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Immobilized Phosphate Ligands with Enhanced Ionic Affinity through Supported Ligand Synergistic Interaction

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Immobilized Phosphate Ligands with Enhanced Ionic Affinity through Supported Ligand Synergistic Interaction

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Abstract: The ability of a secondary group to influence the metal ion affinities of a primary ligand immobilized on crosslinked polystyrene beads is reported. The secondary groups were glycol units, -$(CH_2CH_2O)_{1\text{-}4}$-, and their effect on phosphate ligands was studied. The affinities of Pb(II), Cd(II), Cu(II), Ni(II), Zn(II), Fe(III), Y(III), La(III), Eu(III), Lu(III), and U(VI) were quantified from HNO_3, HCl, and H_2SO_4 solutions in concentrations up to 4 N. Affinities were highest for U(VI) and the trivalent ions. The glycol units enhanced the extent of metal ion complexation by the phosphate ligands through coordination of the metal ion and not through an auxiliary group effect (where there would be a direct interaction between the glycol units and the phosphate ligand) as indicated by the similarity in the FTIR spectra of the four phosphorylated glycol resins. At least two glycol units are needed for synergistic cooperation between the glycol and phosphate in binding metal ions.

Keywords: Polymer, extractant, synergism, selective, metal

INTRODUCTION

The need to reduce the levels of heavy metal ions in wastewater has led to the development of new chelating resins. The efficiency of the metal complexation reaction is dependent on the structure of the immobilized ligand and the solution conditions; for example, ligands based on 2,2′-diaminobiphenyl

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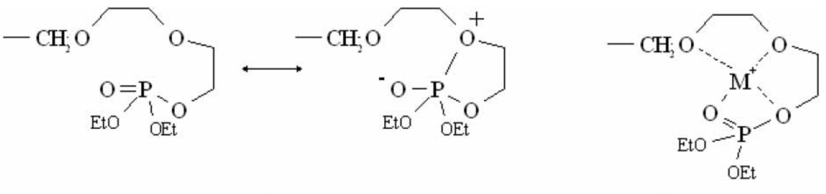
have a high affinity for Cu(II) from acidic solutions (1), tetraazacyclotetradecane has a high affinity for gold in solutions of pH 3 (2), and glucamine (but not sorbitol) is selective for arsenate from solutions of pH 4 to 6.5 (3). Multi-dentate ligands are effective complexants for transition metal ions because of their high coordination numbers (4). The flexible poly(ethylene glycol)s (PEGs) coordinate with metal ions at multiple sites by wrapping around them in a helical configuration (5). Single crystal X-ray analysis shows all of the oxygens are involved in coordinating the metal ion. The stability constants of PEGs with alkali metal ions increase as the length of the PEG increases (6). Ionic affinity is retained after immobilization onto polymer supports (7, 8).

Complexation at the phosphoryl oxygen has been studied through the development of neutral complexants soluble in organic solvents such tributyl phosphate and triphenylphosphine oxide (9). Research in the development of this moiety as part of an immobilized ligand is on-going. Polystyrene-bound phosphate diester ligands have a low affinity for metal ions from acidic solutions but their affinities increase significantly when coupled with -OH groups on diverse platforms such as immobilized calixarene (10) and pentaerythritol (11). Unlike phosphonic and phosphoric acid ligands, where the high affinities are due to ion exchange, the metal ion interaction with the diester ligand is through coordination at the phosphoryl oxygen. The mechanism by which -OH groups enhance the ionic affinities of the phosphoryl oxygen is hydrogen bonding which increases the electron density at the oxygen; this is supported by FTIR and solid state ^{31}P spectra as well as reports in the literature on soluble molecules such as the α-aminophosphonochloridates (12). Phosphate is thus the primary ligand whose ion-binding affinity is tuned by the auxiliary -OH groups.

