

Effect of Hydrogen-Bonding in the Development of High-Affinity Metal Ion Complexants: Polymer-Bound Phosphorylated Cyclodextrin

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Received 15 June 2010; accepted 12 September 2010

DOI 10.1002/app.33665

Published online 28 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: In a series of phosphorylated polyols bound to a polystyrene support, the position of the FTIR band assigned to hydrogen bonding between the —OH and phosphoryl oxygen correlates with the affinity of that phosphoryl oxygen for metal ions. Polymer with phosphorylated β -cyclodextrin (pCD) ligands is now reported as a further test of this correlation. The metal ion affinity is probed with the uranyl ion. pCD is the most red-shifted of a series of five phosphorylated polyols: the strongest polyol had been phosphorylated pentaerythritol (pPE) with a band at 873 cm^{-1} ; pCD has a band at 868 cm^{-1} . Consistent with the FTIR bands, pCD has a significantly higher affinity for the uranyl ion than pPE: the percents complexed

from a 10^{-4}M uranyl solution in a background of 1.0N HNO_3 , HCl , and H_2SO_4 are 94.7%, 90.5%, and 93.6%, respectively, for pCD and 68.6%, 52.1%, and 40.1%, respectively, for pPE. This further supports the hypothesis that the strong complexing ability of phosphorylated polyols is due to activation of the phosphoryl oxygen through hydrogen bonding between the $\text{P}=\text{O}$ and the —OH groups within the polyol. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1137–1142, 2011

Key words: separations; metal ion; functionalization; polymer; resin

INTRODUCTION

The preparation of polystyrene-bound complexants with a high affinity for metal ions is important to numerous applications including environmental remediation, catalysis, chromatographic separations, and sensor technology. For example, YbCl_3 on pyridine-bis(oxazoline) was used as an asymmetric catalyst,¹ VO on 2-(2'-hydroxyphenyl)benzimidazole acted as an oxidation catalyst,² and 2-(aminomethyl)pyridine had a high affinity for Cu(II) from aqueous solutions.³

An alternative approach is to attach ligands to immobilized scaffolds and vary the ionic affinity of the ligand as a function of the scaffold.⁴ This occurs through the influence on the ligand of the groups on the scaffold that remain unfunctionalized. Simple polyols (glycerol, pentaerythritol, tris(hydroxymethyl)ethane, and pentaerythritol triethoxylate) were immobilized onto crosslinked poly(vinylbenzyl chloride) and monophosphorylated to the diethyl phos-

phate ligand. Scaffolds thus allow for a controlled variation in the stereochemical arrangement of auxiliary groups such as —OH around the ligand.

Phosphorylated pentaerythritol (pPE) has the highest affinities for divalent and trivalent ions, then phosphorylated glycerol (pGly), phosphorylated pentaerythritol triethoxylate (pPT), and phosphorylated tris(hydroxymethyl)ethane (ptris), though the site of interaction remains the $\text{P}=\text{O}$ moiety for all polymers (Fig. 1). Phosphorylated ethylene glycol (pEG1), with no —OH groups, has a very low affinity for metal ions. The increase in affinity was consistent with an increase in polarizability of the phosphoryl oxygen arising from hydrogen bonding to the —OH groups. Hydrogen bonding to the $\text{P}=\text{O}$ has been reported with (2-hydroxyalkyl)phosphonates⁵ and phosphonylammonium salts,⁶ and found to affect the electron density at the phosphoryl moiety. Metal ion affinities correlate with a band in the FTIR spectrum due to hydrogen bonding at the phosphoryl oxygen: the higher the ionic affinity, the more bathochromic the shift: pGly and pPE have the band at 889.1 and 873.7 cm^{-1} , respectively. The phosphorylated pentaerythritol has the highest affinity in this series for U(VI); as measured by the percent complexation (and the distribution coefficient, D), the values from 0.01N HNO_3 are 99.4% (3870), from 0.01N HCl are 91.5% (245), and from 0.01N H_2SO_4 are 97.5% (815).⁷

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Contract grant sponsor: Department of Energy, Office of Basic Energy Sciences; contract grant number: DE-FG02-ER15287.

