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Enhanced metal ion affinities by supported ligand synergistic interaction in bifunctional polymer-supported aminomethylphosphonates

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ENHANCED METAL ION AFFINITIES BY SUPPORTED LIGAND SYNERGISTIC INTERACTION IN BIFUNCTIONAL POLYMER-SUPPORTED AMINOMETHYLPHOSPHONATES

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ABSTRACT

The Mannich reaction is applied to the phosphorylation of amine resins with monoamine, ethylenediamine, diethylenetriamine, and tetraethylenepentamine ligands to give a series of bifunctional aminomethylphosphonic acid resins. The microenvironment around each ligand was varied by preparing fully functionalized resins, a second set of resins with 82 mol% phenyl groups in the polymer, and a third set with 82 mol% carbomethoxy groups. The affinity of the resins for Cu(II), Cd(II), Pb(II), and Eu(III) was evaluated from solutions buffered at pH 5. Synergism is observed under certain conditions where both groups operating together complex more metal ions than either one alone. Ion exchange by the phosphonate portion of the ligand and coordination by the amine portion cooperate as a dual mechanism for metal ion complexation. Synergistic complexation of Cd(II) by all

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bifunctional aminomethylphosphonate resins (regardless of microenvironment) and of all metal ions by all bifunctional resins within the carbomethoxy microenvironment is quantified. For example, 26% Cd(II) is complexed by the ethylenediamine resin (distribution coefficient of 26), and 49% Cd(II) is complexed by the phosphonic acid resin (distribution coefficient of 48), but the bifunctional aminomethylphosphonic acid resin complexes 98% Cd(II) (distribution coefficient of 2300), which far exceeds the combined distribution coefficients of the monofunctional resins.

INTRODUCTION

The use of polymer-supported reagents has been widespread in organic synthesis (1), catalysis (2), and separation science (3). Interest in separations with polymers for the recovery of toxic metal ions from water has grown significantly over the last 30 years (4). In designing a selective polymer, selection of a suitable ligand receives the greatest emphasis. The complexation of metal ions by immobilized ligands can vary from what is expected based on the results from their soluble analogs because the different local concentration within the macromolecular framework may not produce the same behavior as in solution (5). However, it is commonly assumed that the complexation behavior of a chelating polymer is similar to that of the corresponding monomeric functional groups (6). This assumption has been evaluated by comparing the thermodynamic properties of *N*-benzyl iminodiacetic acid and its immobilized analog, Dowex A-1, toward divalent transition metal ions and finding agreement between the constants evaluated from potentiometric titration of the soluble compound and from equilibration studies with the cross-linked polymer (7).

Polyethyleneimine (PEI) is a well-known ligand for different metal ions (8). The resulting complexes are soluble in water and thus require ultrafiltration for recovery (9). In order to simplify isolation, PEI is either cross-linked or grafted onto cross-linked polymers (10). Di-, tri-, and tetramines immobilized on silica gel have been found effective for the complexation of transition metal ions, with uptake capacities increasing as the amine length was increased (11). The same ligands bonded to polystyrene also showed an increase in effectiveness for Cu(II) complexation with increasing length (12). Bonding to the polystyrene through more than one nitrogen in the polyamine has been reported (13).

In quantifying the binding of PEI with Cu(II) and Ni(II), the polymer was found to more strongly complex metal ions than monomeric ethylenediamine (14). With Cu(II), the overall formation constant with PEI was about 10^6 times greater than that for ethylenediamine. This increase in stability was attributed to

the higher concentration of ligating sites within the polymer relative to the concentration of ethylenediamine in solution. This *chelate effect* can be used to explain the difference in behavior of ammonia vs. ethylenediamine and other PEI ligands (15): a ligand able to form five- or six-membered rings upon complexation shows enhanced ionic affinities due to this effect (16).

Soluble phosphoryl-containing compounds with high metal ion affinities include tributyl phosphate (17) and trioctylphosphine oxide (18). Phosphorylated polystyrene–divinylbenzene copolymer was found to have a high affinity for uranyl and ferric ions due to strong coordination by the electron donating phosphoryl oxygen (19). Dual mechanism bifunctional polymers with a wide array of phosphorus-based ligands have been developed that couple an access mechanism to bring metal ions rapidly into the polymer matrix and a recognition mechanism to selectively react with targeted metal ions (20). In one example, the bifunctional phosphonate monoester/diester resin utilizes coordination as the recognition mechanism (21). Both ligands cooperate to complex greater levels of Ag(I) from acidic solutions than either ligand can alone; this phenomenon is termed *supported ligand synergistic interaction*.

The microenvironmental effect, defined as the influence of inert (nonligating) groups surrounding an active ligand on the interaction between that ligand and a substrate, has been observed in the complexation of ions by immobilized ligands (22). A polymer with an equimolar ratio of imidazole ligands and carboethoxy groups binds copper ions 2.6 times more strongly than a polymer with only imidazole ligands because the polymeric microenvironment is less polar in the former which results in greater compatibility with the complexed species.

In the present report, the aminomethylphosphonic acid ligand was immobilized via the Mannich reaction and its performance evaluated as a dual mechanism bifunctional ion exchange/coordination polymer. The Mannich reaction is well known to yield aminomethylphosphonates via the reaction of amines, formaldehyde, and phosphorous acid (23–25). Polyethyleneimine has successfully undergone this reaction to give $-CH_2P(O)(OH)_2$ ligands bound to the nitrogen and the polymer was found to have a high saturation capacity for Cu(II) from pH 6 solution (26). The influence of a microenvironmental effect superimposed on the bifunctional interaction was determined by varying the copolymer onto which the ligands were immobilized: vinylbenzyl chloride (VBC) was copolymerized with divinylbenzene (DVB) as the cross-linking agent and either styrene (STY) or methyl methacrylate (MMA) to give different microenvironments within the polymer matrix (Fig. 1). The VBC/STY copolymer creates a hydrophobic microenvironment around the ion-binding ligands while the VBC/MMA copolymer creates one that is more polar. The molar ratio of the two comonomers was set at 0.18:0.82 because that ratio gives a content of inert groups large enough to influence the microenvironment at the active site (27).

