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**Chemical Synthesis, Characterization and Separation Studies
of Functionalized Polymeric Supports**

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INTRODUCTION

Polymer resins with immobilized phosphorus acid ligands have been used to remove metal ions from solutions over a wide range of pH values. These resins offer selective removal of metal ions under acidic conditions through coordination with the phosphoryl oxygen. The use of poly(vinylbenzyl chloride) foams as supports for phosphorus-based ligands is examined in the present report. The use of foams with large pore volumes as supports for these ligands offers an advantage over gel and macroporous beads in that the increased porosity of the functionalized foams could lead to greater accessibility of the metal ions into the polymer matrix, which would result in enhanced rates of metal ion complexation. Additionally, the larger pore size of the foam allows for the use of more hydrophobic ligands such as phosphonate esters in metal ion complexations from aqueous solutions. The effects of crosslinking and sulfonation on metal ion complexation are also studied.

EXPERIMENTAL

The synthesis of vinylbenzyl chloride (VBC) beads is carried out by suspension polymerization. Both gel and macroporous beads are utilized. The gel beads contain 2% divinylbenzene (DVB) as a crosslinking agent and have a particle size of 100 - 200 mesh. The macroporous beads contain 5% DVB with a 50% void volume and a particle size of 40 - 60 mesh. VBC foams with 2.5% and 20% DVB are prepared at Los Alamos National Laboratory.¹

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The phosphonic acid resin is synthesized by refluxing the VBC beads in an excess of triisopropyl phosphite for 17 h. The beads are washed with acetone followed by 1 N HCl. The phosphonate diester intermediate is hydrolyzed by refluxing the beads in an excess of concentrated HCl for 24 h. The beads are then eluted with 1 L each of water, 1 N NaOH, water, 1 N HCl, and water at a rate of 1 L/h. The foam is functionalized in the same manner, but with a greater excess of phosphite due to loss of fluidity with swelling. Typical phosphorus capacities for the gel and macroporous beads are 4.77 and 4.34 meq/g with a solids content ($(\frac{g_{\text{dry weight}}}{g_{\text{wet weight}}} \times 100)$) of 59.49% and 43.20%, respectively. Typical phosphorus capacities for the 2.5% and 20% DVB foams are 5.04 and 4.37 meq/g with a solids content of 4.03% and 9.72%, respectively.

Diphosphonic acid gel beads, macroporous beads, 2.5% DVB foam, and 20% DVB foam are synthesized from the tetraisopropyl ester of methylene diphosphonic acid ($R_4\text{MDA}$) and have typical phosphorus capacities of 4.44, 3.28, 4.02, and 2.33 meq/g with a solids content of 60.48%, 37.47%, 4.50%, and 9.80% respectively.

Bifunctional phosphonic/sulfonic acid resins are synthesized from the phosphonic acid resin. The beads are first azeotroped dry with heptane, then contacted with a 5% (v/v) solution of chlorosulfonic acid in dichloroethane at room temperature. The reaction time for the gel and macroporous beads is 1 h and 4 h, respectively. The beads are sequentially washed with dichloroethane, dioxane, and 50/50 dioxane/1 N HCl. After washing, the beads are eluted with 1 L each of water, 1 N NaOH, water, 1 N HCl, and water at a rate of 1 L/h. The acid capacities of the gel and macroporous beads are 9.87 and 9.08 meq/g with phosphorus capacities of 3.81 and 3.24 meq/g, respectively. This

indicates that there are 2.25 and 2.60 meq/g of sulfonic acid sites on the gel and macroporous resins, respectively. The solids content for the gel and macroporous beads decrease to 37.71% and 38.25%, respectively, from the phosphonic acid precursors.

The bifunctional phosphonic/sulfonic acid foam is prepared in a different manner due to the possibility of irreversibly collapsing the pores of the foam upon drying. The phosphonic acid foam is contacted with an excess of concentrated H_2SO_4 for 48 h at room temperature, then washed with 50% aq H_2SO_4 , 30% aq H_2SO_4 , and water. The foam is also eluted with the same sequence noted with the beads. The acid and phosphorus capacities of the foam are 12.10 and 4.21 meq/g, respectively, with 3.68 meq/g of sulfonic acid sites. The solids content is 3.70%.

