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POLYMER-SUPPORTED REAGENTS WITH ENHANCED IONIC RECOGNITION

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ABSTRACT

Polymer-supported reagents with ligands designed for ion-specific interactions are reviewed. Applications in separations science are especially relevant though such polymers can be applied as catalysts and to the preparation of chemical sensors. Ligands covalently bound to polymers which display unique metal ion selectivities include macrocycles, glycols, imines, quinolines, and heterocycles.

INTRODUCTION

An understanding of ion-molecule interactions is important to establishing one aspect of fundamental chemistry and, at the same time, important to the preparation of new reagents which may be applied to separations science. With such an understanding, it becomes feasible to design and synthesize ligands with

high levels of selectivity, or recognition,for targeted metal ions. Such ligands could then be applied to problems in separation and purification involving the complexation of metal ions from the environment.[1]

Homogeneous reagents have been developed within the context of host-guest chemistry[2] for the selective complexation of metal ions. Crown ethers[3] and cryptands[4] form the best-known examples of such reagents; siderophores (macrocycles with an especially high iron affinity),[5] catenands (interlocking macrocycles),[6] and lacunar complexes (bicyclic macrocycles)[7] are a few of many other examples.[8] The underlying principle which unifies the ionic complexations by these reagents is that of pre-organization:[9] the molecular host prefers the ionic guest which requires the least conformational change during the course of complexation. The challenge in designing selective homogeneous reagents for targeted substrates involves identifying those ligands with the greatest free energy of reaction for a given metal ion and then arranging those ligands within a molecular structure which maximizes that interaction.

There have been many attempts to extrapolate what is known about specificity with homogeneous systems to polymer-supported reagents. The syntheses involve immobilizing onto an organic or inorganic polymer, a ligand derived from a homogeneous reagent, such as a carbamoylmethylphosphonate, or a moiety (e.g., an oxime, which can be expected to display a high affinity for a given metal ion.[10] In a few cases, the ligands have been pre-organized on the polymer so as to maximize the ligand-ion interactions. The advantages to employing polymers have been identified[11] and include ease of recovery and reuse of the reagent, adaptability to continuous processes, and the non-toxicity of the reagent once immobilized on the polymer support.

Due to the broadness of the topic, the scope of this review is limited to crosslinked organic polymers with emphasis on polystyrene and poly(meth)acrylates; supports which are used to a lesser extent, such as polybenzimidazole and polyvinyl chloride, will be noted. Inorganic polymers such as silica gel will be considered outside the scope of the present review, as will linear polymers and membranes, each of which can be a separate review. The interaction of metal ions with organic polymers will form the current focus. Extensive lists of commercial ion-complexing polymers are available[10a,f] and their applications have been reviewed recently.[10g] The specific interactions of polymers with organic molecules will be the subject of a future review.

ION-SPECIFIC POLYMER-SUPPORTED REAGENTS: AN OVERVIEW

The organic polymers on which ion-specific ligands can be covalently bound are mostly based on styrene and (meth)acrylate esters because of the ease with which they undergo modification reactions with electrophilic or nucleophilic reagents and the techniques available for their preparation as beads by suspension polymerization. There are two approaches to selecting the groups for covalently bonding onto the polymers: (i) immobilize homogeneous reagents such as crown ethers, whose ionic affinities are known, and (ii) immobilize ligands such as oximes, quinolines, and Schiff bases whose metal ion affinity series must be established. The latter approach is less restrictive and offers the possibility of producing a wide range of selective polymer-supported reagents.

Hard-soft acid-base theory[12] is the foundation on which the choice of appropriate ligands is based. Ligands with sites of low polarizabilities (i.e., hard

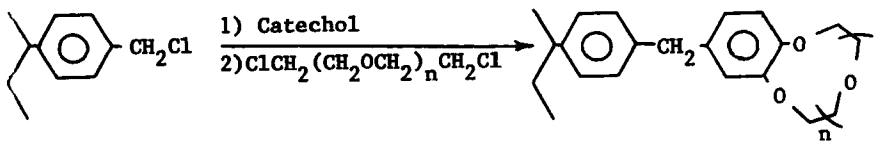
sites) have the greatest affinity for trivalent ions, such as Fe(III), which also have low polarizabilities (and are, therefore, hard); ligands with soft, polarizable sites have the greatest affinity for soft ions such as the precious metals. (The polarizability of a metal ion is directly proportional to its radius and inversely proportional to its valence.) This theory can be used in separation schemes, such as those of precious metals from base metals (the former being softer than the latter have a greater affinity for soft ligands such as sulfur).

