Intraligand Cooperation in Metal-Ion Binding by Immobilized Ligands: The Effect of Bifunctionality

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ABSTRACT: Intraligand cooperation between carbonyl and phosphoryl moieties in ion bonding was studied by the synthesis of β-ketophosphonic acid (βkPh), phosphonoacetic acid (PhAc), and phosphonic acid (Ph) resins. A subsequent reaction gave bifunctional analogues with sulfonic acid as an additional ligand (βkPh$_s$, PhAc$_s$, and Ph$_s$ resins). Ionic affinities were quantified with dilute solutions of Cu(II), Cd(II), and Pb(II) in 0.10M HNO$_3$. The effect of an increased solution ionic strength was studied with a second set of 0.10M HNO$_3$/0.04M NaNO$_3$ solutions. The results from the monofunctional resins and nitric acid alone showed that βkPh had the highest metal-ion affinities, whereas PhAc had affinities similar to those of Ph. Comparing βkPh to Ph led to the conclusion that the carbonyl group was a strong contributor to binding through intraligand cooperation with the phosphoryl group, whereas comparing PhAc to Ph led to the conclusion that the carbonyl group played no role in the ion binding. These opposing conclusions were reconciled as follows: (1) the extent of complexation from the 0.10M HNO$_3$ solutions increased significantly when the monofunctional resins were sulfonated and (2) a comparison of the results for the monofunctional resins when contacting Cu(II), Cd(II), and Pb(II) in the absence of NaNO$_3$ with those for the bifunctional resins when contacting those ions in the presence of NaNO$_3$ showed that the ionic affinities were comparable for Ph and Ph$_s$, greater for PhAc$_s$ than for PhAc, and comparable for βkPh$_s$ and βkPh. The resins PhAc$_s$ and βkPh displayed comparable ionic affinities that were higher than that of Ph. The results were consistent with the conclusion that, in the monofunctional resin, the affinity of the phosphonoacetate ligand for the metal ions was reduced because of intraligand hydrogen bonding. Intraligand cooperation was, therefore, an important variable in enhancing the metal-ion affinities, but its effect could be attenuated by intraligand hydrogen bonding. This attenuation could be eliminated by the introduction of a highly hydrophilic group into the matrix. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 463–468, 2004

Key words: ion exchangers; polystyrene; separation techniques

INTRODUCTION

The immobilization of ligands on crosslinked polymer supports is important for the selective complexation of metal ions from solutions, with applications for environmental science and chromatographic separations.[1] Classes of ligands that have been developed for this purpose include amines, amidoximes, phenolics, and phosphonates.[2] Phosphorus acid derivatives are especially versatile, displaying a wide range of ionic selectivities as a function of the precise ligand structure.[3]

The phosphonic acid ligand complexes transition-metal ions from aqueous solutions by coordination through the phosphoryl oxygen when the acid strength of the solution precludes ion exchange.[4] Studies with acetyl phosphate have shown that metal-ion affinities increase when the phosphoryl group is able to cooperate with a carbonyl oxygen on the same ligand,[5] and this is consistent with results from polymers with immobilized ketophosphonate ligands.[6] To fully explore the phosphoryl–carbonyl cooperative interaction and its effect on ionic affinities, we synthesized three resins: phosphonic acid (Ph), phosphonoacetic acid (PhAc), and β-ketophosphonic acid (βkPh; Fig. 1). The phosphoryl and carbonyl groups were in the same spatial relationship in the PhAc and βkPh resins (i.e., separated by a single carbon atom). To understand the effect of the electronic environment around the carbonyl on its interaction with the phosphoryl group, the carbonyl is part of an acid moiety in PhAc and a keto moiety in βkPh. The Ph resin is the control against which the importance of the carbonyl interaction is quantified.