The objective of this contribution was to determine whether glycol affects the ion-complexing ability of the phosphate ligand and, if so, whether it acts as an auxiliary group to increase the polarizability of the P═O (I) or as a coordinating group to synergistically bind the metal ion with the phosphate ligand (II). Additionally, in order to determine whether the number of oxygens in the glycol unit have an effect on the ionic affinities, ethylene glycol (EG1), di(ethylene glycol) (EG2), tri(ethylene glycol) (EG3), and tetra(ethylene glycol) (EG4) were immobilized onto crosslinked poly(vinylbenzyl chloride) beads followed by phosphorylation of the terminal hydroxyl groups (Fig. 1). The metal ions used to probe the affinities of the



I

II

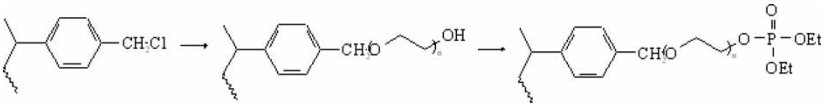


Figure 1. Synthesis of the phosphorylated glycols.

glycol and phosphorylated glycol were the divalent set used with the phosphorylated polyols from solutions of 0.01 N HNO_3 (Pb(II), Cd(II), Cu(II), Ni(II), Zn(II)), a set of trivalent ions (Fe(III), Y(III), La(III), Eu(III), and Lu(III)) spanning a range of electronic properties from solutions of HNO_3, HCl and H_2SO_4, and U(VI) due to the importance of identifying polymers that have high affinities for UO_2^{2+} to allow for its recovery within the nuclear fuel cycle. Only acidic solutions were studied because in solutions at or close to neutral pH, there is essentially quantitative complexation of the ions by immobilized phosphate ligands, with or without the presence of glycol units. Studies at these pH values would thus not be able to distinguish among the different polymers being reported.

EXPERIMENTAL

Copolymer beads of vinylbenzyl chloride (VBC) and divinylbenzene (DVB, 2 wt%) were prepared by suspension polymerization (13). The particle size used was 250–425 μm. The glycols, metal nitrate salts, and standard metal ion solutions were purchased from the Acros Chemical Co.

Synthesis of ethylene glycol resin (EG1). Ten grams of NaH (60% dispersion) is added slowly to a solution of ethylene glycol (100 g) in dioxane (100 mL) in a 250 mL roundbottom flask fitted with a condenser, overhead stirrer, and N_2 gas inlet tube. The solution is stirred under N_2 for 2 h to form the sodium glycolate and 6 g copolymer beads swollen in 50 mL of dioxane for 2 h are added to it. The reaction is refluxed for 17 h, cooled, the excess solution removed, the beads washed with dioxane, dioxane/water (1:1), and water, and vacuum dried at 70°C for 12 h.

Synthesis of di(ethylene glycol) (EG2), tri(ethylene glycol) (EG3), and tetra(ethylene glycol) (EG4) resins. The procedure is the same as that for the EG1 resin except for the use of di(ethylene glycol), tri(ethylene glycol) and tetra(ethylene glycol), respectively.

Synthesis of phosphorylated glycol resins (pEG1), (pEG2), (pEG3), (pEG4). Two grams of EG1, EG2, EG3, or EG4 are swollen in 100 mL of pyridine for 2 h in 250 mL roundbottom flasks, to which 10 mL of diethyl chlorophosphate are added. The mixtures are stirred for 17 h at room temperature, the excess solution removed, the beads washed with methanol, methanol/water (1:1), and water, and conditioned by eluting with 1 L each of 4% NaOH, water, 4% HCl, and water.

Characterization. The percent solids, acid capacity, and phosphorus capacity for each resin was determined (14). Spectra of the resins as KBr pellets were taken on a Bomem FTIR spectrophotometer.

Metal ion affinities. Solutions were prepared from reagent grade metal salts and nanopure water, except for uranium which was prepared from a standard solution of 1000 mg/L in 2% nitric acid. Affinities were quantified by batch equilibration of 10^{-4} N metal ion solutions in acid concentrations varying from 0.01 N to 4 N. Enough buchner-dried resin to give 1.0 mmol phosphorus was shaken with 10 mL of the given metal ion solution for 17 h after it was pre-equilibrated with background solutions at the same acid concentration as the metal-containing solution (3 × 15 min each). Metal ion concentrations were determined by inductively coupled plasma-atomic emission spectroscopy on a Spectroflame M120E. Sorption percentage was calculated from the ratio of final to initial concentration; the distribution coefficient was calculated from the ratio of mmol metal sorbed per g resin to mmol metal remaining in solution per mL solution.