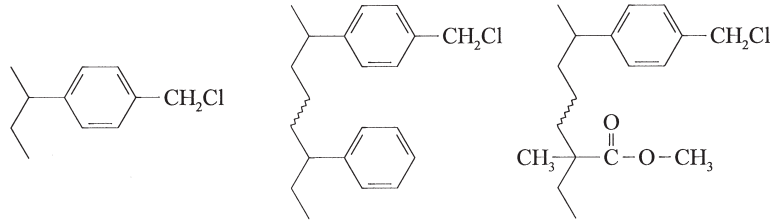

Figure 1. Copolymer supports prior to functionalization.

EXPERIMENTAL SECTION

Copolymer Synthesis

The three copolymer supports consist of VBC, VBC/STY, and VBC/MMA (the latter two at mole ratios of 0.18:0.82), all cross-linked with 2% DVB. Suspension polymerization was used to prepare beads with diameters 0.250–0.425 mm for the VBC and VBC/STY copolymers and 0.180–0.250 mm for the VBC/MMA copolymer using published procedures (27). Each copolymer is then used to support one of the three types of ligands: amine, aminomethylphosphonic acid, and phosphonic acid.

Amination

The monoamine (MA) resins were prepared by adapting the Gabriel synthesis. Enough copolymer beads to give 52 mmol $-CH_2Cl$ groups (e.g., 8 g VBC beads) were added to a three-neck round bottom flask fitted with an overhead stirrer, condenser, and thermometer, then swelled in 80 mL of dimethylformamide (DMF) for 17 hr. Potassium phthalimide (40 g, 216 mmol) in 320 mL of DMF was added and the reaction was stirred at 80°C for 17 hr. The solution was removed and the beads were washed three times with 300 mL of water and four times with methanol. After drying in a Buchner funnel, the beads were transferred to a flask containing 100 mL of methanol, 20 mL of hydrazine, and 4 mL of water. After refluxing at 65°C for 17 hr, the beads were washed four times with water. Concentrated HCl (200 mL) was added and the mixture heated at 90°C for 17 hr. The solution was removed with a fritted glass filter tube, the beads stirred with 300 mL of 2 *M* NaOH for 2 hr and then washed with water four times. The resin was conditioned by eluting with 1 L H_2O, 1 *M* HCl, H_2O, 1 *M* NaOH and H_2O until neutral.

The polyamine resins [ethylenediamine (EDA), diethylenetriamine (DETA), and tetraethylenepentamine (TEPA)] were prepared following the same general procedure. A 10-fold excess of the given amine relative to the VBC copolymer was used in each case. In one example, 10 g (63 mmol) of VBC copolymer beads was weighed into a three-neck round bottom flask fitted with an overhead stirrer, condenser, and addition funnel. A solution of 40 mL (600 mmol) EDA in 150 mL dioxane was added to the flask and the mixture refluxed for 17 hr. Once cooled, the solution was removed and washed twice with 50% aqueous dioxane and water. The resin was then conditioned by eluting with 1 L H_2O, 1 *M* HCl, H_2O, 1 *M* NaOH and H_2O until neutral. Note that while the EDA and DETA were of 99% purity (Sigma-Aldrich Corporation, Milwaukee, Wisconsin, USA), the TEPA was of 60% purity with the remainder comprised of tris(aminoethyl)amine, diaminoethylpiperazine, and piperazinoethylenediamine according to technical personnel at the Aldrich Chemical Company. Given this, the precise composition of the TEPA resins is unclear; the metal ion studies are reported as indicators of what can be expected using commercially available TEPA, but cannot be used for comparative conclusions. All resins were characterized by their percent solids ($g_{dry}/g_{wet} \times 100$) and nitrogen elemental analysis.

Mannich Reaction

The amine resins were phosphorylated via the Mannich reaction in order to prepare the bifunctional resins (Fig. 2). In one example, 4.25 g (17 mmol) of EDA resin was weighed into a three-neck round bottom flask fitted with an overhead stirrer, condenser, and thermometer. Formalin (12 mL, 150 mmol HCHO), H_3PO_3 (8 g, 98 mmol), and 40 mL of 20% HCl solution were added to the flask and heated at 90°C for 17 hr. The beads were washed four times with water and conditioned with 1 L H_2O, 1 *M* NaOH, H_2O, 1 *M* HCl, and H_2O until neutral. Resins were characterized by their percent solids, and nitrogen, phosphorus, and acid capacities (28).

Arbusov Reaction

Monofunctional phosphonic acid resins were prepared by the Arbusov reaction on each copolymer with an excess of triisopropyl phosphite. Twenty

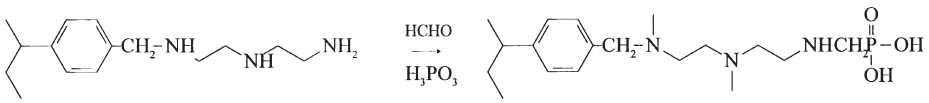

Figure 2. Mannich reaction on the diethylenetriamine resin.

grams of dry copolymer was weighed into a 500 mL three-neck round bottom flask equipped with an overhead stirrer, condenser, and addition funnel. Triisopropyl phosphite (300 mL) was added and the mixture refluxed for 17 hr. After cooling, the solution was removed and 300 mL of concentrated HCl was added followed by a 24 hr reflux. The resins were washed four times with water and conditioned with 1 L H_2O, 1 *M* NaOH, H_2O, 1 *M* HCl and H_2O until neutral. They were characterized by their percent solids, phosphorus capacity, and acid capacity.