For each resin, polystyrene (prepared by the suspension polymerization of styrene or vinylbenzyl chloride) was the support matrix. The accessibility of metal ions to the polymer was evaluated by the adjustment of three variables: (1) the particle size of the microporous (i.e., gel) beads (250–425 vs 75–150 μm), (2) the contact time (0.25 vs 24 h), and (3) the porosity of gel beads versus that of macroporous (50 vol %)
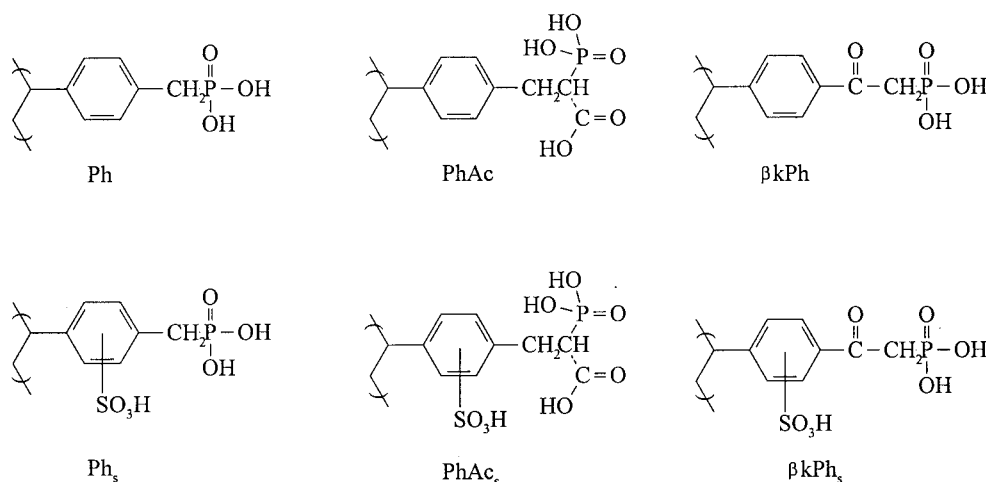
Figure 1 Structures of the monofunctional and bifunctional resins.

beads. A variable superimposed on the microporous–macroporous comparison was that, although the former were crosslinked with 2% divinylbenzene (DVB), the latter were crosslinked with 12% DVB. This higher level of crosslinking was important for maintaining the integrity of the beads during functionalization (a gel bead crosslinked with 12% DVB did not allow reagent accessibility for functionalization to occur).

Sulfonic acid ligands were introduced into the monofunctional Ph, PhAc, and βkPh resins by a reaction with chlorosulfonic acid to give a bifunctional set of resins (Ph$_s$, PhAc$_s$, and βkPh$_s$; Fig. 1). The sulfonic acid ligand could enhance the accessibility of ions to a polymer matrix,[7] and its effect on this set of resins was explored.

The ionic affinities were quantified with dilute solutions of Cu(II), Cd(II), and Pb(II) because these ions represented a range of polarizability.[8] The background solution was $0.10M$ HNO$_3$ because that acid strength minimized ion exchange at the phosphonic acid but did not provide a high enough concentration of protons to compete effectively with the transition-metal ions for coordination to the phosphoryl oxygen.[9] To determine the influence of the solution ionic strength on the ligand–metal affinities, we used a background solution of $0.10M$ HNO$_3$/$0.04M$ NaNO$_3$. The resins were also contacted with Eu(III) in $1M$ HNO$_3$; trivalent ions have a higher affinity for the phosphoryl group than divalent ions and were able to compete in more acidic solutions than transition-metal ions.[10] Additionally, it was of interest to determine whether the trivalent ion's greater hydrophilicity affected binding with ligands in a monofunctional microenvironment versus a bifunctional microenvironment.

EXPERIMENTAL

Polystyrene and poly(vinylbenzyl chloride) beads were prepared by suspension polymerization.[11] The gel beads were crosslinked with 2% DVB and sieved to particle size diameters of 250–425 and 75–150 μm, whereas the macroporous resin (MR) beads were crosslinked with 12% DVB and sieved to 250–425 μm. All starting material were purchased from Aldrich Chemical Co. (St. Louis, MO).