RESULTS

pEG Resin Synthesis

The glycol units were immobilized to give the ethylene glycol (EG) resins by reaction of sodium glycolates $NaO(CH_2CH_2O)_nH$ (n = 1–4) with crosslinked poly(vinylbenzyl chloride) beads. No residual $-CH_2Cl$ groups remained, as indicated by the lack of chlorine content. The FTIR spectra were very similar: strong peaks centered at 3415, 1100, and 1070 cm^{-1} are assigned to the -OH, C-O(C), and C-O(H) bonds, respectively. The phosphorylated glycol resins (pEG1–pEG4) were prepared by subsequent reaction with diethyl chlorophosphate (Fig. 1). The FTIR spectra show the P=O and P-O(C) stretching vibrations centered at 1263 and 1033cm^{-1}, respectively.

Table 1 gives the acid and phosphorus capacities of the pEG resins. Since pyridine is a weak base and soluble with the glycols, it removes HCl formed as

Table 1. Characterization of the pEG resins

	pEG1	pEG2	pEG3	pEG4
Acid capacity (mmol/g)	0.12	0.03	0.20	0.12
Phosphorus capacity (mmol/g)	2.58	2.11	1.91	1.70
Theoretical P capacity (mmol/g)	3.05	2.68	2.39	2.15

by-product in the reaction. The lack of acid capacity indicates that the reaction occurs with no hydrolysis of the ester groups. The phosphorus capacity decreases from 2.58 to 1.70 mmol/g as the number of glycol units increase from one to four, as expected from the increase in molar mass of the ligand. The phosphorus capacity is 18% less than the theoretical value for pEG1 and 26% less for pEG2–4; this is probably due to an inability to attain complete phosphorylation. There is a large excess of glycolate and glycol in contact with the copolymer beads (the mole ratio of NaH:glycol: -CH_2Cl for the formation of EG1, EG2, EG3, and EG4 is 7:45:1, 7:26:1, 7:19:1, and 7:14:1, respectively) but at least some possibility of two CH_2Cl groups bonded to a single glycol molecule cannot be discounted.

Metal Ion Sorption from Different Acid Media

While polyethylene glycols are known to complex metal ions, the EG1, EG2, EG3, and EG4 resins have no affinity (<9%) for Pb(II), Cd(II), Cu(II), Ni(II), Zn(II), Fe(III), Y(III), La(III), Eu(III), Lu(III), and U(VI) from nitric acid solutions at final pH values of 2.0–2.7. The basicity of the glycol oxygens is thus too weak to displace the waters of hydration and coordinate with the metal ions.

Phosphorylation of the terminal -OH groups at the immobilized glycols has a significant effect on the amounts complexed from dilute acid solutions (Table 2). There is a greater affinity for trivalent than divalent ions: pEG4, for example, complexes 97% La(III) and only 37% Pb(II). pEG1 has the lowest affinities, pEG4 the highest, and the general trend is pEG4 > pEG3 > pEG2 > pEG1, though, with some ions, pEG3 and pEG4 have

Table 2. Metal ion affinities as percent complexed (and distribution coefficients) of the pEG resins from 0.01 N HNO_3 solution ($pH_f = 2.1$)

	pEG1	pEG2	pEG3	pEG4
Pb(II)	1.74% (0.37)	30.4% (11.9)	46.0% (15.3)	36.9% (10.7)
Cd(II)	—	18.6% (5.45)	23.5% (5.62)	19.6% (4.31)
Cu(II)	—	22.6% (6.85)	28.8% (7.36)	26.4% (6.54)
Ni(II)	—	6.60% (1.66)	9.72% (1.92)	9.38% (1.92)
Zn(II)	—	10.2% (2.60)	14.2% (3.09)	16.0% (3.25)
Al(III)	9.68% (1.68)	60.5% (35.3)	90.7% (179.8)	89.5% (154.9)
Fe(III)	14.4% (2.69)	84.3% (123.3)	94.2% (305.9)	90.3% (160.1)
Y(III)	14.7% (3.61)	46.6% (20.7)	79.1% (79.9)	87.3% (147.8)
La(III)	16.9% (3.22)	53.6% (24.8)	81.8% (83.3)	97.0% (554.8)
Eu(III)	15.7% (3.85)	64.9% (43.8)	90.6% (178.2)	98.1% (875.9)
Lu(III)	15.6% (3.86)	61.3% (33.7)	83.2% (101.6)	93.6% (258.2)
U(VI)	24.9% (7.57)	99.5% (4650)	99.5% (3960)	99.5% (2690)

