Development of a new ion-exchange / coordinating phosphate ligand for the sorption of U(VI) and trivalent ions from phosphoric acid solutions

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Abstract

A polymer-bound monoprotic phosphoric acid ligand was developed for the sorption of U(VI) from 0.10 - 6.0 M phosphoric acid solutions. The ligands reported are new phosphorylated mono- and triethylene glycol ethyl esters (pEG1M and pEG3M) prepared by combining diethylchlorophosphate and 4-dimethylaminopyridine; they ion exchange through the acid site and coordinate through the phosphoryl oxygen. The binding mechanism is probed by comparing their results to coordinating phosphorylated mono- and triethylene glycol diethyl esters (pEG1 and pEG3) and the diprotic phosphonic acid (DPA) that operates by ion exchange. The affinities for Lu(III), La(III), Fe(III) and Al(III) were also determined. All metal ions were sorbed much more efficiently by the monoprotic ligand relative to the diprotic and coordinating ligands. It is proposed that a decrease in inter-ligand hydrogen bonding within the monoprotic ligand is responsible for the increased metal ion affinities. This is consistent with the FTIR spectra wherein the P=O band appears at 1262 cm^{-1} for pEG1 and this shifts down to 1229 cm^{-1} in pEG1M and 1180 cm^{-1} for DPA. Incorporating ether oxygen into the ligand further enhances metal affinities: pEG3M with three oxygen donors adjacent to the monoprotic site shows the highest affinity for metal ions. The increased affinities compared to pEG1M are due to complexation by the weakly binding ether oxygen donors. High metal ion affinities thus require both ion exchange with acidic protons and coordination with neutral donors. More rapid kinetics evident with pEG3M relative to DPA is further evidence for decreased hydrogen bonding which permits more rapid sorption. The affinity orders of the three acidic polymers are

similar: U(VI), Lu(III) > Fe(III) > La(III) > Al(III). Ligand strength is pEG3M > pEG1M > DPA > pEG3 > pEG1.

Keywords: polymer; separations; complex; uranium; phosphoric acid.

Introduction

Uranium concentrations in phosphate minerals range from 70-200 mg/kg and were considered a uranium resource.¹ Moreover, phosphoric acid is a component of agricultural and industrial products (e.g. fertilizer, cleaners, toothpaste, beverages, food additives, and animal feed).² Most phosphoric acid is produced by acidification of phosphate minerals with sulfuric acid but this wet-process phosphoric acid contains varying levels of metal impurities including iron, aluminum, and lanthanides as well as uranium, and their presence affects how the phosphoric acid can be applied. It is thus important to separate uranium and metal impurities from wet-process phosphoric acid particularly when it is to be used as a raw material in the food industry.

Soluble phosphorus acid reagents have been used for the separation and recovery of metal ions from aqueous solutions because of their high affinities and selectivity.³ The complexation of metal ions by coordinating phosphates is well known^{4,5} and binding to uranyl from nitric acid solutions is the basis for the PUREX process.⁶ Di(2-ethylhexyl)-phosphoric acid is often used in the presence of coordinating complexants for uranyl binding.^{7,8} They are capable of ion exchange over a relatively wide pH range and coordinate metal ions through the phosphoryl oxygen in acidic solution.⁹ Polymer-bound phosphorus acids have a very high U(VI) affinity¹⁰ and several have been examined for metal recovery from phosphoric acid though their affinity is limited from concentrated solutions.^{11,12}

Our research is focused on understanding the interactions between metal ions and immobilized ligands in order to optimize both affinity and selectivity which can then lead to important applications. Studies with coordinating phosphorus-based ligands has shown how the polarizability of the phosphoryl oxygen can be varied by neighboring –OH groups which then affects affinities for divalent ions,¹³ hydrogen bonding affects the affinities of amides for lanthanides,¹⁴ and moieties bound to the amine nitrogen affect the affinity of U(VI) from seawater through ion exchange.¹⁵