Synthesis of the Ph resins

Poly(vinylbenzyl chloride) beads (10 g) were refluxed with 300 mL of triethyl phosphite for 24 h. The solution was removed; the beads were washed twice with acetone and dilute HCl and then refluxed for 24 h with concentrated HCl.

Synthesis of the PhAc resins

Triethyl phosphonoacetate (31.60 g) was added to 150 mL of dry dioxane and 3.67 g of sodium metal, and the mixture was stirred 17 h under nitrogen. Poly(vinylbenzyl chloride) beads (10 g) were added to the deprotonated triethyl phosphonoacetate and refluxed for 24 h. The solution was removed; the beads were washed four times with toluene, dried *in vacuo* at 60°C for 17 h, swelled in CHCl$_3$ for 1 h under nitrogen, refluxed with 27 mL of Me$_3$SiBr for 24 h, and washed twice each with dioxane and water. The beads were then refluxed with 150 mL of 3M NaOH for 24 h.

Synthesis of the βkPh resins

Polystyrene beads (10 g) were swollen in 200 mL of CS$_2$ while being cooled in an ice bath for 1 h; 40 g of AlCl$_3$ in 65 mL of CS$_2$ was then added and was followed by stirring for 2 h and the dropwise addition of 40.4 g of bromoacetyl bromide in 10 mL of CS$_2$. The mixture was stirred for 48 h under nitrogen. The solution was removed, and the beads were washed with dioxane until the solution remained clear. Washing

TABLE I
Characterization of the Monofunctional Resins

Resin	Type	Size (μm)	Phosphorus capacity (mmol/g)		Acid capacity (mmol/g)	Percentage of solids
			Experimental	Theoretical		
Ph	2% DVB gel	250–425	4.49	4.90	9.07	54.3
Ph	2% DVB gel	75–150	4.72	4.90	9.13	56.9
Ph	12% DVB MR	250–425	3.66	4.16	7.33	26.5
PhAc	2% DVB gel	250–425	2.09	4.07	6.04	52.2
PhAc	2% DVB gel	75–150	2.47	4.07	5.88	49.0
PhAc	12% DVB MR	250–425	0.77	3.54	2.27	36.7
βkPh	2% DVB gel	250–425	3.51	4.35	6.85	53.0
βkPh	2% DVB gel	75–150	2.76	4.35	5.51	47.4
βkPh	12% DVB MR	250–425	1.86	3.92	3.46	31.3

was continued with five successive solutions of dioxane/water (100/0, 75/25, 50/50, 25/75, and 0/100), twice with ethanol, and twice with acetone. The beads were dried *in vacuo* at 70°C for 4 h, added to 100 mL of triethyl phosphite, and refluxed for 24 h. The solution was removed, the beads were washed twice with acetone, twice with dilute HCl, and refluxed for 24 h with 250 mL of concentrated HCl.

Sulfonation of the phosphorus acid resins

A phosphorus acid resin (10 g) was dried by azeotropic distillation with heptane and then stirred for 1 h in 200 mL of ethylene dichloride (EDC), after which time a solution of 16.5 mL of chlorosulfonic acid in 65 mL of EDC was added dropwise. The mixture was stirred at room temperature for 48 h. The beads were washed with five solutions of dioxane/water (as previously mentioned).