Table 3. Metal ion affinities as percent complexed (and distribution coefficients) of the pEG resins from HNO_3 solution at $pH_f = 2.55$

	pEG1	pEG2	pEG3	pEG4
Pb(II)	16.5% (3.96)	37.4% (14.3)	64.1% (38.1)	71.1% (53.2)
Y(III)	13.4% (3.16)	80.8% (98.4)	97.4% (812.)	97.7% (929.)
Lu(III)	19.7% (5.03)	84.9% (128.)	97.2% (732.)	97.2% (765.)
U(VI)	27.1% (7.58)	99.95% (52960)	99.5% (3410)	99.2% (2380)

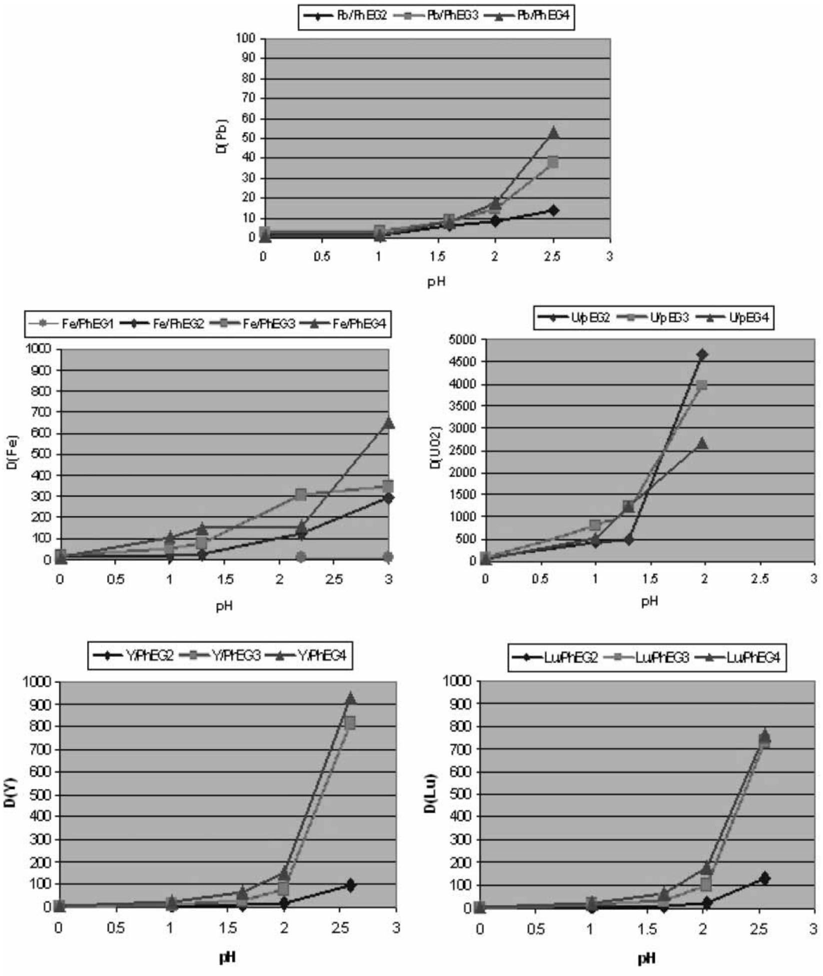


Figure 2. Distribution coefficients for Pb(II), U(VI), Fe(III), Y(III), and Lu(III) for the different pEG resins as a function of pH.

comparable affinities. The results far exceed the affinities displayed by the phosphonate diester resin where the extent of complexation is $<20\%$. The results are sensitive to pH and, as indicated with a representative set of ions (Table 3), complexation generally increases with decreasing solution acidity (though only marginally with pEG1).