Metal Ion Studies

The metal ion complexing abilities of the amine, aminomethylphosphonic, and phosphonic acid resins were evaluated with 10^{-4} *N* solutions of $Cu(NO_3)_2$, $Cd(NO_3)_2$, $Pb(NO_3)_2$, and $Eu(NO_3)_3$ solutions buffered to pH 5 with 0.6 *N* acetate ion. Buffered solutions were used because reproducibility in the amount of metal ion complexed requires a constant equilibrium pH and nonbuffered aqueous solutions displayed a final pH that varied irregularly with the amine resins.

An amount of resin corresponding to either 0.5 or 1 mequiv of functional groups (based on the nitrogen capacity for the amine resins and phosphorus capacity for the aminomethylphosphonic and phosphonic acid resins) was weighed into a vial and solvent exchanged four times with pH 5 acetate buffer solution. The resins were shaken with 10 mL of 10^{-4} *N* metal ion solution for 24 hr on a Burrell Wrist Action Shaker (Burrell Scientific, Inc., Pittsburgh, Pennsylvania, USA) for 24 hr in order to ensure that equilibrium had been reached. The solutions were then removed from the beads and the final concentrations were measured on a Perkin–Elmer model 3100 atomic absorption spectrometer (Perkin-Elmer Corporation, Shelton, Connecticut, USA). The results are reported in terms of percent metal ion complexed and the corresponding distribution coefficient (D = mequiv M^{n+} per g_{resin}/mequiv M^{n+} per mL_{soln}). The distribution coefficients are independent of the mass of resin used in the experiments, but affinities measured by the percent complexed can be compared only when initial variables are the same.

RESULTS AND DISCUSSION

Amine Resins

The properties of the MA resins are listed in Table 1. The percent solids of the VBC/STY resin (MH-1-233) were higher than the VBC (MH-1-173) or VBC/MMA (MH-1-253) resins due to the hydrophobicity of the unsubstituted

phenyl groups. This trend holds for the remaining amine resins. The nitrogen capacities of the three MA resins show that the percent functionalization for the VBC, VBC/STY, and VBC/MMA resins were 81, 76, and 100%, respectively. That the VBC and VBC/STY resins are less functionalized than the VBC/MMA resin may be due to steric hindrance because of a high ligand density in the former polymers.

The polyamines are bonded to the polymer at more than one nitrogen. In each case, the nitrogen capacity is lower than the theoretical value despite a negligible chlorine content. For example, the nitrogen capacity of the EDA resin from the VBC support is 7.54 mequiv/g, the theoretical value assuming complete monosubstitution is 11.13 mequiv/g, and the chlorine capacity of the phosphorylated EDA resin (MH-1-009) is 0.4 mequiv/g (phosphorylation will not occur at the $-CH_2Cl$ groups). The most likely explanation is secondary cross-linking by the polyamines to give the structures shown in Fig. 3. The ratio of experimental to theoretical nitrogen capacity, or *percent functionalization*, can be used as a measure of the extent of secondary cross-linking; the lower the apparent percent functionalization, the greater the degree of secondary cross-linking. The extent of secondary cross-linking is most pronounced with the EDA resin when comparing results from the VBC support to those from the VBC/STY and VBC/MMA supports because of the higher content of $-CH_2Cl$ groups in the VBC copolymer and the relatively short length of the EDA molecule. The difference disappears with the lengthier TEPA molecule which can bridge sites even in the supports with a lower content of $-CH_2Cl$ groups.

Aminomethylphosphonic Acid Resins

The data for the aminomethylphosphonic acid resins are summarized in Table 2. Calculating the mmol MA, EDA, and DETA ligands from the nitrogen capacities and comparing those values to the phosphorus capacities show that

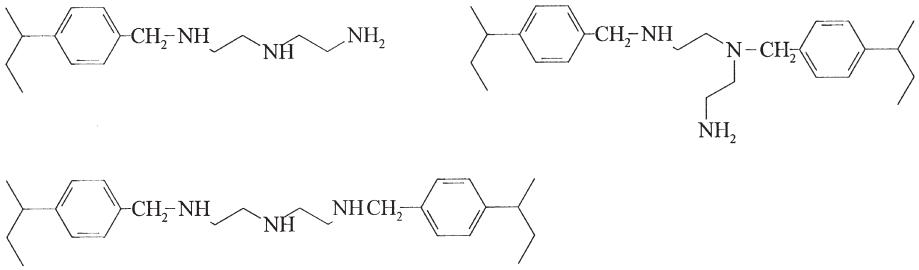

Figure 3. Possible cross-linked structures with the DETA ligand.

Table 1. Characterization of the Amine Resins

Resin	Functional Group[a]	Percent Solids	N Capacity (mequiv/g)	Percent Functionalization[b]
VBC				
MH-1-173	MA	60.23	5.79 (7.12)[c]	81.3
MH-1-032	EDA	46.99	7.54 (11.13)	67.7
MH-1-037	DETA	46.94	8.89 (13.56)	65.6
MH-1-041	TEPA	44.61	10.88 (16.30)	66.8
VBC/STY				
MH-1-233	MA	87.20	1.21 (1.60)	75.6
MH-1-110	EDA	73.86	2.50 (2.91)	85.9
MH-1-116	DETA	73.66	2.55 (4.14)	61.6
MH-1-120	TEPA	67.87	4.08 (6.17)	66.1
VBC/MMA				
MH-1-253	MA	68.87	1.82 (1.58)	100
MH-1-142	EDA	66.82	2.45 (2.96)	82.8
MH-1-146	DETA	59.99	3.48 (4.18)	83.3
MH-1-150	TEPA	57.11	4.42 (6.22)	71.1

[a] MA: monoamine, EDA: ethylenediamine, DETA: diethylenetriamine, TEPA: tetraethylenepentamine.
[b] Apparent percent functionalization for EDA, DETA, and TEPA resins.
[c] Theoretical value assuming complete monosubstitution.

phosphorylation on the aminated VBC and VBC/MMA supports consistently gives 3–4 phosphonic acid groups for every two ligands. Phosphorylation may occur to a somewhat lower extent on the aminated VBC/STY support due to the decreased accessibility of the polar reactants into the hydrophobic support. This is most pronounced for the bifunctional MA/acid resin (MH-1-286). With one exception, the resins have acid capacities that are, within experimental error, twice the phosphorus capacities. The sole exception, MH-1-286, has the least polar environment so that formation of the diphosphonate anion during titration may be disfavored, consistent with the observation that it is phosphorylated to the least extent of the resins synthesized.