Pre-organization can enhance the inherent ligand/ion affinity. This is accomplished by pre-organizing the polymer micropores (template polymerization (vide infra)) or by using macrocyclic ligands, such as crown ethers. Reactive polymers offer an additional route to selectivity enhancement and will be discussed below.

MACROCYCLES

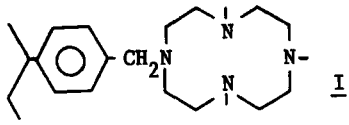
The chemistry of soluble macrocycles[8] has been extended with methods of immobilizing the macrocycles on a polymer network. One method reacts chloromethylated polystyrene beads with a low molecular weight polyethylene glycol (eq 1).[13] The polymers display selectivities expected from the soluble analogues. They can, however, form 2:1 complexes with ions whose diameter exceeds that of the crown cavity.[14] Complexed ions can be recovered from the polymer quantitatively. Benzocrown ethers undergo a polycondensation reaction with formaldehyde.[15] Vinylbenzocrown ethers have been synthesized and can be polymerized.[16]

(1)



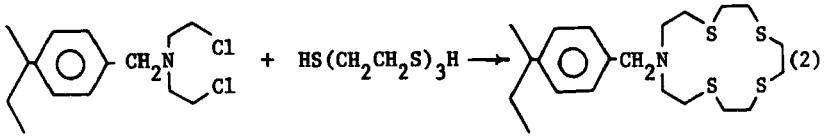
A 24-crown-8 moiety immobilized onto polystyrene through an azobenzene unit is photoresponsive: cesium ions complexed in the dark, are released when the polymer is irradiated with UV light.[17] It is suggested that this is due to conformational changes in the crown ether as the azobenzene moiety photoisomerizes.

Azacrowns such as I have been prepared and the metal ion selectivities reported.[18,19] The cyclic amines have greater affinities for the transition metal ions, especially Cu(II), than the Group I and II ions.



I

The sulfur analogues of the crown ethers have been prepared (eq 2) and found to complex Cu(II), Ag(I), and Hg(II) from non-aqueous solutions.[20]

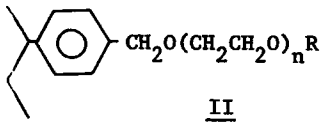


(2)

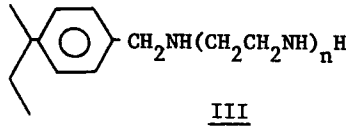
Cryptands can display much higher selectivities and binding constants than crown ethers due to their greater degree of pre-organization.[21] Such reagents have been immobilized on crosslinked polystyrene and found to complex metal ions including UO_2(II), Cu(II), and Nd(III).[22,23]

GLYCOLS AND IMINES

Polystyrene-supported ethylene glycols (II) and imines (III) are acyclic analogues of the crown ethers and azacrowns, respectively. They are more easily synthesized than the crowns but have 100 to 1000 times lower metal ion affinities due to their lower degree of



II

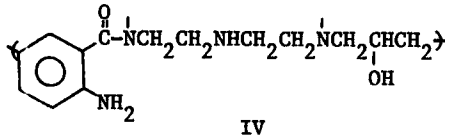


III

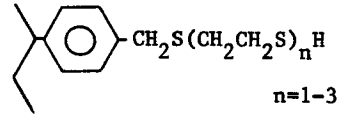
pre-organization.[14] Polymer II (n=3) is selective for $HgCl_2$ (binding constant of 158 M^{-1}) over $NiCl_2$, $CdCl_2$, $CuCl_2$, $FeCl_3$, $CaCl_2$, $UO(NO_3)_2$, $Pb(NO_3)_2$, $PbCl_2$ and $AgNO_3$.[24] Polymeric imines III (n=1-3) were able to complex Cu(II) from 200 ppm (pH 5) solutions.[25] Additionally, the greater the degree of substitution with ligands at n=1, the greater the capacity of the polymer for copper; an inverse relationship was found with n=3 indicating a steric hindrance to complexation with the longer ligands as they were substituted in closer proximity to each other. Diethylenetriamine was also bound to macroporous polyvinyl chloride where it was found to complex Rh quantitatively at pH >5 and Ir at all acid concentrations (from 4M HCl to pH 9 solutions).[26]