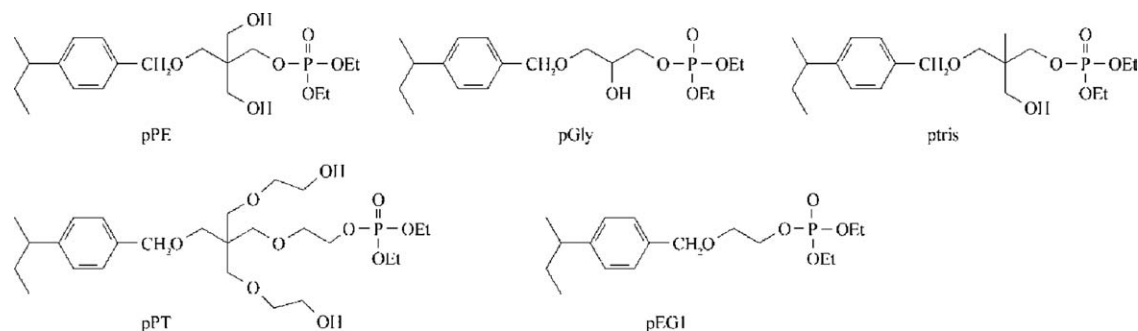


Figure 1 Structures of polystyrene-bound phosphorylated polyols.

Cyclodextrin is an oligosaccharide with α -, β -, and γ - isomers of 6, 7, and 8 glucose units, respectively.⁸ Their cyclic structures result in a hydrophobic cavity and hydrophilic rims, allowing them to act as hosts for the inclusion of hydrophobic guest molecules held by noncovalent interactions. This has proven useful in biomedical, agricultural, food processing, and environmental applications. Functionalizing soluble cyclodextrins with amines and binding to Cu(II) allows for their study as enzyme mimics.⁹ Unfunctionalized cyclodextrins bind transition metals through ion exchange at the $-\text{OH}$ groups but only from alkaline solutions.¹⁰

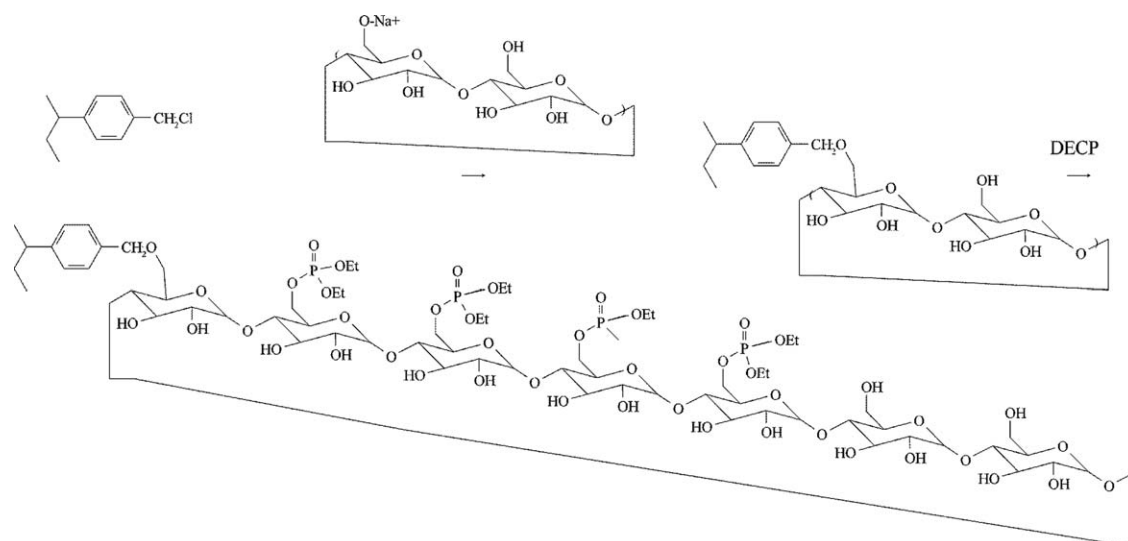
The study of hydrogen bonding as a mechanism for increasing the ionic affinity of a given ligand was extended to β -cyclodextrin (CD) as the first in a series of complex polyol scaffolds. CD was chosen because of its well-defined structure of $-\text{OH}$ groups around a phosphate ligand bonded to the CD in a subsequent step. The extent to which hydrogen bonding between the $-\text{OH}$ and phosphoryl moieties occurred would be examined by FTIR and metal ion affinities then determined, especially with the uranyl ion due to its high affinity for pPE.⁷

