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The role of polarizability in determining metal ion affinities in polymer-supported reagents: monoprotic phosphates and the effect of hydrogen bonding

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Abstract

The rational design of sensors, solid phase extractants, and cross-linked polymers for environmental remediation requires a pairing of the electronic properties of a targeted metal ion with a given ligand. Polarizability is a key property and values for metal ions have been tabulated. It is now proposed to evaluate ligand polarizabilities by their affinities for Au(III) and Eu(III) as representative soft and hard metal ions. This report centers on: phosphonate diethyl ester (PDE); pentaerythritol diethyl phosphate (pPenta); diprotic phosphonic acid (DPA); phosphinic acid (PA); pentaerythritol monoethyl phosphate (pPentaM); glycerol monoethyl phosphate (pGlyM); and ethylene glycol monoethyl phosphate (pEG1M). Results show that hydrogen bonding is an additional variable that is superimposed on the affinities observed when ion exchange sites are introduced into ligands. PDE and pPenta are classified as soft ligands since they have a high affinity for Au(III) and a low affinity for Eu(III). DPA has a significant affinity for Au(III) and Eu(III) from less acidic solutions which indicates that the phosphoryl oxygen remains soft but intra- and inter-ligand hydrogen bonding cause a loss in both coordinating and ion exchange strength. Changing from a diprotic to a monoprotic acid decreases hydrogen bonding and increases metal ion affinities as indicated by results with PA, which has a high affinity for Au(III) via coordination to the P=O and Eu(III) via ion exchange at the P-OH. FTIR spectra support the change in hydrogen bonding. Monoprotic pPentaM is an alternative with decreased hydrogen bonding and it has high affinities for both Au(III) and Eu(III). The FTIR spectrum for pPentaM exchanged with Eu(III) confirms ion exchange by an hypsochromic shift of 25 cm^{-1} for the P-O band. The ability to tune metal ion affinities with hydrogen bonding is promising for the design of new ligands.

keywords: polymer, ion exchange, adsorption, hydrogen bonds

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Introduction

Ion – selective polymer – supported reagents are important to sensor technology, solid phase extraction, environmental remediation and the nuclear fuel cycle.[1] Sensors can be formed from micrometer-sized cross-linked polymers: e.g., a vinylpyridine/ acrylate copolymer was attached to a sensor tip comprised of bundled optical fibers and connected to a spectrophotometer for detection of Cu(II)[2] and scintillation fibers were coated with a cesium-selective bifunctional polymer pulverized to 3 – 5 µm for quantifying ^{137}Cs in solutions.[3] Solid-phase extraction (SPE) is applied to the preconcentration of Cu(II), Fe(III) and Zn(II) on a Duolite resin modified with bis(2-hydroxyacetophenone)-2,2-dimethyl-1,3-propanediimine with a preconcentration factor of 208,[4] a calixarene-bipyridyl ligand bound to a Wang resin was used for the SPE of Ag(I) and Zn(II) from a solution also containing Pb(II) via a mechanism that utilized the coordinate geometry of the targeted metal ions,[5] and a cross-linked polymer with 8-hydroxyquinoline as the ligand was used in the SPE of Ni(II) from seawater.[6] An amine-modified silica was developed as a selective adsorbent for Cr(VI) from aqueous solutions[7] and immobilized salicylideneimine was found to be selective for uranium from a synthetic nuclear industrial effluent.[8]

Selectivity can be incorporated into polymeric reagents with ligands analogous to soluble complexants such as Schiff bases,[9] N, N-bis-[1,10-phenanthrolin-2yl]-amine,[10] and imidazole,[11] as well as through the use of amino acids such as cysteine.[12] While this empirical design of ligands can be successful, rational design is an important alternative and polarizability, described by hard-soft acid-base theory,[13] is a useful variable in building an *a priori* understanding of ion – ligand selectivity for applications to sensors, SPE, remediation, etc., by matching the polarizability of a targeted metal ion to a given ligand.[14] Though scales of relative softness can be constructed from standard electrode potentials, first ionization potentials, and bulk metal densities,[15] and ligand polarizabilities of soluble compounds can be determined from emission spectra and NMR chemical shifts,[16] an evaluation of ligands immobilized on cross-linked polymers is problematic due to their inherent insolubility. An indirect measure of the polarizabilities of these ligands is an objective of this research. Part I of our research program probed the polarizabilities of four ligands (ethylene glycol, phosphorylated ethylene glycol diethyl ester (pEG1), sulfonic acid, and dimethylamine).[17] Au(III) and Eu(III) were identified as

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representative soft and hard ions from a quantitative scale for a wide range of metal ions.[15] An affinity for the former coupled to a lack of affinity for the latter identified a coordinating ligand as soft; a hard ligand would have an affinity for Eu(III) and this would be due to ionic bond formation through an exchange mechanism.