Phosphonic Acid Resins

The properties of the phosphonic acid resins are summarized in Table 3. The acid capacities for the resins from the VBC and VBC/MMA supports are almost exactly twice the resins' phosphorus capacities (theoretical values of 9.02 and 3.38 mequiv/g, compared to experimental values of 8.86 and 3.47 mequiv/g,

respectively); the acid capacity of the resin from the VBC/STY support is again lower than theoretical, and, as noted earlier, formation of the diphosphonate anion may be disfavored in this relatively low-polar environment.

Metal Ion Studies

The amine, aminomethylphosphonic acid, and phosphonic acid resins were contacted with solutions containing the nitrate salts of Cu(II), Cd(II), Pb(II), and Eu(III) ions and the results are presented in Tables 4–6.

Among the ions studied, the polyamine resins have a high affinity only for Cu(II). As the length of the ligand increases from MA to EDA, the level of Cu(II) complexation increases from negligible to near-quantitative levels, indicating the presence of a chelate effect, which is also evident with the DETA and TEPA ligands (Table 4). Interestingly, TEPA behaves in a manner similar to DETA, indicating that it is the TEPA in the mixture that dominates the coordination chemistry. The high Cu(II) affinities indicate that accessibility into the matrix is not a limiting factor, even with resins prepared from the VBC/STY copolymer support. All amine resins have low affinities for Cd(II), Pb(II), and Eu(III), regardless of the microenvironment. These affinities are consistent with the stability constants (β_n) of the analogous soluble compounds (29). As indicated in Table 7, the stability of the Cu(II) complex with ammonia at low coordination numbers is poor compared to EDA. Three ammonia molecules are required by Cu(II) to yield a complex that approaches the stability found with one EDA molecule. This enhanced stability with EDA is due to chelate ring formation between the metal ion and the multidentate ligand. The MA resin thus displays the lowest Cu(II) affinity because steric constraints in the cross-linked polymer preclude three $-NH_2$ ligands from coordinating with a single metal ion. The large increase in distribution coefficients from the MA to the EDA resin can be attributed to the increase in ligand length, not the increase in total number of nitrogens in the resin. The extent of complexation of metal ions other than Cu(II) with the amine resins is very low in all cases, consistent with the stability constants of the soluble analogs: for example, the β_1 of EDA with Cu(II) is 10^5 times greater than that for Cd(II) and 10^3 times greater than that for Pb(II).

The bifunctional aminomethylphosphonic acid resins (Table 5) have higher ionic affinities than the amine resins, but their behavior must be considered in light of the affinities of the phosphonic acid resin (Table 6). The fully functionalized phosphonic acid resin has very high affinities for Cu(II) and Pb(II), a high affinity for Eu(III), and a much lower affinity for Cd(II). The affinity for all ions decreases significantly in the MMA microenvironment, and remains low in the STY microenvironment for all ions except Pb(II) where complexation is quantitative. The effect of bifunctionality is best understood by

Table 2. Characterization of the Aminomethylphosphonic Acid Resins

Resin	Functional Group[a]	Percent Solids	N Capacity (mequiv/g)	P Capacity (mequiv/g)	Acid (mequiv/g)	$>P{=}O$ Ligand^{-1}
VBC						
MH-1-180	MA/PhA	63.18	3.14	4.85	9.55	1.5
MH-1-070	EDA/PhA	49.23	4.17	3.81	7.38	1.6
MH-1-073	DETA/PhA	53.96	5.71	3.77	7.46	2
MH-1-094	TEPA/PhA	50.66	6.92	3.56	8.40	
VBC/STY						
MH-1-286	MA/PhA	77.94	1.21	0.81	0.90	0.67
MH-1-130	EDA/PhA	82.30	1.75	1.29	2.62	1.5
MH-1-134	DETA/PhA	76.93	4.53	1.59	3.14	1
MH-1-138	TEPA/PhA	67.65	2.90	1.78	3.44	
VBC/MMA						
MH-1-270	MA/PhA	59.31	1.44	2.13	4.62	1.5
MH-1-154	EDA/PhA	66.60	2.00	1.79	3.44	1.8
MH-1-158	DETA/PhA	63.81	3.60	2.03	4.25	1.7
MH-1-162	TEPA/PhA	57.70	3.76	2.27	4.42	

[a] MA: monoamine, EDA: ethylenediamine, DETA: diethylenetriamine, TEPA: tetraethylenepentamine, PhA: phosphonic acid.

Table 3. Characterization of the Phosphonic Acid Resins

Resin	Copolymer Support	Percent Solids	P Capacity (mequiv/g)	Acid (mequiv/g)	P : Acid Ratio
MH-1-034	VBC	53.91	4.51 (4.82)[a]	8.86	1:1.96
MH-1-256	VBC/STY	64.57	1.49 (1.42)	1.93	1:1.30
MH-2-002	VBC/MMA	58.12	1.62 (1.45)	6.47	1:2.05

[a] Theoretical value.

comparing the metal ion affinities of the amine, aminomethylphosphonic, and phosphonic acid resins for a given ligand in Tables 8–11. With all of the metal ions studied, the aminomethylphosphonic acid resins show higher complexing affinities than the amine resins, except for Cu(II) which also complexes well with the EDA, DETA, and TEPA resins. For example, the fully functionalized EDA/phosphonic acid resin complexes 100% Pb(II) whereas the EDA resin complexes only 15.3% (Table 9). Care must be taken in the interpretation of this