The step-growth polymerization of anthranilic acid, epichlorohydrin, and diethylenetriamine produced polymer IV with a selectivity series of Cu>Ni>Zn>Ca>Co >Mg from 1M NH_4OAc/DMF solutions.[27]

The sulfur analogues of the ethylene glycols have also been prepared. Thioethers (V) have been bound to macroporous polystyrene supports and found to be selective for Hg(II) and Ag(I) with capacities ranging from 4.4 to 7.3 mequiv/g.[28] A binding constant of 60 M^{-1} is reported for mercury.



IV

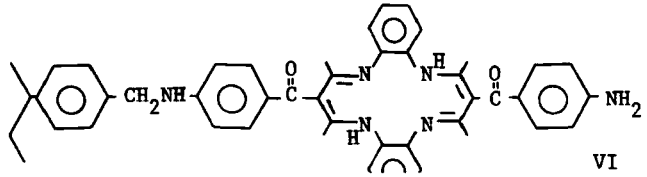


V

SCHIFF BASES

Macrocyclic and acyclic Schiff base ligands have been immobilized on polystyrene. A tetraaza Schiff base (VI) is selective for copper ions.[29] Acyclic analogues have been prepared by reaction of aminomethylated polystyrene with different aldehydes, including salicylaldehyde and 2-pyridinecarboxaldehyde.[30] The relative affinities were Cu > Ni >Co.

Epoxidized microporous polybenzimidazole was reacted with glyoxal-bis-2-hydroxyanil and salicylaldehyde-ethylenediimine to give Schiff base polymers with good sorption capacities for UO_2(II) from pH 4.7 sulfate solutions.[31]

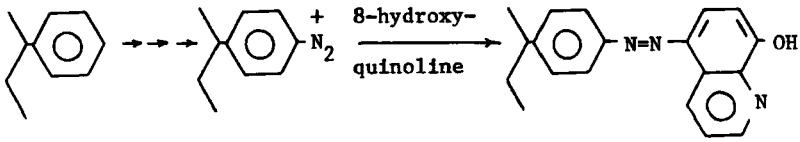


VI

QUINOLINES AND OXIMES

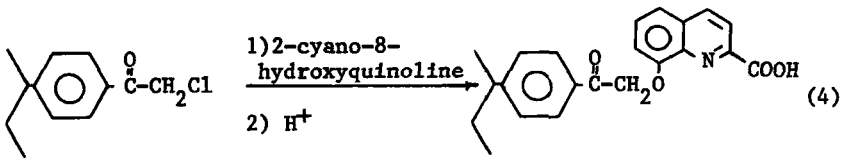
The high sorption capacity of 8-hydroxyquinoline for Cu(II) is retained when bound to polystyrene; a typical synthesis is summarized by eq 3.[32] The sorption capacity is influenced by the resin's hydrophilicity and crosslink level so that results obtained with one type of matrix will not necessarily translate into the same performance with a different matrix: polymer crosslinked with the hydrophilic ethylene glycol dimethacrylate equilibrates ten times faster with Cu(II) (to a $t_{1/2}$ of 5.2 minutes) than when crosslinked with divinylbenzene.[32] Similarly, increasing the degree of substitution on an acrylonitrile-divinylbenzene

(3)



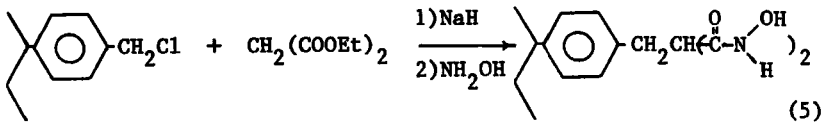
copolymer from 1.7 to 2.4 mmol diethylenetetramine ligands per gram polymer, increases the amount of Cu(II) complexed from 22.3 to 55.3 mg/g polymer.[33]

Quinolines with carboxylic acid moieties at the 2-position have been bonded to substituted polystyrenes (eq 4).[34] Such a polymer-supported reagent has a very high Cd affinity even out of 30% H_3PO_4 solutions. The hydroxyquinoline ligand has also been synthesized as a formaldehyde-based polymer.[35]



(4)

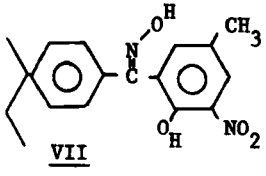
Selectivity for nickel has been reported for a polymeric dihydroxamic acid (eq 5).[36] The affinity series is $Ni>Zn>Co>Cu>Fe^{3+}>UO_2(CO_3)_3^{4-}>>Sr=Ca=Mg$.