EXPERIMENTAL

The suspension polymerization of vinylbenzyl chloride (VBC) and 2 wt % divinylbenzene (DVB) gave beads with a particle size of 250–325 μm .¹¹ All chemicals, including the monomers, were purchased from the Sigma-Aldrich or Acros Chemical Companies. The β -cyclodextrin was in the hydrated form and dried in a vacuum oven at 70°C for 24 h before being used.

Polymer-supported β -cyclodextrin

In a 500-mL round-bottom flask fitted with a condenser, overhead stirrer, gas inlet tube, and thermometer, cyclodextrin (CD; 75.0 g, 66 mmol) was heated in 250 mL *N*-methylpyrrolidone (NMP) at 80°C to get a homogeneous solution. NaH (2.6 g of a 60% dispersion, 65 mmol) was then added slowly under a gentle N_2 flow and the mixture stirred at 80°C for 2 h. PolyVBC beads (1.3 g) in 30 mL NMP were added to the mixture and the reaction kept at 80°C for 72 h. After cooling, the solution was removed and the beads washed with NMP,



Scheme 1

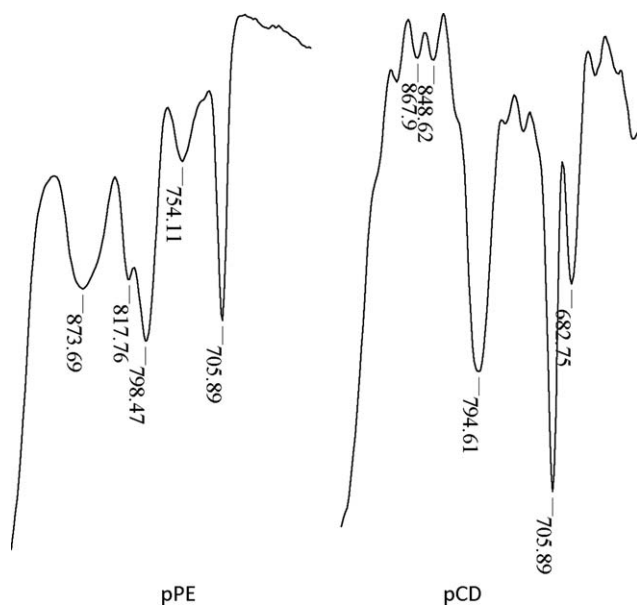


Figure 2 IR spectra of pPE and pCD between 600–960 cm^{-1} .

NMP:H₂O (1: 1), and water, filtered, and dried in a vacuum oven at 70°C for 12 h.

Phosphorylation of CD

The CD beads (1.5 g) were swelled in 100 mL pyridine for 2 h in a 250-mL round-bottom flask. Diethyl chlorophosphate (DECP, 30 mL) was added and the mixture stirred for 3 days at 25°C. The solution was removed and the beads washed with 100 mL each of methanol, 50% aqueous methanol, water, then placed in a glass frit funnel and conditioned by eluting with 1 L each of 4% NaOH, H₂O, 4% HCl, and H₂O.