Characterization

Each resin was analyzed by its IR spectrum, phosphorus capacity, acid capacity, and percentage of solids.[12]

Metal-ion studies

The resins were contacted with 10 mL of 10^{-4} N Cu(NO$_3$)$_2$, Cd(NO$_3$)$_2$, and Pb(NO$_3$)$_2$ in 0.01M HNO$_3$ or 0.01M HNO$_3$/0.04M NaNO$_3$ and 10^{-4} N Eu(NO$_3$)$_3$ in

1.00M HNO$_3$. Enough resin was weighed to give 1 milliequiv of the phosphorus ligand and was then shaken with 10 mL of the solution for 0.25 or 24 h (as noted). The amount of metal ion remaining in solution was determined by atomic absorption or atomic emission (depending on the metal being analyzed) on a PerkinElmer 3100 spectrometer. The results are reported in terms of percent complexation.

RESULTS AND DISCUSSION

The characterization of the monofunctional resins is reported in Table I. A comparison of the theoretical and experimental phosphorus capacities shows that only the Ph resins are at least 90% functionalized; the phosphonoacetate and β-ketophosphonate gel resins are 50–80% functionalized, whereas the MR resins are 25–45% functionalized. The ligands are nonetheless accessible, despite the lower levels of functionalization, because the acid capacities are as expected from the experimental phosphorus capacities in all cases but one (the phosphonoacetate resin with a small particle size has an acid capacity somewhat lower than expected). The phosphonoacetate MR resin was considered to be functionalized to too low a degree (probably because of low accessibility of the sodium triethylphosphonoacetate into the highly crosslinked matrix) to yield reliable ion affinities and so was not used in this study.

The bifunctional resins are characterized in Table II.

TABLE II
Characterization of the Bifunctional Resins

Resin	Type	Size (μm)	Phosphorus capacity (mmol/g)	Acid capacity (mmol/g)	Percentage of solids
Ph$_S$	2% DVB gel	250–425	4.03	9.53	35.8
Ph$_S$	12% DVB MR	250–425	2.87	10.12	28.1
PhAc$_S$	2% DVB gel	250–425	1.57	6.93	53.9
PhAc$_S$	12% DVB MR	250–425	0.64	4.79	31.3
βkPh$_S$	2% DVB gel	250–425	2.80	8.26	33.9
βkPh$_S$	12% DVB MR	250–425	1.26	6.38	26.3

TABLE III
Complexation by Monofunctional Resins[a] of Cu(II), Cd(II), and Pb(II) in 0.01M HNO$_3$ and Eu(III) in 1.00M HNO$_3$

	Ph			PhAc			βkPh		
	250–425[b]	75–150[c]	MR	250–425	75–150	MR	250–425	75–150	MR
Cu(II)	35.1[d,e]	30.7	32.3	39.5[f]	37.3	—	70.0[g]	67.6	56.2
Cd(II)	40.5	34.3	36.6	37.9	43.1	—	76.8	71.7	54.7
Pb(II)	67.4	56.8	80.0	71.8	74.3	—	94.4	92.9	100
Eu(III)	23.8	23.0	1.8	28.7	28.0	—	96.0	87.5	83.2

[a] 24-h contact time (unless otherwise noted).
[b] Gel resin at 250–425-μm particle size.
[c] Gel resin at 75–150-μm particle size.
[d] Percentage complexed
[e] 38.7% at 0.25-h contact time.
[f] 43.8% at 0.25-h contact time.
[g] 68.0% at 0.25-h contact time.

In all cases but one, a comparison of the total acid capacity with the phosphorus capacity indicates that all aromatic groups have been sulfonated (the phosphonate resin has significant, but not complete, sulfonation).

Metal-ion studies in the absence of sodium nitrate are reported in Tables III and IV; those in the presence of sodium nitrate are reported in Tables V and VI. Because of the nonuniform level of substitution, all contact studies were done with enough resin to give 1 milliequiv of the phosphorus ligands. Given this constant factor, the results are reported in terms of the percentage of the metal ions complexed. The performance of the gel resins is discussed first, and the MR resins are compared afterward.