Polarizability is a continuous property: hard metal ions such as the lanthanides are at least somewhat polarizable[18] and differences are used to effect the separation of the slightly more polarizable actinides from lanthanides.[19] Each metal ion thus has some tendency for both ionic bonding and covalent coordination. Phosphorus-based ligands provide a way of taking advantage of this tendency. For example, combining soft Lewis bases such as phosphine oxides with acidic complexants leads to a synergistic interaction in the complexation of the hard uranyl ion from phosphoric acid solutions.[20] Although the organic substituents differ in acidic organophosphorus reagents, their metal-complexing functionality –P(O)(OH) remains the same: P-OH forms predominantly ionic bonds through ion exchange while the P=O has a strong coordinating affinity for metal salts. Both moieties in the immobilized phosphinic acid ligand are involved in metal complexation.[21]

The results of Part I suggested three approaches to developing high-affinity ligands: single-site coordinating ligands whose polarizability matched that of targeted metal ions; combining multiple weakly coordinating sites into a single ligand; and preparing ligands capable of both ion exchange and coordination. This report (part II) introduces ligands within the third approach, part III applies it to the recovery of U(VI) from phosphoric acid solutions[22] and part IV extends the approach with a new ligand.[23] The polystyrene-bound ligands in this study are shown in Fig. 1. The phosphonate diester (PDE) is the simplest purely coordinating ligand and its affinity for Au(III) and Eu(III) will identify the polarizability of the P=O moiety; phosphorylated pentaerythritol diethyl ester (pPenta) is also purely coordinating but the neighboring –OH groups will identify the strength of any auxiliary group effect on the polarizability. Hydrolysis of PDE to the diprotic phosphonic acid (DPA) will introduce ion exchange and its affinities will be compared to the monoprotic phosphinic acid (PA) and phosphorylated monoethyl esters of pentaerythritol (pPentaM), glycerol (pGlyM), and ethylene glycol (pEG1M), each with the –P(O)(OH) ion exchange site but differences in surrounding groups.
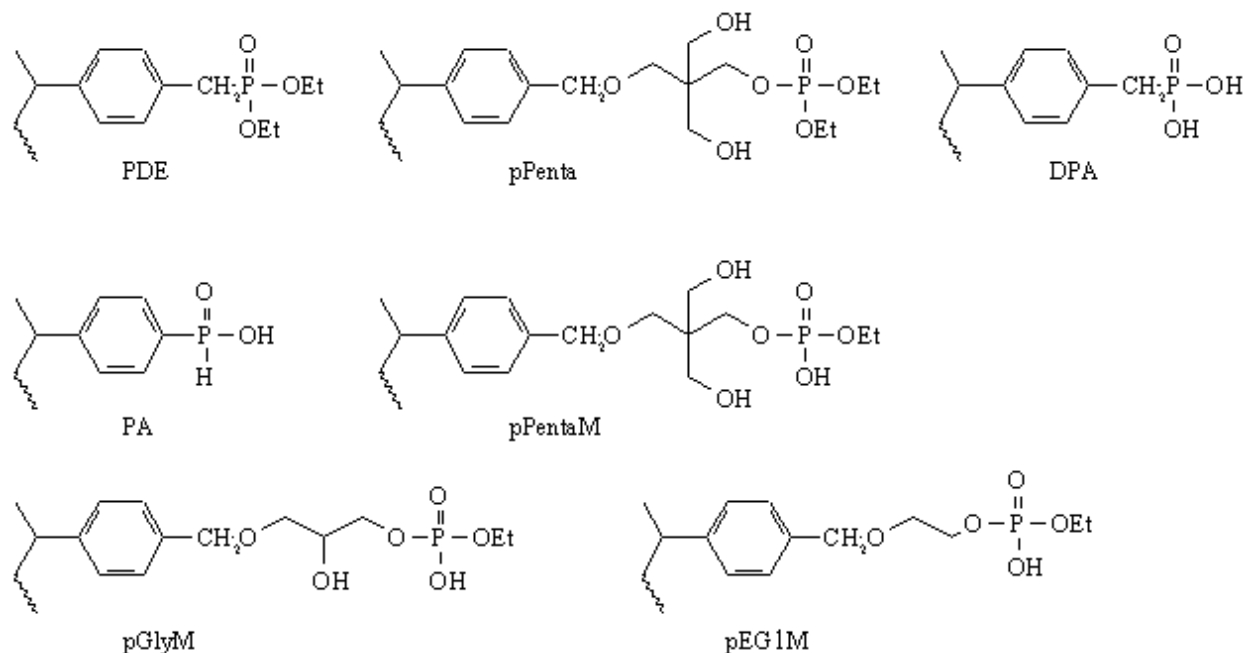
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Fig.1. Structures of the phosphorus ligands: PDE: phosphonate diester; pPenta: phosphorylated pentaerythritol diethyl ester; DPA: diprotic phosphonic acid; PA: phosphinic acid pPentaM: phosphorylated pentaerythritol monoethyl ester; pGlyM: phosphorylated glycerol monoethyl ester; pEG1M: phosphorylated ethylene glycol monoethyl ester

Experimental

The copolymer of vinylbenzyl chloride (VBC) and 2% divinylbenzene (DVB) was prepared by suspension polymerization with 0.5 wt% benzoyl peroxide as initiator.[24] After polymerization, the beads were washed with toluene, dried and sieved to a particle size of 250–400 μm. VBC, DVB, pentaerythritol, triethyl phosphate, diethyl chlorophosphate, organic solvents, metal nitrate salts, and metal standard solutions were purchased from Sigma-Aldrich or Fisher Scientific and used directly.