Table 4. Complexation of Metal Ions from Solutions at pH 5 by the Amine Resins

	Percent Complexed (Distribution Coefficient)			
Functional Group[a]	Cu(II)	Cd(II)	Pb(II)	Eu(III)
VBC				
MA	32.5[b] (14.0)	23.3[b] (8.8)	10.9[b] (3.6)	4.4[b] (0.1)
EDA	100[b]	26.0[b] (26.4)	15.3[b] (13.6)	0.0[b] (0.0)
DETA	98.4[b] (5,470)	24.0[b] (28.8)	3.3[b] (3.0)	3.0[b] (2.7)
TEPA	96.9[b] (3,370)	35.0[b] (57.8)	10.4[b] (12.6)	0.0[b] (0.0)
VBC/STY				
MA	5.4[c] (1.4)	12.8[c] (3.4)	12.1[c] (3.3)	0.0[c] (0.0)
EDA	99.2[b] (3,100)	16.0[c] (9.5)	20.5[b] (6.5)	6.7[c] (3.4)
DETA	99.2[b] (3,170)	18.7[c] (11.7)	23.4[b] (7.8)	8.2[c] (4.6)
TEPA	99.2[b] (5,030)	27.3[c] (30.6)	23.4[b] (12.5)	10.4[c] (9.5)
VBC/MMA				
MA	20.3[c] (9.3)	16.1[c] (7.0)	14.0[c] (6.0)	0.0[c] (0.0)
EDA	99.2[b] (3,040)	15.0[c] (8.7)	11.0[c] (6.1)	6.4[c] (3.4)
DETA	100[b]	15.0[c] (11.7)	2.7[c] (1.9)	5.1[c] (3.7)
TEPA	100[b]	20.0[c] (22.0)	6.8[c] (6.4)	7.5[c] (7.2)

[a] MA: monoamine, EDA: ethylenediamine, DETA: diethylenetriamine, TEPA: tetraethylenepentamine.
[b] Weight based on 1 mequiv of capacity.
[c] Weight based on 0.5 mequiv of capacity.

Table 5. Complexation of Metal Ions from Solutions at pH 5 by the Aminomethylphosphonic Acid Resins

	Percent Complexed (Distribution Coefficient)			
Functional Group[a]	Cu(II)	Cd(II)	Pb(II)	Eu(III)
VBC				
MA/PhA	98.4[b] (2,960)	92.0[b] (550)	98.1[b] (2,500)	92.4[b] (585)
EDA/PhA	100	98.0 (2,300)	100[b]	90.5[b] (447)
DETA/PhA	100[b]	98.0[b] (1,840)	98.1[b] (1,970)	90.2[b] (347)
TEPA/PhA	96.9[b] (1,100)	99.6[b] (8,750)	100[b]	92.2[b] (419)
VBC/STY				
MA/PhA	91.4[c] (171)	53.1[c] (18.0)	93.2[b] (222)	3.2[c] (0.5)
EDA/PhA	97.4[b] (491)	89.1[b] (212)	100[b]	92.2[b] (459)
DETA/PhA	99.2[b] (1,970)	96.8[c] (1,100)	100[b]	91.8[b] (321)
TEPA/PhA	99.2[b] (2,210)	95.1[b] (689)	100[b]	91.3[b] (374)
VBC/MMA				
MA/PhA	99.0[c] (4,240)	83.0[c] (210)	93.5[c] (612)	81.8[c] (193)
EDA/PhA	100[b]	96.1[c] (880)	100[c]	91.5[c] (384)
DETA/PhA	100[b]	97.4[c] (1,540)	93.8[c] (614)	91.2[c] (420)
TEPA/PhA	100[b]	96.1[c] (1,120)	93.8[b] (687)	91.3[c] (478)

[a] MA: monoamine, EDA: ethylenediamine, DETA: diethylenetriamine, TEPA: tetraethylenepentamine, PhA: phosphonic acid.
[b] Weight based on 1 mequiv of capacity.
[c] Weight based on 0.5 mequiv of capacity.

result, however, as the phosphonic acid resin itself also complexes 100% Pb(II). By comparing the distribution coefficients of all the bifunctional resins with their monofunctional analogs, it is seen that, under certain conditions, a supported ligand synergistic interaction is operative where both groups operating together

Table 6. Complexation of Metal Ions from Solutions at pH 5 by the Phosphonic Acid Resins

	Percent Complexed (Distribution Coefficient)			
Copolymer Support	Cu(II)	Cd(II)	Pb(II)	Eu(III)
VBC	98.1[a] (3,140)	49.2[a] (48)	100[a]	92.3[a] (588)
VBC/STY	76.4[a] (96.3)	30.2[b] (13.0)	100[b]	2.3[b] (0.7)
VBC/MMA	51.5[b] (36.0)	21.7[b] (9.3)	64.4[b] (62.0)	74.5[b] (98.0)

[a] Weight based on 1 mequiv of capacity.
[b] Weight based on 0.5 mequiv of capacity.

Table 7. Metal Ion Stability Constants of Soluble Amine Compounds

Molecule	$\log \beta_n$	Cu(II)	Cd(II)	Pb(II)
NH_3	$\log \beta_1$	4.04	2.62	
	$\log \beta_2$	7.47	4.56	
	$\log \beta_3$	10.27	5.90	
EDA	$\log \beta_1$	10.54	5.45	7.0
	$\log \beta_2$	19.6	9.98	8.45
DETA	$\log \beta_1$	15.9	8.4	8.5
	$\log \beta_2$	20.9	13.8	10.37
TETA	$\log \beta_1$	20.1	20.63	10.4
TEPA	$\log \beta_1$	22.8	14.0	10.5

EDA: ethylenediamine, DETA: diethylenetriamine, TETA: triethylenetetramine, TEPA: tetraethylenepentamine.

complex more metal ions than either one alone. A comparison of the distribution coefficients indicates synergistic complexation of Cd(II) by all bifunctional aminomethylphosphonic acid resins, regardless of microenvironment, and of all metal ions by all bifunctional resins within the MMA microenvironment (though