For all gel resins, the absence of a particle size effect in ionic complexation indicates that equilibrium has been reached. At a 24-h contact time, the percentages of Cu(II) complexed for the Ph, PhAc, and βkPh resins with a 250–425-μm particle size diameter are 35.1, 39.5, and 70.0%, respectively, whereas the same resins with a 75–150-μm diameter show 30.7, 37.3, and 67.6%, respectively. Equilibrium is confirmed by the

TABLE IV
Complexation by Bifunctional (Sulfonated) Resins[a] of Cu(II), Cd(II), and Pb(II) in 0.01M HNO$_3$ and Eu(III) in 1.00M HNO$_3$

	Ph$_S$		PhAc$_S$		βkPh$_S$	
	250–425[b]	MR	250–425	MR	250–425	MR
Cu(II)	94.1[c,d]	100	100[e]	—	100[f]	100
Cd(II)	96.2	100	100	—	98.4	91.0
Pb(II)	100	100	100	—	100	100
Eu(III)	91.8	100	97.7	—	96.0	100

[a] 24-h contact time (unless otherwise noted).
[b] Gel resin at 250–425-μm particle size.
[c] Percentage complexed.
[d] 94.4% at 0.25-h contact time.
[e] 100% at 0.25-h contact time.
[f] 98.4% at 0.25-h contact time.

Cu(II) contact time study: the results at 0.25 h are identical to those at 24 h.

The results for the monofunctional gel resins indicate that the β-ketophosphonate resin has the highest metal-ion affinities, whereas the phosphonoacetate resin has an affinity similar to that of the phosphonate resin. For example, the percentages of Pb(II) complexed for the βkPh, PhAc, and Ph resins are 94.4, 71.8, and 67.4%, respectively. In a comparison of βkPh and Ph, the carbonyl group appears to be a strong contributor to binding through intraligand cooperation with the phosphoryl oxygen. However, in a comparison of PhAc and Ph, the carbonyl group seems to play no role. The results with the bifunctional resins reconcile these divergent conclusions (as discussed later).

The degree of complexation significantly increases when the monofunctional resins are sulfonated: complexation is greater than 90% in each case and quantitative in most cases with bifunctional resins (Table IV). The kinetics remain rapid, the values at 0.25 h being within experimental error of those at 24 h. Bifunctional resins complex far greater levels of metal ions than monofunctional resins (Tables III and IV); as indicated by the decrease in the percentage of solids, sulfonation increases the resins' hydrophilicity, and this increases the compatibility of the metal ions with the polymer matrix.

The high level of complexation (>90%) for Eu(III) from 1M HNO$_3$ by the three bifunctional resins is not due to ion exchange by the sulfonic acid ligand: a monofunctional sulfonic acid resin complexes only 44.9% Eu(III) under the conditions of this study.[13] Because the phosphonic acid ligand has pK_a values of 3 and 8,[14] complexation must occur predominately through coordination by the phosphoryl oxygen. Participation of the carbonyl group in the binding is especially important in the less hydrophilic microenvironment of the monofunctional resins [e.g., 23.8% Eu(III) complexed by Ph and 96.0% complexed by βkPh] and may be less important for a highly hydro-

TABLE V
Complexation by Monofunctional Resins[a] of Cu(II), Cd(II), and Pb(II) in 0.01M HNO$_3$/0.40M NaNO$_3$

	Ph			PhAc			βkPh		
	250–425[b]	75–150[c]	MR	250–425	75–150	MR	250–425	75–150	MR
Cu/Na	16.7[d,e]	14.6	21.9	27.5[f]	27.5	—	43.8[g]	44.1	39.3
Cd/Na	42.5	17.7	22.0	19.2	24.0	—	43.0	42.0	40.1
Pb/Na	29.5	26.2	43.4	55.4	48.9	—	72.6	68.4	71.3

[a] 24-h contact time (unless otherwise noted).
[b] Gel resin at 250–425-μm particle size.
[c] Gel resin at 75–150-μm particle size.
[d] Percentage complexed.
[e] 18.0% at 0.25-h contact time.
[f] 20.1% at 0.25-h contact time.
[g] 37.8% at 0.25-h contact time.

philic trivalent ion in a highly hydrophilic microenvironment [e.g., 91.8% Eu(III) complexed by Ph$_s$ and 96.0% Eu(III) complexed by βkPh$_s$].