The present study develops ligands capable of ion exchange and coordination for the binding of U(VI) from concentrated phosphoric acid solutions. In our previous report, it was concluded that the phosphoryl oxygen in phosphorylated ethylene glycol diethyl ester (pEG1) was soft

(i.e., polarizable) given its greater affinity for Au(III) over Eu(III) and that ligand – ion interactions could be enhanced by preparing ligands with dual ion exchange/coordination character.¹⁶ In this study, these conclusions are tested with new phosphorus-based ligands that are applied to the binding of the hard uranyl ion from 0.10 - 6.0 M phosphoric acid solutions. Though immobilized phosphorus acids have the same binding site as H₃PO₄, high U(VI) sorption onto the polymers from the phosphoric acid solutions will require different metal ion affinities. The ligands are the purely coordinating pEG1 and phosphorylated triethylene glycol diethyl ester (pEG3), the new phosphorylated mono- and triethylene glycol ethyl esters pEG1M and pEG3M that can ion exchange through the -OH and coordinate through the phosphoryl oxygen, and the diprotic phosphonic acid (DPA) that operates primarily by ion exchange (Fig. 1). pEG3M differs from pEG1M by having internal coordinating ether sites that are known from studies with pEG1 and higher homologue diesters to affect metal ion affinities from less acidic solutions.

Fig.1 The immobilized ligands: phosphorylated ethylene glycol diethyl ester (pEG1), triethylene glycol diethyl ester (pEG3), ethylene glycol monoethyl ester (pEG1M), triethylene glycol monoethyl ester (pEG3M), and diprotic phosphonic acid (DPA).

Experimental

Materials Vinylbenzyl chloride (VBC) was copolymerized with 2 wt.% divinylbenzene (DVB) by suspension polymerization with 0.5 wt.% benzoyl peroxide as initiator. After reaction, the beads were extracted with toluene, dried, and sieved to a particle size 250 – 425 μm . All reactants (VBC, DVB, ethylene glycol, triethylene glycol, triethyl phosphite, diethyl chlorophosphate), 4-dimethylaminopyridine, solvents, metal nitrate salts, and uranium standard solution were purchased from Sigma-Aldrich or Fisher Chemical Co., and used without further treatment.

Synthesis of ethylene glycol polymer (EG1) Ten grams of NaH (60% dispersion) was slowly added to 100 g of ethylene glycol and 100 mL of dioxane in a 250 mL round-bottom flask fitted with a condenser, overhead stirrer, and gas inlet tube. The mixture was stirred at 23°C under N_2 flow for 2 h, after which time 6.0 g of polyVBC swollen in 40 mL of dioxane for 2 h was added. The mixture was refluxed for 17 h. The solution was removed, the beads were washed with dioxane, dioxane/water (1:1) and water, and then vacuum-dried at 70 °C for 12 h.

Synthesis of triethylene glycol polymer (EG3) EG3 was prepared in the same way as EG1 except that triethylene glycol was used.

Synthesis of ethylene glycol phosphate diethyl ester polymer (pEG1) EG1 was phosphorylated with diethyl chlorophosphate (DECP) in pyridine. The beads (2.0 g) in 50 mL of pyridine were stirred for 1 h, 10 mL DECP added, and the reaction stirred at 23°C for 17 h. The product was washed with 100 mL each of methanol, methanol/water (1:1), and water and then conditioned with 1 L of each 1.0 M NaOH, H_2O , 1.0 M HCl, and H_2O .

Synthesis of triethylene glycol phosphate diethyl ester polymer (pEG3) pEG3 was prepared in the same way as pEG1 except that 2.0 g EG3 was used.

Synthesis of ethylene glycol monoprotic phosphate polymer (pEG1M) Two grams of EG1 in 100 mL of pyridine were stirred with 10 g of 4-dimethylaminopyridine (DMAP) for 2 h in a 250 mL round-bottom flask; 10 mL DECP was then added and the mixture refluxed for 17 h. The resulting beads were washed with 100 mL each of methanol, methanol/water (1:1), water and then conditioned with 1 L of each 1.0 M NaOH, H_2O , 1.0 M HCl, and H_2O .