Table 8. Complexation of Metal Ions from Solutions at pH 5 by Monofunctional Monoamine and Bifunctional Resins

	Percent Complexed (Distribution Coefficient)			
Functional Group	Cu(II)	Cd(II)	Pb(II)	Eu(III)
VBC				
MA	32.5[a] (14.0)	23.3[a] (8.8)	10.9[a] (3.6)	4.4[a] (0.1)
MA/PhA	98.4[a] (2,960)	92.0[a] (550)	98.1[a] (2,500)	92.4[a] (585)
PhA	98.1[a] (3,140)	49.2[a] (48.0)	100[a]	92.3[a] (588)
VBC/STY				
MA	5.4[b] (1.4)	12.8[b] (3.4)	12.1[b] (3.3)	0.0[a] (0.0)
MA/PhA	91.4[b] (171)	53.1[b] (18.0)	93.2[b] (222)	3.2[b] (0.5)
PhA	76.4[b] (96.3)	30.2[b] (13.0)	100[b]	2.3[b] (0.7)
VBC/MMA				
MA	20.3[b] (9.3)	16.1[b] (7.0)	14.0[b] (6.0)	0.0[b] (0.0)
MA/PhA	99.0[b] (4,240)	83.0[b] (209)	93.5[b] (612)	81.8[b] (193)
PhA	51.5[b] (36.0)	21.7[b] (9.3)	64.4[b] (62.0)	74.5[b] (98.0)

[a] Weight based on 1 mequiv of capacity.
[b] Weight based on 0.5 mequiv of capacity.

Table 9. Complexation of Metal Ions from Solutions at pH 5 by Monofunctional Ethylenediamine and Bifunctional Resins

	Percent Complexed (Distribution Coefficient)			
Functional Group	Cu(II)	Cd(II)	Pb(II)	Eu(III)
VBC				
EDA	100[a]	26.0[a] (26.4)	15.3[a] (13.6)	0.0[a] (0.0)
EDA/PhA	100[a]	98.0[a] (2,300)	100[a]	90.5[a] (447)
PhA	98.1[a] (3,140)	49.2[a] (48)	100[a]	92.3[a] (588)
VBC/STY				
EDA	99.2[a] (3,100)	16.0[b] (9.5)	20.5[a] (6.5)	6.7[b] (3.4)
EDA/PhA	97.4[a] (491)	89.1[b] (212)	100[a]	92.2[b] (459)
PhA	76.4[b] (96.3)	30.2[b] (13.0)	100[b]	2.3[b] (0.7)
VBC/MMA				
EDA	99.2[a] (3,040)	15.0[b] (8.7)	11.0[b] (6.1)	6.4[b] (3.4)
EDA/PhA	100[a]	96.1[b] (880)	100[b]	91.5[b] (384)
PhA	51.5[b] (36.0)	21.7[b] (9.3)	64.4[b] (62.0)	74.5[b] (98.0)

[a] Weight based on 1 mequiv of capacity.
[b] Weight based on 0.5 mequiv of capacity.

Table 10. Complexation of Metal Ions from Solutions at pH 5 by Monofunctional Diethylenetriamine and Bifunctional Resins

	Percent Complexed (Distribution Coefficient)			
Functional Group	Cu(II)	Cd(II)	Pb(II)	Eu(III)
VBC				
DETA	98.4[a] (5,470)	24.0[a] (28.8)	3.3[a] (3.0)	3.0[a] (2.7)
DETA/PhA	100[a]	98.0[a] (1,840)	98.1[a] (1,970)	90.2[a] (347)
PhA	98.1[a] (3,140)	49.2[a] (48.0)	100[a]	92.3[a] (588)
VBC/STY				
DETA	99.2[a] (3,170)	18.7[b] (11.7)	23.4[a] (7.8)	8.2[b] (4.6)
DETA/PhA	99.2[a] (1,970)	96.8[b] (1,100)	100[a]	91.8[b] (321)
PhA	76.4[b] (96.3)	30.2[b] (13.0)	100[b]	2.3[b] (0.7)
VBC/MMA				
DETA	100[a]	14.4[b] (11.7)	2.7[b] (1.9)	5.1[b] (3.7)
DETA/PhA	100[a]	97.4[b] (1,540)	93.8[b] (614)	91.2 (420)
PhA	51.5[b] (36.0)	21.7[b] (9.3)	64.4[b] (62.0)	74.5[b] (98.0)

[a] Weight based on 1 mequiv of capacity.
[b] Weight based on 0.5 mequiv of capacity.

Table 11. Complexation of Metal Ions from Solutions at pH 5 by Monofunctional Tetraethylenepentamine and Bifunctional Resins

	Percent Complexed (Distribution Coefficient)			
Functional Group	Cu(II)	Cd(II)	Pb(II)	Eu(III)
VBC				
TEPA	96.9[a] (3,370)	35.0[a] (57.8)	10.4[a] (12.6)	0.0[a] (0.0)
TEPA/PhA	96.9[a] (1,100)	99.6[a] (8,750)	100[a]	92.2[a] (419)
PhA	98.1[a] (3,140)	49.2[a] (48.0)	100[a]	92.3[a] (588)
VBC/STY				
TEPA	99.2[a] (5,030)	27.3[b] (30.6)	23.4[a] (12.5)	10.4[b] (9.5)
TEPA/PhA	99.2[a] (2,210)	95.1[b] (689)	100[a]	91.3[b] (374)
PhA	76.4[b] (96.3)	30.2[b] (13)	100[b]	2.3[b] (0.7)
VBC/MMA				
TEPA	100[a]	20.0[b] (22.0)	6.8[b] (6.4)	7.5[b] (7.2)
TEPA/PhA	100[a]	96.1[b] (1,120)	93.8[b] (687)	91.3[b] (478)
PhA	51.5[b] (36.0)	21.7[b] (9.3)	64.4[b] (62.0)	74.5[b] (98.0)

[a] Weight based on 1 mequiv of capacity.
[b] Weight based on 0.5 mequiv of capacity.

for Cu(II), this is pronounced only with the MA/PhA resin). Thus, in one example with resins prepared from the VBC/MMA support contacting Pb(II), the DETA resin complexes 14.4% lead (distribution coefficient of 11.7) and the phosphonic acid resin complexes 21.7% (distribution coefficient of 9.3) while the bifunctional resin complexes 97.4% (distribution coefficient of 1540). It is postulated that ion exchange by the phosphonic acid ligand and coordination by the amine ligand cooperate as a dual mechanism for metal ion complexation.