To explore the influence of the solution ionic strength on the complexation process, metal-ion studies were performed in 0.04M NaNO$_3$. The monofunctional resins show less complexation of transition-metal ions in the presence of sodium (Table V); for example, Cu(II) complexation by the βkPh gel resin decreases from 70.0 to 43.8%. The results at 0.25 h again show that equilibrium has been reached despite the presence of competing sodium ions. The level of complexation thus decreases as the solution ionic strength increases. It is proposed that the increased ionic strength removes water from the resins, making them less compatible with the metal ions. This is consistent with a comparison of the weight gain by a 2% DVB Ph gel resin in water versus 1M HNO$_3$: 1 g of dry resin increases by 2.85 g when placed in water and by only 1.87 g when placed in 1M HNO$_3$.[15] A wet resin can thus be expected to lose water when placed in ionic solutions, and this can affect the extent of metal-ion complexation from aqueous solutions.

The bifunctional resins behave similarly, but with important differences (cf. Tables IV and VI). Cu(II),

TABLE VI
Complexation by Bifunctional (Sulfonated) Resins[a] of Cu(II), Cd(II), and Pb(II) in 0.01M HNO$_3$/0.040M NaNO$_3$

	Ph$_S$		PhAc$_S$		βkPh$_S$	
	250–425[b]	MR	250–425	MR	250–425	MR
Cu/Na	46.1[c,d]	74.5	82.5[e]	—	83.2[f]	81.2
Cd/Na	56.9	82.6	72.3	—	68.3	81.1
Pb/Na	67.0	100	94.1	—	100	100

[a] 24-h contact time (unless otherwise noted).
[b] Gel resin at 250–425-μm particle size.
[c] Percentage complexed.
[d] 50.3% at 0.25-h contact time.
[e] 79.4% at 0.25-h contact time.
[f] 73.2% at 0.25-h contact time.

Cd(II), and Pb(II) complexation by the Ph$_s$ gel resin decreases from more than 90 to 46.1, 56.9, and 67.0% for the three ions, respectively. Complexation by the PhAc$_s$ and βkPh$_s$ gel resins also decreases, but to levels that are not as low, and Pb(II) complexation by the βkPh$_s$ resin remains quantitative. Furthermore, comparing results from the monofunctional resins in the absence of NaNO$_3$ (Table III) with those from the bifunctional resins in the presence of NaNO$_3$ (Table VI) shows that (1) the affinities for Cu(II), Cd(II), and Pb(II) are comparable for the Ph and Ph$_s$ gel resins [e.g., 67.4 and 67.0% Pb(II) for Ph and Ph$_s$, respectively], (2) the affinities are greater for PhAc$_s$ than for PhAc [e.g., 94.1 and 71.8% Pb(II) for PhAc$_s$ and PhAc, respectively], and (3) PhAc$_s$ and βkPh (along with βkPh$_s$) display comparable ionic affinities and have higher affinities than Ph. The monofunctional resins thus indicate that the β-ketophosphonate ligand has a greater metal-ion affinity than the phosphonoacetate ligand. Accessibility into the matrix is not a factor because the results are independent of the contact time and particle size. Although sulfonation of the βkPh gel resin leads to no significant increase in the ionic affinities according to a comparison of the results in Tables III and VI, sulfonation of the PhAc gel resin gives it affinities that are comparable to those of βkPh [PhAc$_s$ and βkPh$_s$ have affinities of 82.5 and 83.2% Cu(II), 72.3 and 68.3% Cd(II), and 94.1 and 100% Pb(II)].