Characterization

The acid capacity was determined by shaking 0.5 g of the conditioned beads dried in a Büchner funnel (for 5 min at a reduced pressure of 720 Torr to ensure reproducibility) with 50 mL of 0.1000N NaOH for 17 h, and then titrating a 10-mL aliquot with 0.1000N HCl. The phosphorus capacity was

determined by mineralizing 20 mg of beads in concentrated sulfuric acid in the presence of copper sulfate and subsequent reaction with ammonium vanadate-molybdate. The intensity of the yellow color is directly related to the phosphorus capacity via a calibration curve and measured at 470 nm on a Milton Roy Spectronic 21D. The chlorine content was determined by combusting the beads in a small oxygen-filled tank and titrating the resulting solution with silver thiocyanate. FTIR spectra of the beads were taken as KBr pellets on a Bomem FTIR spectrophotometer.

Metal ion affinities

Affinities were quantified by batch equilibration using 10⁻⁴ N metal ion (Fe(III), Pb(II), Cd(II), Cu(II), and Zn(II)) solutions in 0.01, 0.05, 0.10, 0.50, and 1.0N nitric acid. Also studied were 10⁻⁴N solutions of U(VI) in 0.01N and 1N HNO₃, HCl, and H₂SO₄. An amount of Büchner-dried beads to give 0.50 mmol phosphorus was shaken with 5 mL of a given metal ion solution for 17 h after being pre-equilibrated by shaking with the appropriate background solution three times 15 min each. The solution concentrations were determined by ICP-AES on a Spectroflame M120E. The results are reported in terms of the percent complexed ($100((\text{mmol M}^{n+})_{\text{initial}} - (\text{mmol M}^{n+})_{\text{final}})/(\text{mmol M}^{n+})_{\text{initial}}$) and the logarithm of the distribution coefficient, D , $((\text{mmol M}^{n+})_{\text{final}}/g_{\text{polymer}})/((\text{mmol M}^{n+})_{\text{final}}/\text{mL}_{\text{soln}})$.

RESULTS

CD was immobilized onto polyVBC beads by first converting it to its sodium salt (Scheme 1). A homogeneous solution is important when functionalizing crosslinked polymers to ensure uniform substitution. While dimethyl sulfoxide and pyridine both dissolve CD, they also react with polyVBC. NMP is the best solvent since it dissolves the CD and its sodium salt and does not affect the polyVBC at or below 80°C. At a 1 : 1 ratio of -CH₂Cl moieties on the polyVBC and the sodium salt of the CD (NaCD), the chlorine capacity decreased from 6.19 mmol/g to 2.94 mmol/

TABLE I
Percent Complexation (log D) of Divalent Ions by pCD as a Function of HNO₃ Concentration^a

[HNO ₃]	0.01 N	0.05 N	0.10 N	0.50 N	1.00 N
Pb	93.2% (2.52)	81.4% (2.03)	74.6% (1.85)	32.2% (1.06)	11.9% (0.52)
Cd	83.3% (2.10)	45.8% (1.34)	28.5% (1.00)	11.7% (0.25)	3.2% (-0.03)
Cu	81.5% (2.04)	22.0% (0.85)	3.7% (0.00)	0.0% (0.00)	1.0% (-0.58)
Zn	65.8% (1.70)	19.8% (0.81)	3.8% (0.01)	2.6% (-0.16)	1.8% (-0.33)

^a The values for the percent complexation are reproducible to $\pm 3\%$.

TABLE II
Percent Complexation (log *D*) of Divalent Ions by pPE as a Function of HNO₃ Concentration

[HNO ₃]	0.01 N	0.05 N	1.00 N
Pb	96.1% (2.81)	60.2% (1.57)	11.0% (0.49)
Cd	88.2% (2.31)	28.5% (0.98)	5.2% (0.13)
Cu	89.6% (2.35)	28.8% (0.99)	4.0% (0.00)
Zn	41.9% (1.17)	10.6% (0.46)	–

g at a 17 h reaction time. Increasing the time to 72 h resulted in a further decrease to 2.47 mmol Cl/g. Increasing the ratio to 1: 6.5 gave a chlorine capacity of 1.87 mmol/g at a 17 h reaction time, while a ratio of 1: 8 and a 72 h reaction time gave complete reaction (no chlorine left) and is the preferred reaction condition. The issue is not accessibility of the CD into the polymer bead: using macroporous polyVBC crosslinked with 5% divinylbenzene to maintain structural integrity, a 1: 9 ratio and a 17 h reaction time gave 2.27 mmol Cl/g (from an initial value of 5.13 mmol/g) and an increase to 72 h still left 0.88 mmol Cl/g. FTIR spectra of CD and immobilized CD show common bands, especially in the region 946–1155 cm⁻¹.