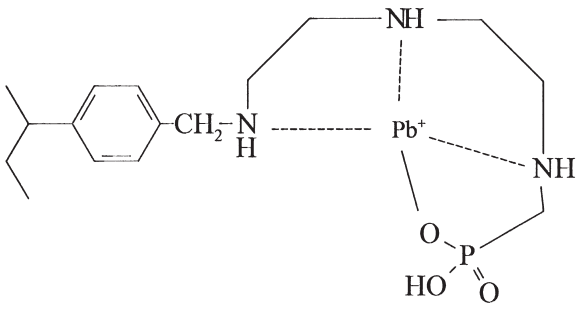

Figure 4. Supported ligand synergistic interaction between the amine and phosphonic acid ligands in the complexation of lead ions.

Figure 4 shows a possible structure that depends upon intra-ligand cooperation, but EPR studies on a related system suggest that amine and phosphonic acid ligands from more than one site can cooperate in binding metal ions (30). For the remaining cases, the bifunctional resin performs like the monofunctional amine or phosphonic acid resin, depending on which had the higher affinity for the metal ion. For example, within the STY microenvironment, the bifunctional resin behaves like the EDA, DETA, and TEPA resins when complexing copper ions and like the phosphonic acid resin when complexing lead ions (the MA resin has such a low affinity for Cu(II) that the bifunctional resin behaves more like the phosphonic acid resin with this metal though some synergism may be evident).

Cadmium ion complexation shows the greatest bifunctional effect. For example, the fully functionalized EDA resin complexes 26.0% Cd(II) (distribution coefficient of 26) and the phosphonic acid resin complexes 49.2% (distribution coefficient of 48) while the bifunctional resin complexes 98.0% Cd(II) (distribution coefficient of 2300), which far exceeds the combined value of the distribution coefficients of the monofunctional resin. Additionally, Eu(III) shows a strong synergistic interaction with the three polyamine/PhA resins in the STY microenvironment: while the DETA resin complexes 8.2% Eu(III) (distribution coefficient of 4.6) and the phosphonic acid resin complexes 2.3% (distribution coefficient of 0.7), the bifunctional resin complexes 91.8% Eu(III) (distribution coefficient of 321).

The different polymer matrices supporting the ligands affect complexation of the metal ions. This *microenvironmental effect* is the influence of inert groups near the ligand on the interaction between the ligand and the substrate. As shown in Tables 8–11, phosphonic and aminomethylphosphonic acid ligands contacted with a given metal ion show different complexing abilities depending on whether they are immobilized on VBC, VBC/STY, or VBC/MMA copolymers. With the phosphonic acid ligand, the fully functionalized resin outperforms the resin with the STY microenvironment for copper, cadmium, and europium ions; the lowest level of complexation is found for divalent ions within the MMA microenvironment. A microenvironmental effect is also evident when examining results with the aminomethylphosphonic acid ligand. When the fully functionalized MA/PhA, EDA/PhA, DETA/PhA, and TEPA/PhA resins contact Cd(II), the distribution coefficients are greater than when the ligands are within the MMA microenvironment and those, in turn, are greater than when the ligands are within the STY microenvironment; thus, for the fully functionalized EDA/PhA resin, the Cd(II) distribution coefficient is 2300 while that value for the ligand in the MMA and STY microenvironments are 880 and 212, respectively. It should be noted that the low level of complexation by the MA/PhA ligands in the STY microenvironment may be due to a lower level of phosphorylation than it is present with the other amine/PhA resins; however,

trends with it are the same as the other amine/PhA resins. The reason why cadmium ions should be more sensitive to the microenvironment is the subject of continuing investigation.

CONCLUSIONS

Amine and aminomethylphosphonate ligands of various lengths were immobilized onto 2% DVB–cross-linked VBC, VBC/STY and VBC/MMA copolymer matrices and their ability to complex metal ions under dilute solution conditions was quantified. A supported ligand synergistic interaction has been identified where the bifunctional aminomethylphosphonate ligand is able to complex greater levels of metal ions than expected from results of the corresponding monofunctional resins. A microenvironmental effect can be superimposed on the synergistic interaction, especially when cadmium ions are the substrate. Research continues to understand how the chemical nature of the ligand, the presence of bifunctionality on the polymer matrix, and the microenvironment surrounding the ligating site can all be used to tune the specificity of polymer-supported reagents for a targeted metal ion.

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REFERENCES

1. Hodge, P.; Sherrington, D.C. *Synthesis and Separations Using Functional Polymers*; Wiley: New York, 1988.
2. Hirai, H.; Toshima, N. In *Tailored Metal Catalysts*; Ieasawa, Y., Ed.; Reidel: Dordrecht, 1986.
3. Marhol, M. *Ion Exchange Resins in Analytical Chemistry*. Their Properties and Use in Inorganic Chemistry, Comprehensive Analytical Chemistry; Svehla, G., Ed.; Elsevier: Amsterdam, 1982, 15–133.
4. Alexandratos, S.D.; Crick, D.W. Polymer-Supported Reagents: Application to Separation Science. Ind. Eng. Chem. Res. **1996**, *35*, 635–644.
5. Blasius, E.; Bronzio, B. In *Chelates in Analytical Chemistry*; Flascka, H.A., Barnard, A.J., Eds.; Dekker: New York, 1967; Vol. 1, 49.