Synthesis of triethylene glycol monoprotic phosphate polymer (pEG3M) pEG3M was prepared in the same way as pEG1M except that 2.0 g EG3 was used.

Synthesis of diprotic phosphonic acid polymer (DPA) Five grams of polyVBC beads were refluxed with 50 mL triethyl phosphite for 17 h. After removal of remaining phosphite, the beads were washed with acetone, acetone/water (1:1), water, hydrolyzed by refluxing in 50 mL conc. HCl for 17 h, and then conditioned with 1 L of each 1.0 M NaOH, H₂O, 1.0 M HCl, and H₂O.

Characterization The acid capacity was determined by contacting 0.5 g Buchner-dried polymer with 50 mL 0.1000 N NaOH containing 5% NaCl for 17 h, and then titrating a 10 mL aliquot with 0.1000 M HCl using phenolphthalein as the indicator. The percent solids, defined as the ratio of dry to wet bead weight, was determined by Buchner-drying beads for 5 min to remove excess water (wet beads) and then oven-drying at 110 °C overnight (dry beads). The phosphorus capacity was measured after digesting 20 mg of polymer in 10 mL conc. H₂SO₄ and 32 mg CuSO₄ followed by reaction with vanadate-molybdate solution. The intensity of yellow coloration was measured at 470 nm on a Spectronic 21D (Milton Roy).

Metal ion sorption study The sorption of Lu(III), La(III), Al(III) and Fe(III) on DPA, pEG1M, pEG3M, pEG1, and pEG3 was studied by batch equilibration using 10⁻⁴ N metal ion solutions in 0.10, 0.50, 1.0, 3.0 and 6.0 M phosphoric acid solutions. A 10⁻⁴ M uranyl nitrate solution was prepared by diluting 1000 mg/L U(VI) standard solution. Enough Buchner-dried polymer to give 0.50 mmol P was shaken with 5 mL of metal ion solution for 17 h after it was pre-equilibrated three times with 0.10 M H₃PO₄ (each 15 min). Metal ion concentrations were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The percent sorption was calculated from the metal ion concentration before and after equilibration.

The kinetics of uranium sorption was evaluated by shaking pEG3M (0.5 mmol P) with 5 mL of 10⁻⁴ M U(VI) in 0.10, 1.0, and 3.0 M H₃PO₄ at 160 rpm for 10-300 min at 23°C. pEG3M was pretreated with 0.10 M H₃PO₄ solution three times, 15 min each. The kinetics of U(VI) sorption by DPA was also studied.

Results

Table 1 gives the acid and phosphorus capacities of the polymers. The results confirm that the diethyl esters have no acid capacity, DPA has two acidic protons per phosphorus ligand, and the monoethyl esters have no more than one acid site per ligand.

Table 1. Acid and phosphorus capacities of the polymers

Resin	Acid capacity (mmol/g)	Phosphorus capacity (mmol/g)	Acid/Phosphorus ratio
pEG1	0.06	2.28	/
pEG3	0.11	1.80	/
pEG1M	2.23	2.82	0.8
pEG3M	1.73	1.90	0.9
DPA	9.65	4.71	2.0

FTIR spectra are consistent with these results. The spectra for pEG1 and pEG1M, shown for the region 600 – 1600 cm^{-1} , are representative (Fig. 2). The P=O band appears at 1262 cm^{-1} for pEG1 and this shifts to 1229 cm^{-1} in the monoprotic ligand. The bands at approximately 1030 and 975 cm^{-1} are assigned to P-O(R) and P-O(H), respectively. The reason for the shift is discussed in the subsequent section.