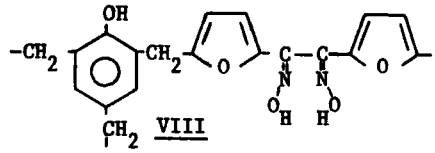
(5)

Hydroxamic acids have a significant affinity for Fe(III).[37] The binding constant, however, is dependent upon the degree of ligand substitution on the polymer: an 11-atom spacing between ligands maximizes the binding constant allowing the reagent to reduce the concentration of ferric ions in water to <0.5 ppm.

The Fries rearrangement was used as a novel method for preparing polymeric hydroxyoximes (VII) which form 1:1 complexes with Cu(II).[38] Phenol-formaldehyde resins prepared by step-growth polymerization have also been used to immobilize oxime ligands. The condensation of 2,4-dihydroxybenzaldehyde oxime with formaldehyde gives a polymer with a higher selectivity for UO_2(II) and Fe(III) than for Cu, Ni, Co, or Mn.[39] Similarly, the



VII

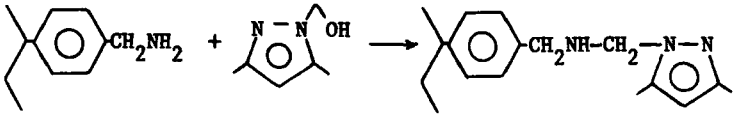


VIII

condensation of furildioxime with formaldehyde and phenol gives polymer VIII which complexes Ni, Co, and Zn ions from ammoniacal solutions.[40]

HETEROCYCLIC BASES

Ligands bearing nitrogen atoms are good coordinators given the tendency of non-bonded electrons to complex metal ions. Guanidine, when immobilized on a polystyrylsulfonyl chloride, is selective for Pd over Pt chloride from solutions at pH 2 due to formation of a trans square planar complex with $PdCl_2$.[41] Polymeric heterocycles take advantage of the nitrogen's basicity while minimizing steric hindrance to complexation. Pyrazole synthesis is a representative example (eq 6). The pyrazole is selective for Cu and Cd over other divalent ions.[42] At pH 4.3, the polymer's capacity for Cu, Cd, Zn, Ni, Co, and Ca (as their chloride salts) is 39, 40, 20, 4, 1, and 0.4 mg/g resin, respectively. The capacities depend upon the anion as well as the metal cation, as is generally true when coordination and not ion exchange is the mechanism of complexation.

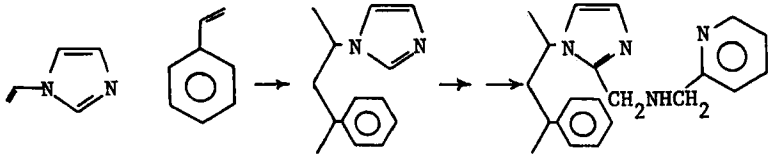


(6)

Imidazoles are an important class of heterocycles that are often used in metal ion selectivity studies. N-methyl-2-thioimidazole has been covalently bound to polystyrene and found to separate Au(III) from 1N HCl solutions containing high concentrations of Cu, Fe, Mn,

and Ni ions.[43] Its binding constant for Au(III) is 8710 M^{-1} with a saturation capacity of 4.08 mmol/g and 98900 M^{-1} for Pt(IV) at a saturation capacity of 2.05 mmol/g.