The effect of solution pH on ionic affinities is especially evident over a wider range (Fig. 2). For Pb(II), Fe(III), Y(III), and Lu(III), the affinities are low below pH 1, then increase as the pH increases. The same trend is evident with the uranyl ion but with much higher distribution coefficients. The increase is especially pronounced with complexation of Y(III) and Lu(III) by pEG3 and pEG4. Sorption from 1 N HNO_3 with pEG4 is 74% with the uranyl ion, 45% with Fe(III), and negligible with the other ions. The affinities of the pEG resins follow the sequence U(VI) $\gg$ Fe(III) $>$ Y(III) $\sim$ Lu(III) $\gg$ Pb(II).

The sorption of uranium from HNO_3 was compared to that from HCl and H_2SO_4 solutions. Table 4 shows the percent complexation and distribution coefficients for pEG2, pEG3, and pEG4. In HNO_3, uptake decreases from 99.5% at pH 2 for all three resins to 65($\pm$5)% in 2 N solution then decreases only slightly at 4 N. The results are similar from HCl and H_2SO_4 solutions except at 4 N: complexation of UO_2^{2+} in both is comparable to the level in HNO_3 at pH 2, then the amounts decrease as the acidity increases. Sorption is lowest from 4 N H_2SO_4 solutions. Differences among the pEG resins within a given acid are not as pronounced with uranyl as they are with other ions. Results with the pEG1 resin have been reported (15): in HNO_3, HCl, and H_2SO_4, respectively, the percents complexed (distribution coefficients) are 24.9% (7.57), 33.2% (11.5), 19.1% (5.53) in 0.01 N; 38.8% (14.4), 22.0% (6.29), 13.0% (3.44) in 0.10 N; 43.6% (17.2), 28.8% (8.99), 3.15% (0.74) in 1 N; 48.2% (20.9), 38.6% (14.5), 8.88% (2.15) in 2 N; and 60.1% (33.5), 57.1% (31.9), 13.7% (3.61) in 4 N.

DISCUSSION

Binding by the Glycol in the Absence of Phosphate

The EG resins have negligible affinity for metal ions under the conditions tested: the basicity of the glycol oxygens alone is too weak to form a stable metal complex from acidic solutions. Similar results were found in solvent extraction studies: a 0.1 M solution of poly(ethylene glycol) with a molecular weight of 600 in dichloroethane or nitrobenzene extracts less than 10% Eu(III) from a 100 ppm solution in the presence of 0.01 M picrate as the counterion (16). Though complexes of lanthanide ions with poly(ethylene glycol)s of varying molecular weight have been reported from anhydrous systems (17), their stabilities decrease significantly upon the introduction of water due to competing coordination by water molecules (18).

Table 4. Uranyl ion affinities as percent complexed (and distribution coefficients) by the pEG resins from HNO_3, HCl and H_2SO_4 solutions

	pEG2			pEG3			pEG4		
Acid (N)	HNO_3	HCl	H_2SO_4	HNO_3	HCl	H_2SO_4	HNO_3	HCl	H_2SO_4
0.01[a]	99.5% (4650)	98.4% (1450)	96.2% (565)	99.5% (3960)	99.3% (3090)	99.4% (3180)	99.5% (2690)	99.1% (1870)	99.0% (1440)
0.05	95.8% (496)	94.6% (461)	91.5% (289)	98.5% (1220)	97.8% (997)	94.3% (383)	98.9% (1220)	97.1% (634)	94.1% (299)
0.10	95.1% (419)	88.9% (213)	82.8% (130)	97.7% (808)	97.7% (993)	93.3% (268)	97.3% (515)	96.7% (504)	92.8% (178)
1.00	81.7% (98.0)	56.5% (30.0)	54.7% (26.8)	80.5% (78.6)	54.6% (27.9)	54.5% (22.9)	74.2% (40.9)	55.1% (20.6)	52.4% (15.5)
2.00	69.5% (50.1)	37.8% (16.7)	39.4% (14.7)	65.7% (36.7)	39.5% (15.1)	39.0% (12.0)	59.8% (20.9)	36.3% (9.49)	35.7% (7.73)
4.00	67.9% (51.3)	41.9% (16.5)	15.7% (4.11)	62.4% (31.6)	34.6% (12.2)	11.8% (2.54)	55.1% (17.0)	31.1% (7.59)	9.65% (1.52)

[a] Actual pH of equilibrated solution was 1.98.