pEG1

pEG1M

Fig. 2. FTIR spectra for pEG1 and pEG1M

Figure 3 shows the percent metal ion sorption on the neutral phosphates as a function of H_3PO_4 concentration. Both pEG1 and pEG3 have low metal ion affinities. Only 64% U(VI) could be sorbed on pEG3 from 0.10 M H_3PO_4 ; pEG1 shows an even lower affinity at 22% sorption. Increasing acid concentration decreases the complexing ability of both neutral phosphates. U(VI) sorption on pEG3 decreases to 31% from 0.50 M H_3PO_4 and 18% from 1.0 M H_3PO_4 ; pEG1 is ineffective from most solutions, sorbing only 15% U(VI) from 0.50 M H_3PO_4 and 13% from 1.0 M H_3PO_4 . Sorption of other trivalent ions by both pEG1 and pEG3 shows the same trend but with lower affinities. The affinity order of the neutral phosphate ligand from phosphoric acid solutions is $\text{U(VI)} > \text{Lu(III)}, \text{Fe(III)}, \text{La(III)} > \text{Al(III)}$.

Figure 4 shows the sorption of U(VI), Lu(III), La(III), Al(III) and Fe(III) by the acidic polymers from 0.10 to 6.0 M H_3PO_4 . The metal ions are efficiently sorbed from 0.10 M H_3PO_4 and the extent of decrease in sorption with increasing phosphoric acid concentrations depends on the ligand. Among the three polymers, the diprotic DPA with the highest phosphorus and acid capacities has the lowest metal ion affinities: only 34% U(VI) could be sorbed from 3.0 M H_3PO_4 while

Fig. 3. Metal ion sorption by the neutral phosphates

6.0 M H_3PO_4 deactivates it. The monoprotic polymers show a high U(VI) affinity that is less affected by the phosphoric acid concentration: U(VI) is efficiently sorbed from up to 3.0 M H_3PO_4 by pEG3M (91%). Increasing the acid concentration to 6.0 M decreases sorption to 47%. pEG1M is a weaker sorbent, complexing 67% and 29% U(VI) from 3.0 and 6.0 M H_3PO_4 , respectively.

The complexation of trivalent ions by the monoprotic polymers shows the same trend as that of U(VI): all were effectively sorbed from dilute solutions while increasing H_3PO_4 concentration gave decreasing uptake. DPA could sorb only 48% Lu(III), 14% La(III), 28% Fe(III) and 1.5% Al(III) from 3.0 M H_3PO_4 . Sorption of all metal ions by DPA from 6.0 M H_3PO_4 is < 10%. Complexation of Lu(III), La(III), Fe(III) and Al(III) by pEG3M is much higher; e.g., 90% Lu(III), 66% La(III), 71% Fe(III) and 53% Al(III) are complexed from 3.0 M H_3PO_4 . The affinity of pEG3M follows an order of U(VI), Lu(III) > Fe(III) > La(III) > Al(III) while pEG1M and DPA have affinity orders of Lu(III) > U(VI) > Fe(III) > La(III) > Al(III). pEG3M is more efficient in metal ion sorption than DPA. Ligand strength is thus pEG3M > pEG1M > DPA.

Fig. 4 Metal ion sorption by phosphorus acid polymers

Figure 5 shows the kinetics of U(VI) sorption by pEG3M and DPA from three H_3PO_4 concentrations. DPA requires 30 min to sorb 94% U(VI) from 0.10 M H_3PO_4 . Increasing the concentration to 1.0 and 3.0 M significantly decreases U(VI) sorption. pEG3M has much faster kinetics: U(VI) sorption reaches 99.9% from 0.10 M H_3PO_4 in 5 min and, from 1.0 M H_3PO_4 , reaches 90% at 1h. Increasing the H_3PO_4 concentration to 3.0 M further slows uranium-ligand binding: U(VI) sorption of 74%, 83%, and 90% are observed at 60, 120, and 300 min, respectively. Equilibrium is reached by 5 h. pEG3M has faster U(VI) sorption kinetics than DPA.

Fig. 5. U(VI) sorption kinetics by pEG3M and DPA

Discussion

Organophosphate esters coordinate uranyl nitrate from high nitric acid concentrations⁴ but complexation from phosphoric acid solutions is much lower and even 0.10 M H_3PO_4 significantly suppresses coordination by the phosphoryl oxygen. This extends to the hard Lewis acids¹⁷ Al(III), Fe(III), La(III), and Lu(III) which prefer to bind to a ligand with an exchangeable proton rather than coordinate to a phosphoryl oxygen. The basicity of the P=O is not high enough to compete with the more strongly basic phosphate ion. The effect of an increasing phosphoric acid concentration is superimposed upon this and the coordinating ability of the neutral oxygen donor decreases further due to competition by the protons for the binding sites.