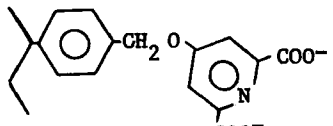
N-vinylimidazole reacts with styrene to give a copolymer which can be functionalized for greater selectivity. A high Cu affinity over Ni was observed after reaction with 2-aminomethylpyridine (eq 7).[44]



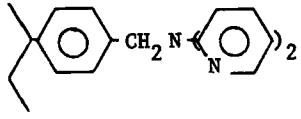
(7)

The pyridyl ligand has been utilized in many polymeric reagents. Suspension polymerization of 4-vinylpyridine with divinylbenzene yields beads with a significant Fe capacity (2.2 mequiv/mL).[45] Aminated pyridine reacts with polyvinyl chloride to give a polymeric reagent capable of reducing a $HAuCl_4$ solution at pH 7 from 100 mg/L to 2.1 mg/mL.[46]

Polymeric dipicolinic acid (IX) displays a selectivity which can be varied depending upon the solution conditions.[47] Pd(II) can be separated from Pt(II) or Pt(IV) in solutions at pH 6, while, at pH <0, Au(III) can be separated from solutions containing Pd(II) and Pt(IV). Polystyrene-bound N-(2-hydroxypropyl)picolylamine is selective for Cu(II): having 4g Fe(III) per L of solution has no effect on the polymer's capacity for copper ions.[48] Increased selectivity by the 2,2'-dipyridylamine ligand (X) is due to a chelate effect with Fe(III)>Cr(III)>>Co(II)>Cu(II)> Ni(II).[49] Metal ion studies were carried out in THF due to its ability



IX

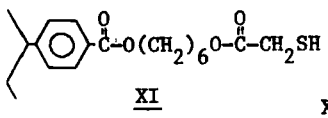


X

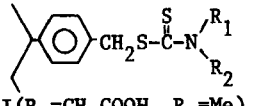
to swell the resin. Accessibility of metal ions to the ligands is minimal from solvents, such as water, which do not swell the resin. Care must be taken when making conclusions about a ligand's ability to complex metal ions if site accessibility is an additional variable.

SULFUR-BASED LIGANDS

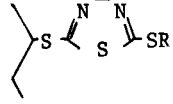
Ligands containing the polarizable sulfur atom can have significant affinities for polarizable ions, such as the precious metals. Ligands within this category include hexylthioglycolate (XI),[50] dithiocarbamates (XII, XIII),[51] thiadiazole (XIV),[52] thiosemicarbazide (XV),[53] and rhodanine (XVI).[54] The hexylthioglycolate



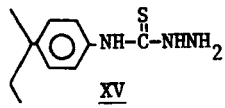
XI



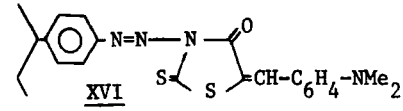
XII(R_1=CH_2COOH, R_2=Me)
XIII(R_1=R_2= CH_2CH_2-OH)



XIV



XV



XVI

is selective for Ag(I), Hg(II), Bi(III), and Au(III); it does not complex Cu(II). Dithiocarbamate XII has a selectivity series of Ag>>Cu>Zn>Ni>Co while XIII shows Ag>>Cu with no affinity for Zn, Ni, or Co. Both series were determined from pH 5.9 solutions except for Ag which was measured at pH 4.68. The capacities of XII and XIII for Ag and Cu were similar. Polyvinyl chloride was the matrix on which the thiadiazole was covalently bound; it had saturation capacities for Ag, Au(III), Pd, Pt(IV) and Rh of 2.74, 2.16, 1.97, 1.03, and 0.38 mmol/g, respectively. No base metals were complexed other than Cu (0.64 mmol/g). The thiosemicarbazide has maximum metal ion capacities from 1-2 M HCl solutions.

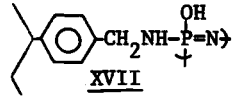
Ir(III) can be separated from other Pt group metals in 1 M HCl solutions: XV complexes all metals in the group except Ir. The rhodanine ligand has a high Ag affinity.

Glycidyl methacrylate is a useful comonomer due to its high reactivity. A copolymer of it with styrene and divinylbenzene was reacted with thiourea and H_2S to give a reagent which complexed 1 mmol $HgCl_2$/g resin.[55] Epoxidation of polybenzimidazole and subsequent reaction with thiourea produces a polymer which is specific for the Pt group metals present in solutions containing higher concentrations of base metals.[56]