Synthesis of immobilized ligands

Phosphonate diester (PDE). Five grams of polyVBC beads were refluxed with 50 mL of triethyl phosphate for 17h. After removing the solution, the beads were washed with acetone, aqueous acetone, and water, then conditioned with 1 L of each 1 M NaOH, H_2O, 1 M HCl and H_2O.

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Diprotic phosphonic acid (DPA). Four grams of PDE were refluxed with 50 mL conc. HCl for 17h. The beads were washed with distilled water and conditioned as above.

Phosphinic acid (PA). Five grams of polystyrene beads were stirred with 50 mL PCl_3 and 50 g $AlCl_3$ at 23^oC for 17 h. Water was added slowly to hydrolyze unreacted PCl_3 and $AlCl_3$ and the beads conditioned as above.

Monoprotic phosphorylated ethylene glycol (pEG1M). Eight grams of NaH (60% dispersion in mineral oil) were added to 100 mL ethylene glycol and 200 mL 1,4-dioxane under a flow of N_2. Five grams of polyVBC beads in 50 mL dioxane were added, the mixture refluxed for 20 h, then the beads washed with dioxane and dried in a vacuum oven. Monoprotic phosphorylated ethylene glycol was then prepared by refluxing two grams of beads in 100 mL pyridine, 10 mL diethyl chlorophosphate (DECP) and 10 g 4-dimethylamino-pyridine (DMAP) for 17 h. The pEG1M beads were washed with methanol and water and conditioned as above.

Monoprotic phosphorylated glycerol (pGlyM). The synthesis followed the procedure for pEG1M except that glycerol and N-methylpyrrolidone (NMP) were used in place of ethylene glycol and dioxane and the mixture stirred at 80^oC rather than reflux.

Phosphorylated pentaerythritol (pPenta). Eight grams NaH (60% dispersion) was slowly added to 60.0 g of pentaerythritol and 250 mL of NMP and the mixture stirred at 80^oC under N_2 flow for 2 h. Copolymer polyVBC beads (6.0 g) pre-swollen in 50 mL NMP for 2 h were then added to the solution and the mixture stirred at 80 °C for 20 h. The solution was removed, and the beads were washed with 100 mL each of NMP, NMP/water (1:1), water, then vacuum-dried at 70 °C for 12 h. Pentaerythritol-modified beads (2.0 g) were added to 50 mL pyridine and 10 mL DECP, stirred at 23^oC for 17 h, then washed with 100 mL each of methanol, methanol/water (1:1), and water, and conditioned as above.

Monoprotic phosphorylated pentaerythritol (pPentaM). Pentaerythritol-modified beads (2.0 g) were added to 100 mL pyridine and 10 g DMAP, then stirred for 2 h at 23^oC. DECP (10 mL) was added and the reaction refluxed for 17 h. The resulting beads were washed with 100 mL each of methanol, methanol/water (1:1), and water, then conditioned as above.

Au(III) loading on PDE and pPenta. PDE or pPenta (0.10 g) was contacted with 10 mL of Au(III) standard solution (1000 mg/L) for 24 h, filtered, washed and dried.

Characterization. Acid capacity was determined by contacting 0.5 g Buchner-dried polymer with 50 mL 0.1000 M NaOH containing 5% NaCl for 17 h, and then titrating a 10 mL aliquot with 0.1000 M HCl with phenolphthalein as the indicator. The percent solids [ratio of dry to wet bead weight x 100] was determined by Buchner-drying the beads for 5 min to remove excess water (wet beads), then oven-drying at 110 ^{o}C for 12 h (dry beads). The phosphorus capacity was measured after mineralization of 20 mg samples in conc. sulfuric acid in the presence of copper sulfate and subsequent reaction with ammonium vanadate-molybdate.[25] The intensity of yellow coloration was measured at 470 nm on a Spectronic 21D (Milton Roy). Infrared spectra were taken on a PerkinElmer Spectrum 65 spectrometer.

Metal ion affinity study. Metal ion affinities were quantified by batch equilibration using 10^{-4} N metal ion solutions in 0.01 – 6.0 M nitric acid. Enough Buchner-dried polymers to give 0.50 mmol P were shaken with 5 mL of Au(III) or Eu(III) solutions for 17 h after being pre-equilibrated with the appropriate background solution (shake three times, each 15 min). Au(III) solutions were prepared from a standard solution (1000 mg Au /L in 0.5 M HCl). Metal ion concentrations at equilibrium were determined by a PerkinElmer Optima 7000 DV inductively coupled plasma - atomic emission spectrometer. The sorption percentages and distribution coefficients were calculated from the metal ion concentrations in solution before and after equilibration.

Results and Discussion

Characterization. Table 1 reports the phosphorus and acid capacities of the polymer-supported complexants. Diethyl esters show no acid capacities, monoethyl esters have an acid capacity equivalent to their phosphorus capacity (within experimental error), the phosphonic acid has an acid capacity twice the phosphorus, and the phosphinic acid has equivalent phosphorus and acid capacities.