The phosphonate diester resins and foams are synthesized by refluxing the polymer in an excess of triethyl or triisopropyl phosphite for 17 h. The resulting diethyl- or diisopropylphosphonate ester is washed with 95% ethanol and eluted with 1 L each of water and 1 N HCl, followed by 2 L of water at a rate of 1 L/h. The diphosphonate ester resins and foams are synthesized by refluxing with R_4MDA and NaH in toluene. The diethylphosphonate, diisopropylphosphonate, and tetraisopropyldiphosphonate macroporous beads have phosphorus capacities of 3.60, 3.30, and 1.87 meq/g and a solids content of 50.86%, 52.80%, and 58.52%, respectively. The corresponding foams have phosphorus capacities of 3.78, 3.44, and 3.32 meq/g and a solids content of 12.71%, 18.54%, and 8.89%, respectively.

Metal ion studies are carried out by contacting enough polymer to give 1 meq of ligands based on the acid or phosphorus capacity with 10 ml 10^{-4} N metal nitrate

solutions in the appropriate matrix for 30 min or 24 h. The amount of metal ion removed from the solution is determined on a Perkin-Elmer atomic absorption spectrometer (model 3100) in the emission mode for Eu(III), and in the absorption mode for Cu(II), Pb(II), and Fe(III).

RESULTS

A comparative study of the gel beads, macroporous beads, and foam with the phosphonic acid functional group in complexing Eu(III), Fe(III), Cu(II), and Pb(II) from 1N nitric acid with a 30 min contact time is shown in Table 1. The increased pore size of the foam results in enhanced kinetics within a highly acidic environment. In less acidic solutions, however, where the beads are more fully hydrated, the performance of the foam is more comparable to that of the beads (Table 2).

Table 1. Distribution Coefficients of Metal Ions from 1N Nitric Acid Solution

	Eu(III)	Fe(III)	Cu(II)	Pb(II)
2% DVB Gel	7.202	329.1	0	1.472
5% DVB MR ^a	10.73	183.7	1.179	2.796
2.5% DVB Foam	29.82	1648.	24.07	22.08

^aMacroporous beads

Table 2. Distribution Coefficients of Metal Ions from 0.04N Nitric Acid Solution

	Eu(III)	Fe(III)	Cu(II)	Pb(II)
2% DVB Gel	890.9	13701.	159.3	437.1
5% DVB MR	∞	1730.	124.6	581.1
2.5% DVB Foam	20135.	3694.	141.5	437.2

The Eu(III) study was repeated with the phosphonic acid samples in a 1 N nitric acid/0.4 N sodium nitrate solution with a 30 min contact time to determine metal ion uptake with a higher ionic strength solution (Table 3). That the results are comparable to those in the absence of sodium nitrate indicates the selectivity of the phosphorus acid ligand which is transparent to the sodium ions present in great excess.

Table 3. Distribution Coefficients of Metal Ions from 1N Nitric Acid / 0.4N Sodium Nitrate

	2% DVB Gel	5% DVB MR	2.5% DVB Foam
Eu(III)	8.780	9.018	38.80

An increase in the crosslinking of beads will increase the rigidity of the polymer matrix resulting in decreased distribution coefficients compared to less crosslinked beads. To determine the effect of increased crosslinking on foams, metal ion studies were done using the 20% DVB phosphonic acid foam in a 1 N nitric acid solution with a 30 min contact time. As shown in Table 4, the foam is much less susceptible to crosslinking effects, given that the distribution coefficients are comparable to those in Table 1 for the 2.5% DVB foam. The open pore structure must thus compensate for the greater rigidity of the matrix.

Table 4. Distribution Coefficients of Metal Ions from 1N Nitric Acid

	Eu(III)	Fe(III)	Cu(II)	Pb(II)
20% DVB Foam	30.05	1007.	6.534	11.23

The sulfonation of polymers with immobilized phosphorus acid ligands leads to a much enhanced rate of metal ion complexation while retaining the selectivity observed with the phosphorus ligands alone. A comparative study undertaken with sulfonated foam (Table 5) shows that the beads do indeed greatly increase their distribution coefficients (compare with Table 1), but improvement with the foam is marginal. Once more, the foam's inherently open structure is not further enhanced by, in this case, bifunctionality.

Table 5. Distribution Coefficients of Metal Ions from 1N Nitric Acid

30 min contact	Eu(III)	Fe(III)	Cu(II)	Pb(II)
2% DVB Gel	513.8	∞	7.362	7.026
5% DVB MR	2914.	∞	11.63	21.44
2.5% DVB Foam	45.75	∞	17.46	15.46
24 h contact				
2% DVB Gel	519.0	---	7.536	8.760
5% DVB MR	5461.	---	12.81	23.98
2.5% DVB Foam	52.91	---	25.66	26.51

Resins with geminal diphosphonic groups have much greater metal ion uptake than analogous monophosphonate resins. This is believed to be due to a chelate effect. Use of this ligand was extended to foams in the present study. All uptake experiments were carried out from a 1 N nitric acid solution. The distribution coefficients presented in Tables 6 and 7 do show a greater metal ion uptake, relative to the phosphonic acid.

