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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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HIGHLIGHTS

- Polymer-bound monoprotic ligands developed for U(VI) sorption from 0.1 to 6 M H₃PO₄.
- Ligands are phosphorylated mono- and triethylene glycol monoethyl esters.
- Metal ion complexation by ion exchange through –OH and coordination through P=O.
- Decreased hydrogen bonding results in increased metal ion affinities.

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ABSTRACT

A polymer-bound monoprotic phosphoric acid ligand was developed for the sorption of U(VI) from 0.10 to 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.

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1. Introduction

Uranium concentrations in phosphate minerals range from 70 to 200 mg/kg and were considered a uranium resource (Guzmán et al., 1995). Moreover, phosphoric acid is a component of agricultural and industrial products (e.g., fertilizer, cleaners, toothpaste, beverages, food additives, and animal feed) (Weiner et al., 2001). 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 (Marcus and Kertes, 1969). The complexation of metal ions by coordinating phosphates is well known (Alexandratos and Zhu, 2007, 2005) and binding to uranyl from nitric acid solutions is the basis for the PUREX process (Dietz

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et al., 1995). Di(2-ethylhexyl)-phosphoric acid is often used in the presence of coordinating complexants for uranyl binding (Gadgila et al., 2014; Beltrami et al., 2014). They are capable of ion exchange over a relatively wide pH range and coordinate metal ions through the phosphoryl oxygen in acidic solution (Yamabe et al., 2001). Polymer-bound phosphorus acids have a very high U(VI) affinity (Egawa et al., 1984) and several have been examined for metal recovery from phosphoric acid though their affinity is limited from concentrated solutions (Kabay et al., 1998; Gonzalez-Luque and Streat, 1983).

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 (Alexandratos and Zhu, 2005), hydrogen bonding affects the affinities of amides for lanthanides (Yang and Alexandratos, 2010), and moieties bound to the amine nitrogen affect the affinity of U(VI) from seawater through ion exchange (Sellin and Alexandratos, 2013).

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 (Zhu and Alexandratos, 2014). 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 to 6.0 M phosphoric acid solutions. Though immobilized phosphorus acids have the same binding site as H_3PO_4 , 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.

2. Experimental

2.1. 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 μ m. 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.

2.2. 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.

2.3. Synthesis of triethylene glycol polymer (EG3)

EG3 was prepared in the same way as EG1 except that triethylene glycol was used.

2.4. 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 .

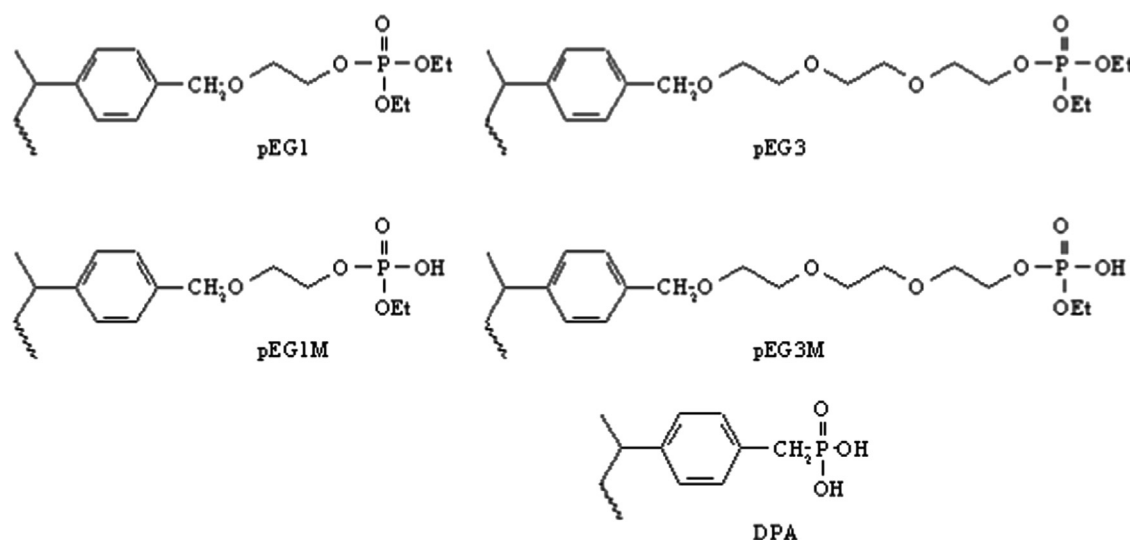


Fig. 1. The immobilized ligands: phosphorylated ethylene glycol diethyl ester (pEG1), triethylene glycol diethyl ester (pEG3), ethylene glycol monoethyl ester (pEG1M), triethylene glycol monoethyl ester (pEG3M), and diprotic phosphonic acid (DPA).

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