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Table 1. Phosphorus and acid capacities of the polymer-supported complexants

	PDE	pPenta	DPA	PA	pPentaM	pGlyM	pEG1M
Phosphorus capacity*	3.78	2.98	4.71	5.21	2.81	2.62	2.34
Acid capacity	0	0	9.65	4.90	2.61	2.69	2.42

*capacities in mmol/g

PDE: phosphonate diester; pPenta: phosphorylated pentaerythritol diethyl ester; DPA: diprotic phosphonic acid; PA: phosphinic acid pPentaM: phosphorylated pentaerythritol monoethyl ester; pGlyM: phosphorylated glycerol monoethyl ester; pEG1M: phosphorylated ethylene glycol monoethyl ester

FTIR spectra support the structures shown in Figure 1. The P=O stretching bands appear at 1227, 1247 and 1219 cm^{-1} for PDE, pPenta and pPentaM, respectively. None have the broad band at 2319 cm^{-1} seen in the phosphonic acid and which is weakly evident in the phosphinic acid. The significance of these bands is discussed in the following section.

Metal ion affinities. Metal ion affinities are reported in Table 2 as both percent sorbed and distribution coefficients. **PDE** has a high affinity (> 90%) for Au(III) and a low affinity (< 10%) for Eu(III). **pPenta** gives the same results as PDE except for Eu(III) in 0.01 M HNO_3 (98.3% sorbed). Hydrolyzing the PDE to **DPA** gives a ligand with a higher affinity for Au(III) over Eu(III), except from 0.01 M HNO_3; the affinity for Au(III) is much less than its precursor PDE and its affinity for Eu(III) is comparable to PDE in the two most acidic solutions. DPA has a much higher Eu(III) affinity than PDE from the least acidic solution and, while the difference in affinities from 1 and

Table 2. Metal sorption percent sorbed and distribution coefficients by the polymeric reagents

[HNO_3]	0.010 M	1.0 M	2.0 M	4.0 M	6.0 M
PDE					
Au(III)	99.9(4.83)*	98.9 (3.73)	98.7 (3.67)	97.7 (3.40)	94.1 (2.95)
Eu(III)	9.63 (0.81)	5.26 (0.53)	4.40 (0.46)	4.80 (0.47)	3.71 (0.36)
pPenta					
Au(III)	97.9 (3.27)	99.2 (3.69)	98.6 (3.44)	96.9 (3.07)	92.4 (2.66)

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| Eu(III)	98.3 (3.42)	4.11 (0.22)	2.06 (-0.09)	3.33 (0.12)	2.15 (-0.07)
DPA					
Au(III)	82.3 (2.40)	81.0 (2.37)	75.5 (2.23)	55.7 (1.83)	36.7 (1.51)
Eu(III)	99.8 (4.61)	16.8 (1.06)	9.54 (0.80)	5.64 (0.54)	4.80 (0.48)
PA					
Au(III)	97.3 (3.30)	99.4 (3.93)	99.4 (3.96)	97.6 (3.34)	83.2 (2.42)
Eu(III)	99.1 (3.81)	95.1 (3.04)	83.8 (2.46)	69.6 (2.12)	59.3 (1.92)
pPentaM					
Au(III)	98.1 (3.32)	94.4 (2.81)	86.9 (2.41)	70.7 (1.98)	78.6 (2.15)
Eu(III)	99.9 (4.42)	98.3 (3.33)	90.9 (2.44)	68.9 (1.64)	51.5 (1.14)
pGlyM					
Au(III)	97.7 (3.10)	97.2 (3.02)	94.9 (2.75)	85.6 (2.25)	71.3 (1.87)
Eu(III)	99.2 (3.58)	97.8 (3.14)	91.6 (2.51)	70.9 (1.87)	55.9 (1.59)
pEG1M					
Au(III)	96.3 (2.84)	96.5 (2.87)	93.8 (2.61)	85.4 (2.20)	77.9 (1.98)
Eu(III)	99.4 (3.65)	95.9 (2.81)	86.1 (2.22)	59.4 (1.60)	45.3 (1.35)

* log(distribution coefficient)

PDE: phosphonate diester; pPenta: phosphorylated pentaerythritol diethyl ester; DPA: diprotic phosphonic acid; PA: phosphinic acid pPentaM: phosphorylated pentaerythritol monoethyl ester; pGlyM: phosphorylated glycerol monoethyl ester; pEG1M: phosphorylated ethylene glycol monoethyl ester

2 M HNO_3 seems marginal, it is significant (see below). **PA** has high affinities for Au(III) and Eu(III); even from 6 M HNO_3, the extent of complexation is much greater than by the sulfonic acid which showed low Au(III) affinity from all solutions and high Eu(III) affinity from the least acidic solution but then declined rapidly as solution acidity increased.[17]

pPentaM has high affinities for both Au(III) and Eu(III), decreasing only when solution acidity exceeds 2 M. It sorbs 51.5% Eu(III) from 6.0 M HNO_3 where neither the diesters (PDE, pPenta) nor the acids (DPA, sulfonic acid) showed any affinity. The log D / pH plot is linear for all points except the first (which is at the upper limit for accuracy by ICP-AES) with a slope of 2.8 (<0.9994>). The monoprotic PA has a similar Eu(III) affinity and this is important to understanding the complexation mechanism (discussed below). **pEG1M** and **pGlyM** show no significant difference in affinities from pPentaM, indicating that the polarizability of the acidic ligand is unaffected by the surrounding –OH groups and that the ion exchange /coordination

properties of the three are similar. This is unlike the situation with the diethyl esters in which the –OH groups play an important role in affecting the polarizability of the P=O and thus its metal ion affinity for divalent ions.[26]