The performance of the resins from solutions of lower and greater ionic strengths at a constant pH is consistent with the conclusion that hydrogen bonding is an important variable in determining the metal-ion affinities of a given ligand. Intraligand hydrogen bonding has been observed by NMR in molecules dissolved in dioxane–water solutions and found to vanish as the amount of water exceeds 80 mol %.[16] In this study, the results are consistent with the presence of intraligand hydrogen bonds that reduce the affinities of the phosphonoacetate ligand in the monofunctional resin (**I**). Sulfonation increases the resin's hydrophilicity and water in the resin hydrogen bonds to the

phosphonoacetate ligand, disrupting the intraligand hydrogen bond (**II**):

(I)

(II)

The carbonyl group then becomes available for ion-binding cooperation with the phosphoryl group, making the affinities of the phosphonoacetate ligand comparable to those for the β-ketophosphonate.

The results with the MR resins are consistent with this conclusion and also point to the importance of the metal ion's hydrophilicity in determining their affinity toward a given ligand. The gel and MR resins differ in their level of porosity and crosslinking: the MR resins are more highly crosslinked to give the porous structure enough rigidity to prevent attrition during functionalization. As a result, the microparticles comprising the MR bead have a lower microporosity than the 2% DVB gel beads. Despite the higher crosslink level, accessibility is unaffected because the phosphonate gel and MR beads give the same results for copper and cadmium ions [e.g., 35.1 and 32.3% Cu(II) complexed for the Ph gel resins and MR resins, respectively]. Interestingly, the phosphonate MR resin has a higher affinity than the gel for lead ions (80.0 vs 67.4%, respectively), and the phosphonate gel resin has a higher affinity than the MR resin for europium ions (23.8 vs 1.8%, respectively). Similar results have been found with the β-ketophosphonate gel and MR resins: the latter have a higher affinity for Pb(II), whereas the former have a higher affinity for Eu(III). This is consistent with the more highly crosslinked microparticles in the MR resins having a lower water content (because of the smaller free volume) and thus favoring the softest, least hydrophilic ion, Pb(II). Europium is the hardest, most hydrophilic, ion and thus favors the ligand within the most hydrated environment (i.e., the gel).

In comparing Tables III and VI, we find that the monofunctional and bifunctional phosphonate gel resins have comparable ionic affinities but that the bifunctional MR performs significantly better than the monofunctional MR. Although not able to prepare the PhAc MR resin, results with the gel show that the bifunctional resin has a greater affinity for metal ions than the monofunctional resin (the Cu, Cd, and Pb affinities increase from 39.5, 37.9, and 71.8% in the PhAc resin to 82.5, 72.3, and 94.1%, respectively, in the

PhAc$_s$ resin). As with the Ph resin, the monofunctional βkPh gel gives results comparable to those of the bifunctional βkPh$_s$ gel, whereas the βkPh$_s$ MR outperforms the βkPh MR [except for Pb(II), which is quantitatively complexed by both]. That the MR resins complex greater levels of the transition-metal ions upon sulfonation, even in solutions of greater ionic strength, indicates that the high crosslinking level enhances the selectivity of the phosphonate-based ligands by making the microenvironment less favorable for highly hydrophilic ions such as europium.[17] Its macroporosity allows the resins to maintain rapid complexation kinetics despite its low microporosity.

CONCLUSION

Intraligand cooperation is an important variable in enhancing metal-ion affinities, and its effect can be attenuated by intraligand hydrogen bonding. Introducing a highly hydrophilic group, such as sulfonic acid, into the matrix can eliminate intraligand hydrogen bonding. Although resin hydrophilicity can have a significant effect on the observed ionic affinities, the polarizability of the metal ion is also a significant variable. Pb(II) is least affected by the solution ionic strength, especially with the PhAc and βkPh resins; it is also the most polarizable and least hydrophilic ion, and so changes in hydration within the polymer matrix have the least effect on it.

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