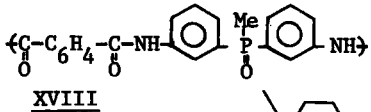
PHOSPHORUS-BASED LIGANDS

Ion exchange resins with phosphorus acid ligands[57] have received new emphasis within the context of dual mechanism bifunctional polymers (vide infra).[58] The aminophosphonic acid ligand has been bonded on chloromethylated polystyrene by reaction of hexamethylenetetramine with phosphorus acid and formaldehyde.[59] It has an affinity series of Pb>Cu>Zn>Ca>Cd>Mg>Ni>Co. Immobilizing two aminophosphonate ligands on an aromatic ring by phosphonylation of diethylenetriamine on polystyrene yields a resin which is selective for trivalent over divalent metal ions.[60]

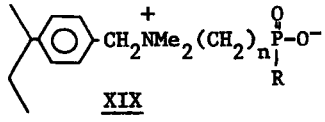
Polymerization of alpha-phenylvinylphosphonic acid with acrylic acid gives a reagent with a selectivity of Th(IV)>Sc(III)>Fe(III)>U(VI)>M^{2+} and a rapid separation of Fe from both Co and Ni.[61]



XVII



XVIII



XIX

Immobilizing the phosphazene moiety gives resin XVII which separates trivalent Sc from Fe.[62] The coordinating resin XVIII is prepared by the step-growth polymerization of bis(3-aminophenyl)methylphosphine oxide with terephthaloyl chloride; it has a far higher affinity for $ZnCl_2$ and $CuCl_2$ than $NiCl_2$, $MnCl_2$, and $FeCl_3$.[63] Carbamoylmethylphosphonates and phosphine oxides are well-known as soluble metal ion complexing agents.[64] They have been bound to polystyrene and studied in lanthanide complexation reactions.[65] Phosphinatobetaines (XIX, n=3-6) complex Co, Cu, and Fe from acetonitrile solutions.[66]

TEMPLATE POLYMERIZATION

The synthesis of selective polymer-supported reagents has focused on the bonding of a wide array of ligands onto different polymeric matrices. In most cases, the ligands are chosen for a targeted interaction and the matrix is not considered a participant in the recognition process. In template polymerization, however, it is the polymer support itself which is responsible for the observed selectivity.[67-69] This is accomplished by preforming a monomer ligand-ion complex and then copolymerizing it with high levels of a crosslinking agent. Once the metal ion is removed from the polymer, it is expected that the ligands will retain an arrangement which is optimal for binding with the original, templating, metal ion. In a recent example,[70] cupric methacrylates were preformed, then crosslinked with ethylene glycol dimethacrylate; after regenerating the acid sites in the copolymer, a higher capacity for Cu(II) was observed relative to other metal ions and untemplated polymers. It is important to note, though, that the crosslinking agent comprised 96% of the total weight of the monomer phase and that the copolymer's

capacity is measured in terms of micromoles/g resin. Results with styrene-based carboxylate monomers were consistent with those from the acrylates.[71]

REACTIVE POLYMERS

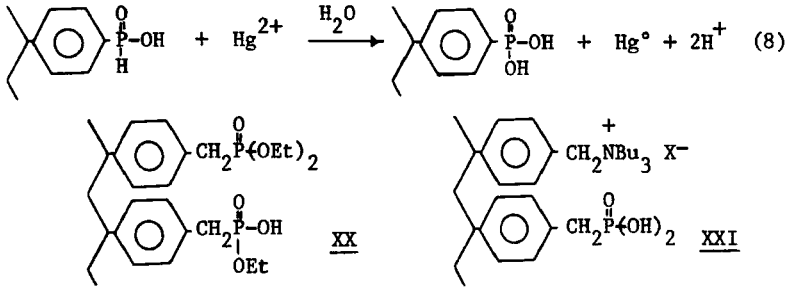
A way to enhance the selectivity displayed by ion exchange resins is to superimpose a chemical reaction on the ion exchange process.[72] Such polymers have been termed "reactive polymers."[73] Appropriate chemical reactions include oxidation, reduction, precipitation, and neutralization.

DUAL MECHANISM BIFUNCTIONAL POLYMERS

An approach which extends reactive polymers is the design and synthesis of dual mechanism bifunctional polymers (DMBPs).[58] In each of three classes of DMBPs, ion exchange by a phosphorus acid ligand operates in concert with a recognition mechanism which endows each class with a selectivity towards targeted metal ions. Given that this topic was reviewed in 1988,[58] a brief introduction will be given here followed by a synopsis of the research since that time.