Analysis of FTIR spectra. FTIR spectra can identify the site at which a ligand binds a metal ion.[27] Figure 2 shows the spectra of PDE, pPenta and pPentaM (metal-free and metal bound). Binding Au(III) to PDE results in a bathochromic shift of 18 cm^{-1} at the P=O and no significant effect at the P-O. Binding of Au(III) to pPenta results in a bathochromic shift of 12 cm^{-1} and no shift in the position of the P-O band though it does sharpen. Binding Eu(III) to pPentaM results in some change in the appearance of P=O band but no change in its position while the P-O band undergoes an hypsochromic shift of 25 cm^{-1}.
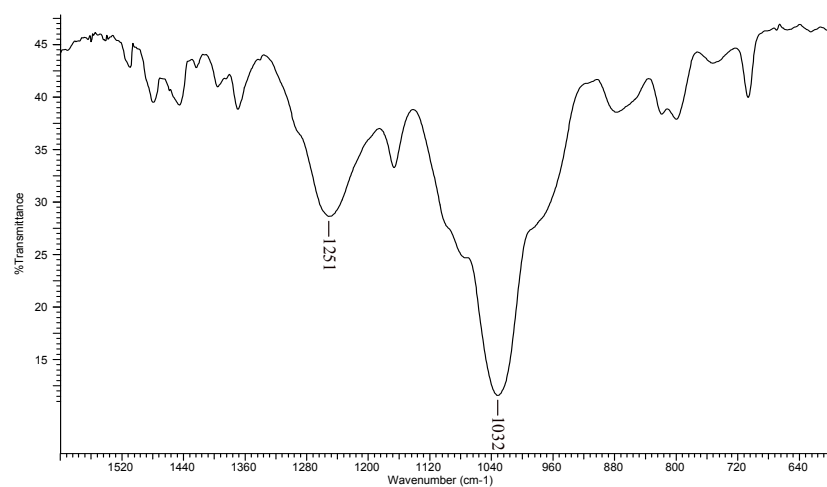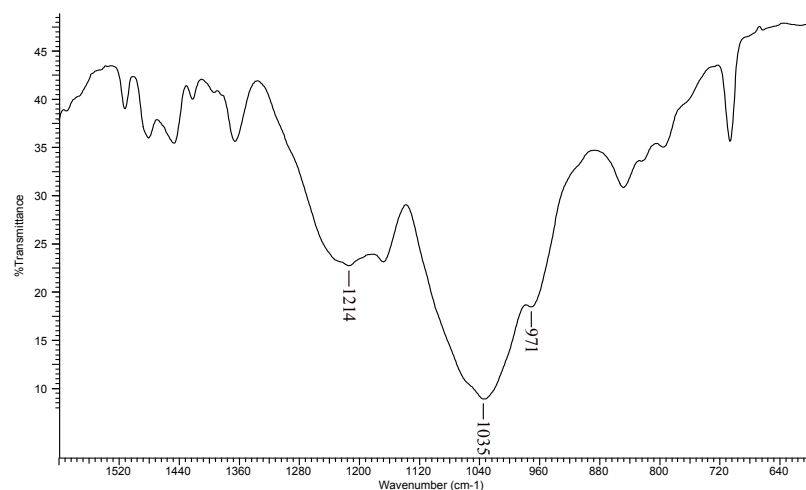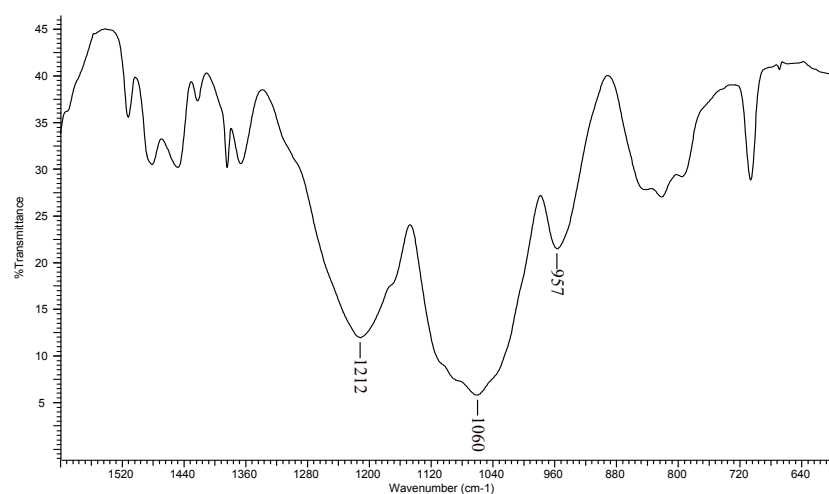