Metal Ion Affinities at pH 2.1

The results in Table 2 show that phosphorylation of the glycol units is important to the complexation of metal ions in solution. The ionic affinity of the pEG1 resin is uniformly low. Earlier research has shown that this is due to a low binding affinity at the ligand; there is no steric interference from proximity to the polymer backbone (11). For pEG2–pEG4, there is a greater affinity for lead within the divalent ions (Pb, Cd, Cu, Ni, Zn), but the overall affinity for those ions is much less than observed with the phosphorylated polyol resins (11). This indicates that though the polarizability of the phosphoryl oxygen is still a factor in determining the metal ion affinities, its polarizability has not been enhanced by auxiliary groups as it was when -OH groups were present. Results with the trivalent ions lead to the inference that the important variable with glycol units is their ability to coordinate with these ions and that this coordination does not occur with divalent ions. Additionally, the extent of complexation depends upon the number of glycol units. One glycol unit does not form stable metal complexes in cooperation with the phosphoryl ligand since there is only one ether oxygen available and that oxygen is a more poorly binding benzylic ether than a more basic alkyl ether (19). At least two glycol units are needed for significant metal ion complexation since this increases the number of alkyl ether oxygens available for coordination. The pEG resins show the affinity order: $U(VI) \gg Fe(III) > Y(III) \sim Lu(III) \gg Pb(II)$, with the higher oxidation states allowing for increased electrostatic attraction to the ether oxygens. Coordination of metal ions to ligands can be controlled by their charge density (20).

Metal Ion Affinities at pH 2.55

Metal ion coordination occurs with the glycol oxygens and the phosphoryl ligand. Though ion exchange is not involved in the mechanism, the extent of complexation is still affected by the solution acidity. As indicated by Table 3, complexation increases as the solution pH increases. This is due to competition by the protons for the phosphoryl oxygen. The affinity of the phosphoryl oxygen for acid is known: nitric acid is extracted by tributyl phosphate from spent etching solution containing copper, lead, tin, and iron (21).

Metal Ion Affinities from Highly Acidic Solutions

The acidity of the solution in contact with the resins is important in determining the extent to which metal ions will be complexed (Fig. 2). Only the uranyl ion has a sufficiently high affinity to overcome competition for binding sites by H^+ from solutions at a pH of 1. The highest affinities remain for U(VI), followed by Fe(III), at least below pH 2.2, then Y(III) and Lu(III), which are similarly complexed, and Pb(II), whose affinity is low. The ability to complex metal ions is highest with pEG4 and slightly less with pEG3; pEG2 has significantly lower affinities, especially in the less acidic solutions, and pEG1 has uniformly low affinities. This corresponds to a decreasing number of alkyl ether oxygens available for complexation (3, 2, 1, and 0, respectively). The uranyl ion is unique in not preferring a given pEG, probably due to the greater electrostatic attraction of the U(VI) for the alkyl ether oxygens (the higher distribution coefficients by pEG2, followed by pEG3 and pEG4, are not reflective of higher affinities but, rather, are an artifact of being a weight-dependent quantity; the percents complexed, determined from the same initial ratio of M^{n+} : ligand, are similar).