6. D'Alelio, G.F.; Hofman, E.T.; Zeman, J.R. Chelating Polymers. I. Monomeric Hydroxyarylaminoacetic Acids as Prototype Chelating Compounds. J. Macromol. Sci., Chem. **1969**, *3*, 959–989.
7. Eger, C.; Anspach, W.M.; Marinsky, J.A. Coordination Behavior of Cobalt, Nickel, Copper, and Zinc in a Chelating Ion-Exchange Resin. I. J. Inorg. Nucl. Chem. **1968**, *30*, 1899–1909.
8. Schlaepfer, C.W.; Von Zelewsky, A. Polymeric Amines as Ligands. Polyethyleneimines as Ligands in First and Second Coordination Sphere. Comments Inorg. Chem. **1990**, *9*, 181–199.
9. Kobayashi, S.; Hiroishi, K.; Tokunoh, M.; Saegusa, T. Chelating Properties of Linear and Branched Poly(Ethylenimines). Macromolecules **1987**, *20*, 1496–1500.
10. Druzin, M.I.; Vakova, I.N.; Shchennikova, N.I.; Koroleva, L.I.; Karapetyan, L.P.; Val'kova, A.K.; Zaitseva, I.V.; Pavlova, I.D. Modifications of Polyethyleneimine, J. Polym. Sci., Polym. Symp. **1974**, *47*, 369, (Transform. Funct. Groups Polym., Prague IUPAC Microsymp. Macromol., 13th, 1973).
11. Soliman, E.M. Synthesis and Metal Collecting Properties of Mono, Di, Tri and Tetramine Based on Silica Gel Matrix. Anal. Lett. **1997**, *30*, 1739–1751.
12. Hudson, M.J.; Matejka, Z. Extraction of Copper by Selective Ion Exchanges with Pendent Ethyleneimine Groups—Investigation of Active States. Sep. Sci. Technol. **1989**, *24*, 1417–1436.
13. Shambhu, M.B.; Theodorakis, M.C.; Digenis, G.A. Polystyrene Resins with Immobilized Polyamines: Preparation, Characterization, and Ability to Bind Copper(II) Ions. J. Polym. Sci., Polym. Chem. Ed. **1977**, *15*, 525–531.
14. Fujimori, K. Complexation of Poly(Ethyleneimine) with Copper(II) and Nickel(II) Ions in 0.5 *M* Potassium Nitrate Solution. J. Polym. Sci., Polym. Chem. Ed. **1985**, *23*, 169–174.
15. Shriver, D.F.; Atkins, P.; Langford, C. *Inorganic Chemistry*, 2nd Ed.; W. H. Freeman: New York, 1994; 264.
16. Huheey, J.E. *Inorganic Chemistry*, 3rd Ed.; Harper and Row: New York, 1983; 530.
17. Apelblat, A. Thermodynamic Description of Tributyl Phosphate Solvent Extraction Systems. In *Sci. Technol. Tributyl Phosphate*; Schulz, W.W., Navratil, J.D., Kertes, A.S., Eds.; CRC Press: Boca Raton, FL, 1991; 5–33.
18. Watson, E.K.; Rickelton, W.A. A Review of the Industrial and Recent Potential Applications of Trioctylphosphine Oxide. Solvent Extr. Ion Exch. **1992**, *10*, 879–889.
19. Kennedy, J.; Lane, E.S.; Robinson, B.K. Synthesis of Metal-Complexing Polymers. I. Phosphorylated Polymers. J. Appl. Chem. (Lond.) **1958**, *8*, 459–464.

20. Alexandratos, S.D.; Wilson, D.L. Dual-Mechanism Bifunctional Polymers: Polystyrene-Based Ion-Exchange/Redox Resins. Macromolecules **1986**, *19*, 280–287.
21. Alexandratos, S.D.; Quillen, D.R.; Bates, M.E. Synthesis and Characterization of Bifunctional Ion-Exchange/Coordination Resins. Macromolecules **1987**, *20*, 1191–1196.
22. Alexandratos, S.D.; Grady-Ciaccio, C.; Beauvais, R.A. The Microenvironmental Effect in Ion-Complexing Interpenetrating Polymer Networks. React. Polym. **1993**, *19*, 137–143.
23. Riedelsberger, K.; Jaeger, W. Polymeric Aminomethylphosphonic Acids. 1. Synthesis and Properties in Solution. Des. Monomers Polym. **1998**, *1*, 387–407.
24. Bligh, S.W.A.; Harding, C.T.; McEwen, A.B.; Sadler, P.J.; Kelly, J.D.; Marriott, J.A. Synthesis, Characterization and Comparative Study of Aminophosphonate Chelates of Gadolinium(III) Ions as Magnetic Resonance Imaging Contrast Agents. Polyhedron **1994**, *13*, 1937–1943.
25. Redmore, D. *N*-Benzyl-α-aminophosphonic Acids. J. Org. Chem. **1978**, *43*, 996–997.
26. Manecke, G.; Stockhausen, K.; Gergs, P. Amphoteric Ion Exchangers. IV. Makromol. Chem. **1969**, *128*, 229–235.
27. Alexandratos, S.D.; Miller, D.H.J. Microenvironmental Effect in Polymer-Supported Reagents. 1. Influence of Copolymer Architecture on the Mitsunobu Reaction. Macromolecules **1996**, *29*, 8025–8029.
28. Crick, D.W. Bifunctional Ion Exchange Resins: Synthesis and Characterization of Ion-Selective Polymers (Dual Mechanism Bifunctional Polymers). Ph.D. Dissertation, University of Tennessee.
29. Kotrly, S.; Sucha, L. *Handbook of Chemical Equilibria in Analytical Chemistry*; Ellis Horwood Ltd: Chichester, UK, 1985; 114–115, 143–149.
30. Trochimezuk, A.W.; Jezierska, J. New Amphoteric Chelating/Ion Exchange Resins with Substituted Carbamylethylenephonates; Synthesis and EPR Studies of Their Cu(II) Complexes. Polymer **2000**, *41*, 3463–3470.

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