PDE

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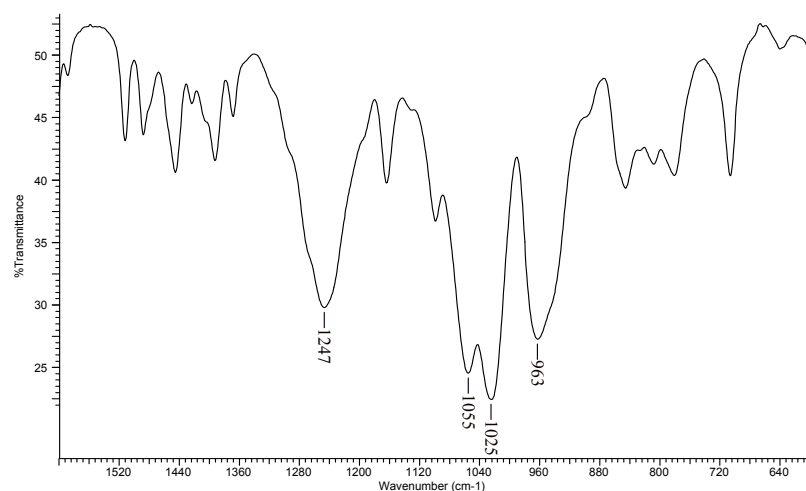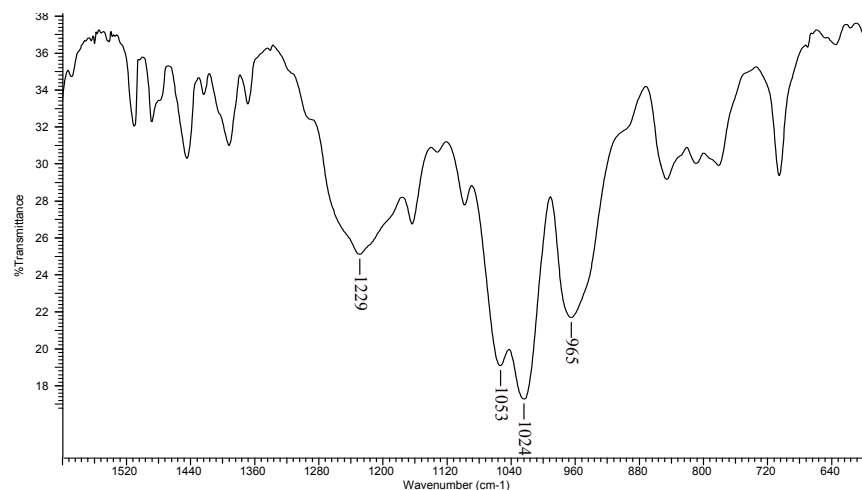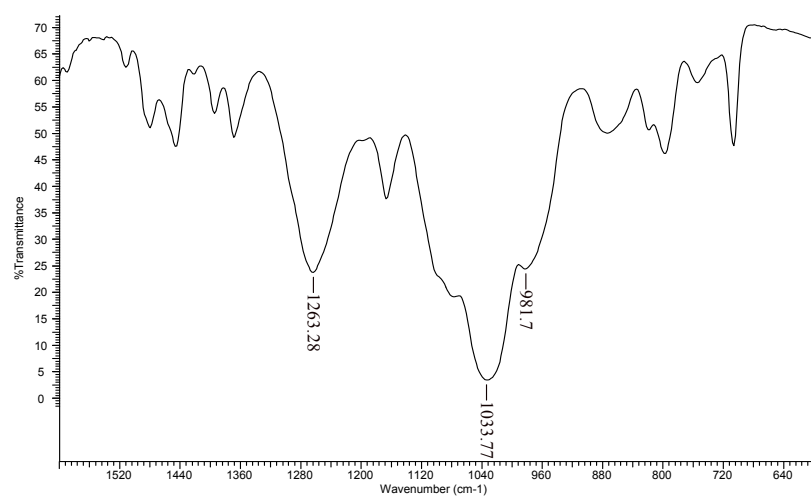
Au(III)-bound PDE

pPenta

Au(III)-bound pPenta

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pPentaM

Eu(III)-bound pPentaM

Fig. 2. FTIR spectra of free and Au(III)-bound PDE and pPenta; and free and Eu(III)-bound pPentaM.

Hard / soft classification. The results in Table 2 allow classification of ligands as hard or soft and build on earlier work focused on the diethyl ester pEG1.[17] **PDE** has a high affinity for Au(III) and a low affinity for Eu(III)) leading to its phosphoryl oxygen being classified as soft. pEG1 has identical results indicating that the polarizability of a phosphonate is similar to that of a phosphate insofar as Au(III) is able to detect. This is reasonable since soluble phosphonate and

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phosphate complexants are both soft, but the former are softer due to the absence of one electron-withdrawing oxygen. Au(III) thus gives a coarse classification as soft but a less soft ion is needed to differentiate among soft ligands. This is seen with **pPenta** which gives the same results as PDE (except for Eu(III) in 0.01 M HNO$_3$ since the low H$^+$ concentration allows weakly coordinating –OH groups to bind Eu^{3+} as indicated by results with immobilized ethylene glycol[17] and in a study with substituted crown ethers.[28]). The phosphoryl oxygen is again classified as soft through Au(III) but earlier studies with Pb(II), an ion that is less soft than Au(III) as determined by the Kinraide scale,[15] showed pPenta is softer than PDE and pEG1.