Reaction with DECP in pyridine gave pCD with a phosphorus capacity of 1.96 mmol/g. The FTIR shows the band for the phosphoryl oxygen at 1259 cm⁻¹, similar to that with the phosphorylated polyols. Figure 2 compares the IR spectra of pCD and pPE between 600–960 cm⁻¹. The H-bonding band at 867.9 cm⁻¹ is lower than pPE and, based on results with the phosphorylated polyols, high metal ion affinities for pCD were expected. (Immobilized CD has no band between 842 and 892 cm⁻¹.)

The metal ion affinity of pCD was first evaluated with the divalent ions used with the polyols as a function of the acidity of the background HNO₃ solution: 0.01, 0.05, 0.10, 0.50, and 1.00N (Table I). The results are compared to those of pPE from 0.01, 0.05, and 1N HNO₃ solutions (Table II). The affinity sequence is Pb(II) > Cd(II) > Cu(II) > Zn(II) for both pCD and pPE. As reported with pPE,¹² there is a linear correlation with the Misono softness param-

eter, indicating that a single-site interaction is operative with polarizability as the dominant variable. The highest affinities are from the least acidic solution due to decreased competition from H⁺ for the P=O. The unphosphorylated cyclodextrin resin has no affinity for these ions from 0.01N HNO₃. Thus, pCD and pPE have equivalent affinities for the divalent ions: the strength of the metal ion interaction with the phosphoryl oxygen has reached its maximum value.

The study was extended to trivalent ions (Table III). The results show that the two polymers have comparable affinities, though pCD may be somewhat stronger from 1.0N HNO₃.

It is more difficult to coordinate metal ions from H₂SO₄ than HNO₃ or HCl.¹³ The sulfate ion is more stable in the aqueous phase, as indicated by its high energy of hydration, rather than be removed from the water as it accompanies the cation into the resin phase. Removal of the ions from H₂SO₄ solutions was thus used as the probe to determine whether there was a significant difference in ligand strengths between the pCD and pPE. The results in Table IV demonstrate that pCD is a stronger ligand than pPE, in line with the positions of the hydrogen bonding bands at 867.9 and 873.7 cm⁻¹, respectively.

The results were extended to the uranyl ion in HNO₃, HCl, and H₂SO₄ solutions and confirm that pCD is a high-affinity ligand (Table V).

DISCUSSION

The bulkiness of CD does not preclude its reaction within the polystyrene network. However, a polymer matrix with maximum flexibility (as would be true when crosslinked with 2% DVB) in a solvent that swells the beads (NMP) is critical to achieving complete functionalization. FTIR spectra show that CD is stable to the immobilization conditions.

Phosphorylation of the immobilized CD with DECP in pyridine gives 1.96 mmol P per g polymer. Assuming that phosphorylation occurs only at the primary –CH₂OH groups since earlier studies found no conditions that allowed difunctionalization of

TABLE III
Percent Complexation (log *D*) of Trivalent Ions by pCD and pPE from 0.01 and 1.0N HNO₃

[HNO ₃]	pCD		pPE	
	0.01 N	1.0 N	0.01 N	1.0 N
Fe	96.9% (2.82)	30.5% (1.13)	75.3% (1.84)	28.0% (0.94)
Al	87.2% (2.16)	7.87% (0.27)	88.5% (2.26)	4.12% (–0.01)
La	96.3% (2.74)	39.2% (1.13)	96.9% (2.85)	24.8% (0.87)
Eu	97.4% (2.90)	40.2% (1.15)	98.4% (3.23)	18.7% (0.71)
Lu	94.8% (2.60)	28.7% (0.94)	98.4% (3.14)	13.5% (0.55)