Affinities for the Uranyl Ion from Different Acids

Table 4 quantifies the uranyl ion affinities for the pEG polymers over a range of solution acidities. Since the phosphorylated glycol is a neutral complexant, sorption of cations is accompanied by the anions in solution. A change in acid type and acid concentration will affect the apparent affinity by changes in mechanism (from direct coordination at the phosphoryl oxygen in low acidity to anion exchange at the protonated P=O in high acidity), speciation, and ion pair formation (contact vs solvent-separated). When comparing a series of resins at a given acid concentration, the solution conditions remain constant and the results reflect the affinity of the immobilized ligand for the metal species. In the present case, it is reasonable to assume that the results in 0.01 N acid reflect direct coordination to the phosphoryl oxygen, those in 4 N acid reflect ion exchange at the protonated ligand, and the intermediate acid concentrations reflect a mix of the two mechanisms. At low acidity, the metal ion coordinates to the polar phosphoryl oxygen and the oxygens of the glycol units. As the hydrogen ion concentration increases, it competes more effectively for the phosphoryl oxygen thus decreasing direct coordination of the P=O to the metal ion. However, the uranyl ion forms anionic complexes at the higher acid concentrations and, for example, as the HNO_3 concentration increases to 4 N, $UO_2(NO_3)_3^-$ can exchange into the resin phase.

The general trends in Table 4 are that there may be a slight preference for pEG3 in 0.01 N, 0.05 N, and 0.01 N acid and there may be a slight decrease in sorption from solutions in the order $HNO_3 > HCl > H_2SO_4$. In 4 N acid, sorption by pEG2 is preferred and, for all pEGs, sorption decreases with $HNO_3 > HCl > H_2SO_4$. In 1 N and 2 N acid, any trend of pEG2 > pEG3 > pEG4 is slight; sorption is greater from HNO_3 but the difference between HCl and H_2SO_4 is minimal. Coordination remains greater with the nitrate perhaps because it forms a stronger complex with the uranyl cation and it loses its waters of hydration more easily. Binding in less acidic solutions thus favors pEG3 and there is no significant dependence on anion because there is sufficient enthalpy gain from binding to the uranyl ion. Binding to two alkyl ether oxygens is preferred; one alkyl ether oxygen (pEG2) is insufficient and three ether oxygens (pEG4) may not gain enough in enthalpy to offset the entropy loss. As solution acidity increases, especially at 4 N, ion exchange at the phosphate dominates and there is decreased participation by the ether oxygens. This is consistent with the preference for pEG2 since, with the dominance of ion exchange, the increasing length of the chain simply results in a loss of entropy with no compensating gain in enthalpy. The pEG1 results confirm these conclusions: only in 4 N acid, where coordination to the ether oxygens is unimportant, does pEG1 complex at a level comparable to the other polymers (e.g., 60.1% from HNO_3 compared to 62.4% for pEG3). When coordination by the ether oxygens is important, pEG1 is far less preferred than the other polymers; thus from 0.01 N HNO_3, pEG1 complexes only 24.9% UO_2^{2+}, compared to 99.5% for the other three polymers.

Mechanism of Metal Ion Binding

There are two mechanisms whereby a secondary group can influence the binding of metals to a ligand: as an auxiliary group affecting the electron density at the ligand and by synergistically cooperating with the ligand in binding directly to the metal ion. The presence of an auxiliary group effect is indicated by FTIR spectra of the phosphorylated resins, either through the appearance of a peak associated with hydrogen bonding at 874–895 cm^{-1} or a downward shift of the P═O peak from 1261 to 1211 cm^{-1} as hydrogen bonding increases (11, 22). With pEG1–pEG4, the nearly identical FTIR spectra and the appearance of the P═O band at 1263 cm^{-1} indicate the absence of any effect of the glycol units on the phosphoryl oxygen despite differences in ionic affinities. Those affinities are thus affected by coordination of the glycol units to the metal ion in cooperation with the phosphate ligand. The interaction illustrated by structure [I] does not occur and the supported ligand synergistic interaction depicted by structure [II] is operative.