Comparing the diethyl esters to the diacid shows **DPA** to have a lower but still significant affinity for Au(III), at least from the less acidic solutions, and an affinity for Eu(III) from the least acidic solution. Insight into the mechanism is gained from a plot of log D *vs.* pH in which the slope is the charge of the exchanging ion.[29] The sulfonic acid, with no Au(III) affinity, has a log D$_{Eu}$/pH slope of 2.9 with all acid solutions, indicating pure ion exchange with Eu^{3+}. The log D/ pH correlation for DPA from 0.01, 1, and 2 M HNO$_3$ is a straight line with a slope of 1.7 <0.9983>. The simplest rationale is that binding of Eu(NO$_3$)$^{2+}$ and Eu(NO$_3$)$_2$$^+$ occurs in a ratio that releases 1.7 protons in an ion exchange mechanism that becomes negligible in the more acidic solutions. Ion exchange is expected from acid sites of intermediate strength though unlike the stronger sulfonic acid, the phosphonic acid is unable to complex Eu^{3+} from solution. The significant affinity for Au(III) indicates that the phosphoryl oxygen remains soft in the diacid but a variable hinders complexation from the more acidic solutions.

Effect of hydrogen bonding. The variable proposed to cause the loss in both coordinating and ion exchange strength in the diprotic phosphonic acid is intra- and inter-ligand hydrogen bonding between the acid P-OH and coordinating P=O sites. Hydrogen bonding is sufficiently strong to determine the secondary structure of proteins,[30] whether a ligand is bidentate or tridentate,[31] and in the binding of anions with soluble complexants.[32] The high affinity of the phosphonate ligand for protons has been reported.[33] In the present case, hydrogen bonding within immobilized phosphorus acids is consistent with the aggregation of soluble acidic organophosphates:[34] Cyanex 272 extracts lanthanides as dimers[35] and P, P′-di(2-ethylhexyl)methanediphosphonic acid dimerizes even after two of the four acidic protons are

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replaced with alkyl groups[36] (additionally, only one of the two protons in the dimer exchanges with metal ions, the other being unavailable due to hydrogen bonding).

A decrease in hydrogen bonding should increase metal ion affinities and a way to accomplish this is changing from a diprotic to a monoprotic acid. The ideal comparison would be with the monoester of DPA but a satisfactory synthesis was not identified; in light of this, a comparison focused on hydrogen bonding was made with **PA**. The results show that PA is soft because of its coordination to Au(III) with a greater affinity than DPA since it has a softer phosphoryl oxygen for the same reason that phosphonate is softer than phosphate. PA also shows significant affinity for Eu(III) due to ion exchange. The log $D_{Eu(III)}$ / pH plot has a slope of 1.4 with all points except the first (<0.98>) indicating that binding of $Eu(NO_3)^{2+}$ and $Eu(NO_3)_2^+$ occurs in a ratio that releases 1.4 protons with an ion exchange mechanism similar to DPA but one that continues to be significant in the more acidic solutions despite the fact that phosphinic acids have a higher pKa than phosphonic acids.[37] Ion exchange with Eu^{3+} is reasonable from 0.01 M HNO_3. Additional P-OH moieties per ligand do not necessarily enhance the extent of ion exchange: e.g., monoprotic PA is known to have higher affinities than DPA despite its lower acidity.[38] The phosphinic acid is also of intermediate strength and ion exchange is assisted by coordination to a P=O from a neighboring ligand since there is less hydrogen bonding.[21]

The change in hydrogen bonding is supported by FTIR spectra. The phosphoryl group in PA has asymmetrical and symmetrical stretching bands at 1167 and 1125 cm^{-1}, respectively, while DPA shows the phosphoryl bands at 1154 and 1123 cm^{-1}, respectively. The bathochromic shift of 13 cm^{-1} in DPA is consistent with hydrogen bonding to the P=O shifting electron density from between the phosphorus and oxygen. The relationship between hydrogen bond strength and bathochromic shifts has been reported in the FTIR spectra of methanesulfonic acid-N-oxides.[39] DPA also has a broad band of medium intensity at 2219 cm^{-1} that is ascribed to hydrogen bonding and this band is barely evident in PA. PDE, having no P-OH groups with which to hydrogen bond, has the P=O bond stretch at 1227 cm^{-1}.