Table 6. Distribution Coefficients of Metal Ions from 1N Nitric Acid

24 h	Eu(III)	Fe(III)	Ag(I)
2.5% DVB Foam	∞	∞	291.8

Table 7. Eu(III) Distribution Coefficients from 1 N Nitric Acid

Eu(III)	2% DVB Gel	5% DVB MR	20% DVB Foam
30 min	1126.	19.36	98.85
24 h	23295.	2169.	3213.

Due to the hydrophobic nature of the phosphonate ester polymers, metal ions have limited access to ligands immobilized on beads. To take advantage of the increased pore size and lower level of solids of the foam, phosphonate esters were also examined. The metal ion studies were done in a 1 N nitric acid solution with a 24 h contact time (Table 8). The far greater efficiency of the foam over the beads in all cases (except one) opens up a new area of metal ion separations chemistry allowing for the use of ligands thought to be too hydrophobic to permit accessibility of metal ions into the polymer matrix.

Table 8. Comparative Study of Beads and Foam with Immobilized Ester Ligands

	Eu(III)	Fe(III)	Ag(I)
Diethylphosphonate MR (5% DVB)	1.855	3.404	3.355
Diethylphosphonate Foam (2.5% DVB)	32.32	158.8	805.6
Diisopropyl-phosphonate MR (5% DVB)	0.9609	0.2026	1.627
Diisopropyl-phosphonate Foam (2.5% DVB)	10.74	8.826	50.19
Tetraisopropyl-diphosphonate MR (5% DVB)	1.697	0.1453	27000.
Tetraisopropyl-diphosphonate Foam (2.5% DVB)	79.72	159.9	194.6

DISCUSSION

In order to ensure that results between the gel and macroporous beads and the foam were comparable, the gel beads used were of a small particle size (and hence, a greater surface area). The macroporous beads had 50% void volume, also for greater accessibility.

Metal ion studies from 1 N nitric acid show significant differences between the distribution coefficients of the beads and the foam (Table 1). The distribution coefficients of the foam are larger than those of both the gel and macroporous beads for each of the metal ions at a 30 min contact time. For both Cu(II) and Pb(II), the gel and macroporous beads have distribution coefficients of ~ 0 , while the foam has distribution coefficients of 24.07 and 22.08 for copper and lead, respectively. For Eu(III), the gel and macroporous beads have similar distribution coefficients, 7.202 and 10.73 respectively, while the foam has a distribution coefficient of 29.82. Fe(III) has distribution coefficients of 329.1 and 183.7 for the gel and macroporous beads; respectively, and a value of 1648 for the foam. When the europium study is repeated in a 1 N nitric acid/0.4 N sodium nitrate solution, the distribution coefficients change only slightly for each of the polymers at a 30 min contact time (Table 3). These results indicate that in solutions with high ionic strength, the foam has an advantage over the beads. The greater distribution coefficients of the foam are attributed to its greater porosity and low solids content. This allows metal ions better access to the ligands in the foam than with the beads.

When metal ion studies were carried out with immobilized phosphonic acid ligands in 0.04 N nitric acid, the 2.5% DVB foam showed no advantage over the gel and

macroporous beads (Table 2).

The higher crosslinked foam was examined because of its greater resistance to attrition during functionalization and contact studies. The increased rigidity of a polymer matrix caused by increased crosslinking can result in lower metal ion uptake due to a decreased accessibility of the metal ions to the ligands. The metal ion studies were carried out using a 20% DVB phosphonic acid foam in 1 N nitric acid solutions with a contact time of 30 min (Table 4). The distribution coefficients for each metal ion decreased but only slightly relative to the 2.5% DVB phosphonic acid foam under the same conditions. The most significant decrease was seen with iron. The distribution coefficient went from 1648 with the 2.5% DVB foam to 1007 with the 20% DVB foam. It should also be noted that the distribution coefficients for the 20% DVB phosphonic acid foam were still larger than those of the gel and macroporous beads.