Adding coordinating sites to a ligand can increase the extent of complexation and this is evident when comparing the results of pEG3 to pEG1. The higher affinity of the former suggests a contribution by the ether oxygen to coordination as seen with poly(oxyethylene) which wraps around metal ions.¹⁸ The different affinities of pEG1 and pEG3 indicate the importance of having more than one donor group per ligand to meet the coordination requirements of the metal ions and form stable chelates.¹⁹

In contrast to neutral coordinating ligands, ion exchange ligands form ionic bonds with ions that include U(VI), La(III), Lu(III), Fe(III) and Al(III). Many examples in the literature show the strength of ion exchange; e.g., the coordinating N,N,N',N'-tetrakis(2-pyridylmethyl)ethylenediamine forms stable complexes with lanthanides and actinides in 0.10 M NaClO_4 but the analogous ethylenediaminetetraacetic acid in which the pyridylmethyl groups are replaced with carboxylic acids has increased complex stabilities by > 11 orders of magnitude.²⁰ In comparing the results from the purely coordinating pEG1 to the ion exchange DPA, it is evident that affinities increase significantly in the less acidic solutions, but equally evident that sorption by DPA decreases as the acid concentration increases.

While DPA has a high protic density and it may be expected that a high concentration of exchange sites leads to uniformly high affinities, the literature suggests otherwise; for example, a phosphinic acid has higher lanthanide affinities from 0.50 M HCl than the corresponding phosphonic acid resin;²¹ and esterifying two of the four P-OH groups in methanediphosphonic

acid gives a new sorbent, Dipex, with much higher selectivity for polyvalent ions and stronger complexes than Diphonix with its *gem*-diphosphonic acid ligands.²² Dipex also shows faster and more efficient sorption of U(VI) than Diphonix.²³

The effect of decreasing the acid capacity while increasing the coordinating ability of the P=O by substituting an alkyl group for an acid site was studied by synthesizing pEG1M. (The increased coordinating ability is suggested by the shift in the FTIR bands (see below).) The addition of 4-dimethylaminopyridine (DMAP) was critical to forming the monoethyl ester. DECP forms the diethyl ester and a controlled hydrolysis with an amine was considered the most direct route to the monoester. Piperidine and piperazine have been used in the deesterification of phenyl thionoacetate,²⁴ poly(ethylenimine) has been used with substituted phenyl acetates,²⁵ and trihydroxymethylmethyllamine has been used on substituted phenyl- α -furoates.²⁶ Pyridine is obviously ineffective in the present case since it is the solvent in the DECP reaction to give the diethyl ester (its inability to catalyze the hydrolysis of tris-2-pyridyl phosphate in an intramolecular reaction has been ascribed to low basicity).²⁷ Dimethylamine was also found to be ineffective. Polymer-bound dialkylaminopyridine was reported to catalyze the hydrolysis of p-nitrophenyl acetate by reaction at the carbonyl group to deacetylate the ester.²⁸ Given its higher basicity over pyridine,²⁹ DMAP was utilized and found to cleave one of the ethoxy groups and thus yield the monoethyl ester:

The proposed mechanism involves formation of the diethyl ester by the highly reactive DECP followed by nucleophilic attack of DMAP at the P=O to give a tetrahedral intermediate that fragments to give the monoethyl ester; attack of a second DMAP is precluded due to steric hindrance. Subsequent contact with water yields the monoprotic ligand. Dimethylamino-

pyridine is far more effective than pyridine and dimethylamine due to its greater nucleophilicity and /or polarizability at the nitrogen: In a study of nucleophilic reactions by aryloxides on thiobenzoates, it was determined that a tetrahedral intermediate forms which then splits to form the product and that the polarizability of the attacking nucleophile, as defined by hard-soft-acid-base theory, has a large effect on the reaction rate.³⁰