New ligand synthesis. Given that DPA and PA have greater metal ion affinities than the purely coordinating diethyl esters, an alternative was developed to maintain ion exchange ability while decreasing the extent of hydrogen bonding. Since the second P-OH in organophosphorus

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diacids is not involved in metal ion complexation, the objective became to replace it with P-OEt. The optimum method was found to be a reaction of the glycol with DECP and DMAP. Formation of the monoethyl ester is most likely due to reaction of the highly reactive DECP with the glycol to give the diethyl ester followed by reaction of DMAP at the phosphoryl moiety to remove one of the ethoxy groups; reaction of a second DMAP at the same site is precluded by steric hindrance:
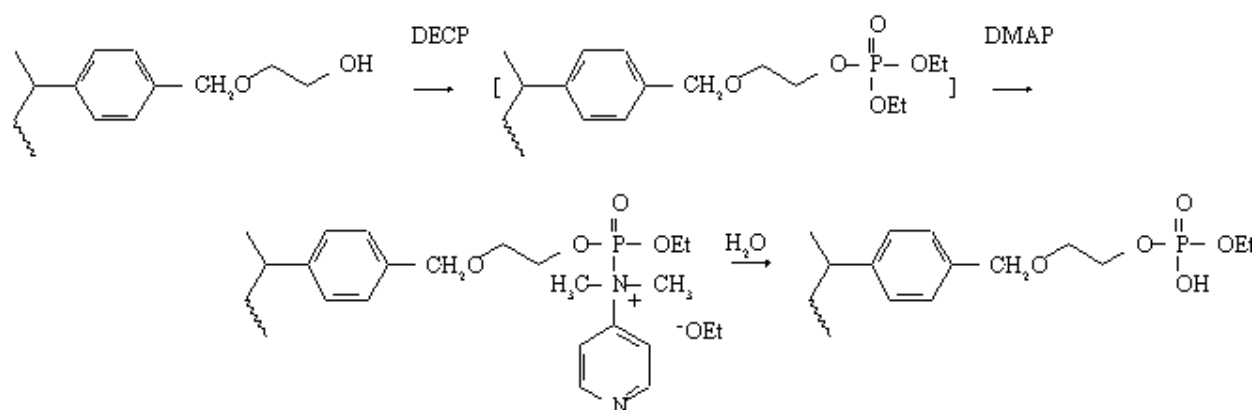

Fig. 3. Conversion of the ethylene glycol ligand (pEG1) to monoprotic phosphate ester (pEG1M)

The results with **pPentaM** show it to have a high affinity for Au(III) that remains significant when acidity exceeds 2 M HNO_3 though at a lower level than that for the purely coordinating pPenta. The affinity for Eu(III) is also high even from 6 M HNO_3 when compared to DPA and the sulfonic acid. It is strong enough to ion exchange with Eu^{3+} given that the log D/pH plot has a slope of 2.8 with all points except the first. The FTIR spectrum for pPentaM exchanged with Eu(III) shows some change in appearance of the P=O band but no change in position; the P-O band has an hypsochromic shift of 25 cm^{-1} which indicates a higher energy stretch arising from an increased electron density between the phosphorus and oxygen due to the change of P-OH to P-O⁻ and ionic bonding to Eu^{3+}. Results with **pGlyM** and **pEG1M** are comparable to pPentaM, indicating that the proximate –OH groups do not affect the phosphate monoester ligating site. This is unlike the case with the purely coordinating diethyl esters in which the polarizability of the phosphoryl oxygen is sensitive to the –OH groups. In the monoprotic ligands, the P=O is hydrogen bonded to the acidic P-OH and the weakly hydrogen bonding –OH groups are unable to have an effect.

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The Au(III) coordination and Eu(III) ion exchange mechanisms are supported by the FTIR spectra (Fig. 2). The binding of Au(III) to the phosphoryl oxygen of PDE results in a loss of electron density between the phosphorus and oxygen as electron density between the oxygen and Au(III) increases; this is reflected in the bathochromic shift from 1247 to 1229 cm^{-1}. The binding to the phosphoryl oxygen of pPenta results in the same change of electron density and a bathochromic shift from 1263 to 1251 cm^{-1}. There is no change in the band position of the P-O single bond for both ligands since, of course, ion exchange is not possible. The band for the P-O single bond undergoes a shift from 1035 to 1060 cm^{-1} in pPentaM upon binding the Eu(III) due to ion exchange at the P-OH to give P-O⁻ and the increase in electron density between the phosphorus and oxygen. The shift in appearance but not position of the P=O band may indicate a weak coordination to the Eu(III) upon ion exchange but this requires further study for confirmation. This type of ion exchange / coordination has been confirmed with the phosphinic acid ligand.[21]

Conclusion

The significance of this work is the progress it makes toward the rational design of polymer-supported complexants by gaining an understanding of the variables important to communication between a supported ligand and a given metal ion that leads to recognition. Polarizability is a key variable; the polarizabilities of ligands immobilized on crosslinked polymers and their classification as hard or soft can be accomplished by determining their affinities for hard (Eu(III)) and soft (Au(III)) ions. FTIR spectra of the metal-bound polymers support the designations. Hydrogen bonding in immobilized ion exchange ligands is an important variable that is superimposed on the metal ion affinities. The decreased hydrogen bonding in the monoprotic phosphinic acid and phosphorylated glycol relative to the diprotic phosphonic acid results in increased affinities. The next phase is to determine whether hydrogen bonding is affected when an amine is proximate to a monoprotic ligand and how this affects metal ion affinities.

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