TABLE IV
Percent Complexation (log *D*) of Trivalent Ions by pCD and pPE from 0.01 and 1.0N H₂SO₄

[H ₂ SO ₄]	pCD		pPE	
	0.01 N	1.0 N	0.01 N	1.0 N
Fe	97.7% (2.96)	88.4% (2.22)	95.8% (2.77)	16.6% (0.69)
La	99.6% (3.70)	57.3% (1.46)	98.7% (3.27)	3.70% (-0.04)
Lu	99.2% (3.47)	46.3% (1.27)	98.4% (3.18)	3.28% (-0.06)

TABLE V
Percent Complexation (log *D*) of U(VI) by pCD and pPE from HNO₃, HCl, and H₂SO₄ Solutions

[HNO ₃]	pCD		pPE	
	0.01 N	1.0 N	0.01 N	1.0 N
[HNO ₃]	99.9% (4.30)	94.7% (2.59)	99.4% (3.59)	68.6% (1.70)
[HCl]	94.6% (2.58)	90.5% (2.33)	91.5% (2.39)	52.1% (1.40)
[H ₂ SO ₄]	99.9% (4.63)	93.6% (2.49)	97.5% (2.91)	40.1% (1.18)

immobilized glycerol and since there are seven -CH₂OH groups in β-cyclodextrin with one used for binding to the -CH₂Cl moieties, there are a maximum of six -CH₂OH groups that can be phosphorylated. Monophosphorylation gives a theoretical phosphorus capacity of 0.69 mmol/g. The experimental value of 1.96 mmol/g best corresponds to a pCD that has four of the six -CH₂OH groups phosphorylated (theoretical phosphorus capacity of 2.14 mmol/g).

An earlier report detailed the correlation between metal ion affinities of phosphorylated polyols and a band at 873–895 cm⁻¹ assigned to hydrogen bonding between -OH groups and the phosphate ester ligand.¹² This interaction increases the electron density at the phosphoryl oxygen and makes it a stronger ligand. The more red-shifted the band, the higher the metal ion affinities.¹² pCD shows a new band at 867 cm⁻¹ which is further red-shifted relative to pPE, allowing a test of the hypothesis developed with the previous set of polyols. The results confirm that pCD is a stronger ligand than pPE. Although the divalent ions from HNO₃ solutions have reached their maximum affinity for the phosphoryl oxygen with pPE, pCD has higher affinities for trivalent ions; it has significantly higher affinities for these ions and U(VI) from H₂SO₄.

The results are consistent with the hypothesis proposed with the previous set of polyols⁴: As the solutions become less acidic, ionic strength decreases, the anions form solvent-separated ion pairs with UO₂²⁺, the inherent interaction between the P=O and the UO₂²⁺ becomes dominant and loss of the outermost waters of hydration by the anions that enter the resin phase may be less important. Ionic strength increases in the more concentrated acid

solutions, UO₂²⁺ exists as a contact ion pair with its anion, and the propensity of the anions to lose their waters of hydration upon ion exchange into the resin phase becomes dominant. The greater ligand strength of the pCD leads to a greater extent of metal ion complexation by overcoming the high energy of dehydration. Additionally, polymers with a high affinity for the uranyl ion would also be important for its removal from brine,¹⁴ phosphoric acid,¹⁵ and the nuclear fuel cycle.¹⁶

CONCLUSIONS

Phosphorylated CD is a complexant with high ionic affinities when immobilized onto crosslinked polystyrene beads. Hydrogen bonding from auxiliary -OH groups to the phosphate ligand is proposed as a general mechanism for the enhancement of ionic affinities. FTIR can be used to predict the ionic affinity of the phosphate ligand: within the region 860–895 cm⁻¹, the more red-shifted the band, the more hydrogen bonding and the higher the metal ion affinity due to an increased electron density at the phosphoryl oxygen. Results to be reported with additional ligands will show that hydrogen bonding is an important determinant of the metal ion affinities displayed by those ligands.

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