A closer examination of the FTIR spectra for the four pEG resins shows an interesting difference in intensities for two bands centered around a large band at 1033 cm^{-1}, one at ~1103 cm^{-1} and one at 979 cm^{-1} (Fig. 3). Qualitatively, the intensity ratio of the two bands (1103:979) increases monotonically across the series pEG1 to pEG4: the 1103 band is less intense than the 979 band in pEG1 and the former grows while the latter recedes along the series pEG2, pEG3, and pEG4. Given that there is a band at 1103 cm^{-1} in the EG resins, the 1103 cm^{-1} band in the pEG resins is assigned to C-O(C) and the 979 cm^{-1} band to either P-O(C) or C-O(P). FTIR spectra of tributyl phosphate (23) assign the P-O(C) stretch to a band at 910 cm^{-1} and the in-phase C-O(P) stretch to the band at 1028 cm^{-1}. In the phosphorylated

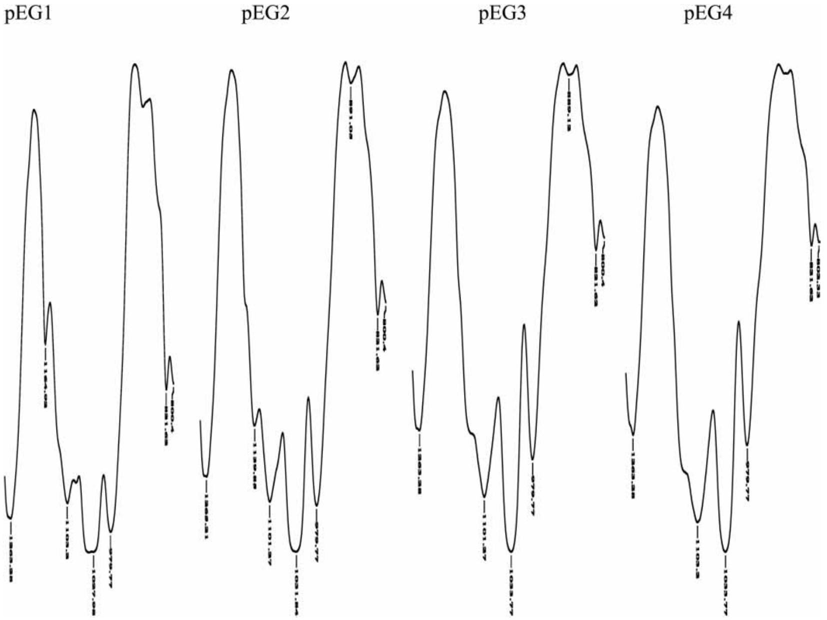


Figure 3. FTIR spectra of the pEG resins in the interval 1270–900 cm^{-1} (band positions- pEG1: 1263, 1165, 1103, 1028, 978; pEG2: 1265, 1140, 1101, 1032, 978; pEG3: 1263, 1101, 1034, 978; pEG4: 1263, 1103, 1034, 978 cm^{-1}).

resins pEG1 to pEG4, the number of C-O(C) bonds increases while the number of phosphorus-oxygen bonds remains the same and this can result in the increasing intensity ratio. The band at 979 cm^{-1} is thus assigned to P-O(C) and the band at 1033 cm^{-1} assigned to C-O(P). Note that the middle band at 1033 cm^{-1} decreases in intensity from pEG1 to pEG4 (while still remaining the strongest of the three bands) paralleling the behavior of the P-O(C) band-as would be expected if both reflect phosphorylation of an increasingly long glycol chain. These assignments will be useful as the auxiliary group effect is correlated with changes in the electron densities at the phosphate P═O and P-O bonds in research to appear in due course.

CONCLUSION

Phosphate diester ligands bound to glycol units have far greater metal ion affinities than diester ligands alone. Neither the phosphate ligands nor the glycol units alone complex metal ions from acidic solutions (pH $\leq$ 2). The influence of the glycol on the distribution coefficients is not as an auxiliary group, i.e., through interaction of the glycol oxygens to increase the phosphoryl oxygen's polarizability, since pEG1 shows low distribution coefficients and the FTIR spectra show no shift of the P═O band to lower energy along the series from pEG1 to pEG4, as would be expected from the increase in extent of metal ion coordination. The high distribution coefficients are ascribed to synergistic cooperation between the phosphoryl oxygen and the glycol units with the affinity order being U(VI)$\gg$Fe(III) $>$ Lu(III) $\sim$ Y(III) $\gg$ Pb(II). Two different sorption mechanisms are operative with U(VI): coordination in low acid solution and anion exchange in high acid solution. For all ions, coordination requires a minimum of two glycol units.

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