The results in Figure 4 show pEG1M to have higher metal ion affinities than DPA across the range of acid concentrations. That a higher density of acid sites does not favor metal sorption is consistent with the observation that phosphorus acids tend to self-associate through hydrogen bonding between the P-OH and P=O groups³¹ leading to the formation of chain-like structures.³² Soluble phosphorus acids have intermediate acidity and ion exchange with metal ions but they dimerize and only one of the two acidic protons in the dimer is available for ion exchange. This is reflected in the infrared P=O stretching frequencies: an increase in the number of P-OH groups per phosphorus acid results in bathochromic shifts of the P=O bands. In this study, the P=O band position shifts from 1229 cm⁻¹ in pEG1M to 1180 cm⁻¹ in DPA. The P=O band appears at 1262 cm⁻¹ in pEG1 and this hypsochromic shift is due to the absence of hydrogen bonding: the -OH in pEG1M is more electronegative than -OEt in pEG1 and so the pEG1M P=O should appear at a higher frequency than pEG1. That it is lower is due to hydrogen bonding:³³ intra- and/or inter-ligand hydrogen bonding to the P=O decreases the electron density in the phosphoryl bond, resulting in the bathochromic shift. This is further compounded in DPA with its yet higher acid density and thus its still lower P=O band frequency; hydrogen bonding competes with the metal ions for binding and results in lower affinities. The neutral diethyl esters have weak affinities because an ion exchange component is necessary for increased binding strength. The monoester strikes a balance between ion exchange capability and decreased hydrogen bonding.

Incorporating ether oxygen into the phosphoric acid ligand further enhances metal affinities: pEG3M with three oxygen donors adjacent to the monoprotic site shows the highest affinity for metal ions from phosphoric acid solutions. While the decrease in affinities with increasing acid concentrations is seen with all polymers, it is less rapid than with pEG1M or DPA. The increasing affinities compared to pEG1M reflect involvement of the weakly binding ether oxygen donor

sites. High affinities thus involve both ion exchange with acidic sites and coordination with neutral donors. The more rapid kinetics of pEG3M relative to DPA (Fig. 5) is evidence for decreased hydrogen bonding which permits more rapid sorption.

A literature survey supports the importance of neutral donors in addition to acidic binding sites in ligand design. Synergistic effects of neutral and acidic reagents in solvent extraction are widely known. Solutions of di-2-ethylhexyl phosphoric acid and trioctylphosphine oxide at different ratios are efficient at extracting uranium from phosphoric acid.³⁴ Combining these two functional groups into one ligand further improves metal binding.³⁵ Dicarboxylic acids form lanthanide and actinide complexes but the bound ions still form covalent bonds with soft donor atoms.³⁶ Incorporating a carbonyl group into a supported phosphonic acid also improves its metal ion affinity.³⁷ The uranyl affinities are thus best summarized in Figure 6 to emphasize the importance of ligand acidity and auxiliary coordinating sites.

Fig. 6. Uranyl affinities of phosphorus-based ligands from 10^{-4} M U(VI) solutions.

Conclusion

This report extends our understanding of the variables involved in the rational design of polymer-supported reagents. Ligands with acid sites are important to high affinities but those sites must also be capable of a coordinative interaction with metal ions. Acidic ligands such as those in DPA bind metal ions but also interact with each other through hydrogen bonding and this limits their metal ion affinities. The stronger the hydrogen bonding, the more the metal ion has to first break the hydrogen bonds in order to react with the acid site; less hydrogen bonding will favor metal binding with the ligand and increase its affinity for metal ions. This is accomplished by partial esterification, as is evident with pEG1M. Metal ion sorption reflects a balance between ion exchange and coordination of ligands with metal ions. The still higher affinities of pEG3M show that auxiliary coordinating sites, such as ether oxygen, are necessary for optimal binding performance. It has the potential for being applied to wet process phosphoric acid and this will be reported in a subsequent publication along with an evaluation of its inherent polarizability through studies of Au(III) and Eu(III) binding.

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