The first class of the DMBP category superimposes a reduction reaction on the ion exchange component. These ion exchange/redox resins allow for the formation of pure metal from a solution of its ions.[74] The phosphinic acid resin is the prototype of this class and it reacts most readily with Hg(II) ions (eq 8). Reduction occurs more slowly, with ions more difficult to reduce than Hg(II); Cu(II) is the lower limit.[75]

Ion exchange/coordination resins are the second class of DMBPs and are exemplified by the bifunctional phosphonate monoester/diester polymer (XX).[76] Ligand combinations are selected for immobilization in this class of polymers which could cooperate synergistically



in the complexation of metal ions. This cooperation would be evident when the bifunctional polymer complexed more metal than the corresponding monofunctional polymers. Synergistic enhancement is well-known with small molecule analogues and the basis for it seems to be understood.[77]

Precipitation is the recognition mechanism in the third class of DMBPs.[78] A representative example is structure XXI. The anion, X^-, may be any species which can form an insoluble salt with a targeted metal ion. For example, the thiocyanate ion can be ionically bound to the quaternary amine by eluting the polymer with KSCN; the resulting reagent can be used to remove Ag(I) from solutions by AgSCN precipitation within the matrix. The versatility of the reagent is indicated by noting that eluting XXI with KIO_3 now results in a reagent which can remove Pb(II) from solution by precipitation as $Pb(IO_3)_2$.

A series of more recent papers has attempted to define the mechanisms by which metal ions can interact with phosphorus-based bifunctional polymers.[79-81] The data allow for a number of conclusions, including: (1) phosphorus acid polymers complex high levels of metal ions from very acidic solutions (1-4 M HNO_3) by coordination through the phosphoryl oxygen; soft ions such as Hg(II) are preferred; (2) the presence of a large excess of sodium ions relative to the lanthanide,

actinide, or transition metal ion concentration has no significant effect on coordination by phosphorus ligands, as measured by the distribution coefficient, D; the sulfonic acid polymer, however, is sensitive to changes in the solution variables since a non-selective ion exchange is the only mechanism by which it interacts with metal ions; (3) the ability of the primary phosphinic acid ligand to reduce metal ions leads to almost quantitative sorption of Hg(II) and Ag(I) from solutions even with 1:1 initial milliequivalent ratios of metal ion to polymer: thus, from pH 2 solutions, the log D of Hg(II) is 3.80 from trace level solutions and 3.88 from equinormal conditions, while log D of Fe(III) decreases from 4.94 to 0.40 under the same conditions due to ion saturation of the phosphinic polymer (the phosphinic ligand does not reduce the ferric ion).

Synergism between ligands on a polymer support has been observed in the complexation of silver ions.[82] The phosphonate monoester/diester resin will complex far higher levels of silver ions than expected from the the corresponding monofunctional resins. For example, from 4N HNO_3 solutions of 10^{-4}N $AgNO_3$, the values of D for the monofunctional monoester and diester resins are 439 and 463, respectively, while for the bifunctional resin, it is 2924. This supported ligand synergistic interaction is unique for Ag(I) among the ions studied; cooperation of the phosphoryl oxygen on the diester ligand with the phosphonate monoester ligand is maximized in the coordination of Ag ions, perhaps due to an optimal match in ligand-ion polarizabilities.

Results with the purely coordinating phosphonate diester resins suggest another mechanism by which selectivity can be incorporated into polymer-supported reagents. The basicity of the phosphoryl oxygen is most evident with the dimethyl ester resin and its non-

selective complexation of Fe(III), Hg(II), and Ag(I) from 0.2M to 4M HNO_3 solutions. The dibutyl ester resin, however, yields a well-defined series of Ag>Hg> Fe: the bulky alkyl groups may moderate the ligand's basicity by sterically hindering the complexation.[82]

The ion complexing behavior of the ion exchange/ redox, coordination, and precipitation polymers, as well as the coordinating diester polymers suggest that "ionic recognition is an inherent property of polymers that couple an access mechanism [such as ion exchange] to a recognition mechanism subject to reaction control or steric control."[82] A strong ion/ligand interaction, such as reduction, coordination, and precipitation is implied by reaction control; steric control requires the presence of bulky ligands to hinder complexation and thus impose a size selectivity on the apparent reactivity.

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