The phosphonic/sulfonic acid polymers were prepared by sulfonation of the phosphonic acid resins and foam. The sulfonic acid sites were expected to increase the kinetics of the metal ion complexation through increased matrix hydrophilicity and enhanced ion exchange allowing for greater accessibility of the metal ions to the phosphoryl oxygen sites. The studies were done in 1 N nitric acid solutions for 30 min and 24 h contact times (Table 5). The principal conclusion is that bifunctionality is critical to the performance of the beads but an unimportant variable for the foam. For the 30 min contact study with Pb(II), the distribution coefficients for the gel and macroporous beads increased, relative to the phosphonic acid study, from 1.472 to 7.026 and 2.796 to 21.44 respectively, while the foam decreased from 22.08 to 15.46. The

30 min contact study with Cu(II) also showed an increase from 0 to 7.362 and 1.179 to 11.63 for the gel and macroporous resins, respectively, while the foam decreased from 24.07 to 17.46. The Fe(III) distribution coefficients went from 329.1, 183.7, and 1648 with the phosphonic acid gel beads, macroporous beads, and foam, respectively, to an infinite value (100% complexed) with all of the phosphonic/sulfonic acid samples during the 30 min contact time. The distribution coefficients for Eu(III) increased relative to the phosphonic acid study from 7.202 to 513.8 for the gel and 10.73 to 2914 for the macroporous beads during the 30 min contact, while the distribution coefficient for the foam increased from 29.82 to 45.75. The larger distribution coefficients of the phosphonic/sulfonic acid beads, relative to the phosphonic acid beads, indicate that the sulfonic acid group increases the accessibility of the metal ions into the polymer. The values for the phosphonic/sulfonic acid foam indicate that the sulfonic acid group is not needed for increased accessibility at 30 min in foams and may even be hindering the complexation of certain metal ions.

The phosphonic/sulfonic acid results with the 24 h contact studies show little change in the distribution coefficients for the gel and macroporous beads with each metal ion, except for Eu(III). The distribution coefficients of the macroporous resin went from 2914 at 30 min to 5461 at 24 h (98.89% and 99.41% of the Eu(III) being complexed). The distribution coefficients for the foam increased for Pb(II), Cu(II), and Eu(III) at 24 h, showing that it had not reached equilibrium at 30 min. It is unclear why the complexation of Eu(III) with the foam is not as high as expected compared to the beads.

The diphosphonic acid polymers have shown an increased ability to complex metal ions under highly acidic conditions relative to the phosphonic acid resins. Because of the potential advantage of enhanced kinetics due to a larger pore size, it was desirable to functionalize the foam with the diphosphonic acid ligands. Metal ion studies were carried out with the 2.5% DVB diphosphonic acid foam in 1N nitric acid with a 24h contact time (Table 6). The foam complexed 100% of the Eu(III) and Fe(III), and 87.89% of the silver ions (distribution coefficient of 291.8). A comparative study was also done using the gel and macroporous resins and the 20% DVB foam over 30 min and 24 h periods with Eu(III) in 1 N nitric acid (Table 7). At 30 min, the distribution coefficients for the gel resin, macroporous resin, and 20% DVB foam are 1126, 19.36, and 98.85 respectively. When the contact time is increased to 24 h, the distribution coefficients increase to 23295 for the gel resin, 2169 for the macroporous resin, and 3213 for the 20% DVB foam. The increased kinetics of the gel resin could be the result of the higher level of functionalization relative to the macroporous resin and 20% DVB foam.

Phosphonate esters are important ligands in metal ion complexation because they offer selectivities that are different from those of the corresponding acid. The use of different alkyl groups on the ester functionality can also contribute to different selectivity trends. However, the use of phosphonate esters can be limited due to a decreased accessibility of the metal ions to the ligands given their hydrophobicity and resulting high solids level of the polymer matrix. However, the more open structure of the phosphonate ester foams (with solids content ranging from 8.89% to 18.54%) could allow greater access to the ligands. Comparative studies between phosphonate ester macroporous

resins and foams were done with Eu(III), Fe(III), and Ag(I) in 1 N nitric acid with a contact time of 24 h (Table 8). Both the Eu(III) and the Fe(III) studies show that each of the phosphonate ester foams have larger distribution coefficients than the corresponding macroporous resins. In addition, the diethyl- and diisopropylphosphonate ester foams have larger distribution coefficients with Ag(I) than their corresponding macroporous beads. It is not yet clear why the tetraisopropyldiphosphonate macroporous resin has such a large distribution coefficient for Ag(I), relative to the foam.

CONCLUSIONS

The use of poly(vinylbenzyl chloride) foam as a support for phosphorus-based ligands can lead to enhanced kinetics in metal ion complexation studies. This is attributed to the foams larger pore size and greater hydrophilicity relative to the beads. When metal ion studies are carried out in 0.04 N nitric acid with a 30 min contact time, the 2.5% DVB phosphonic acid foam gives comparable results to the 2% DVB gel and 5% DVB macroporous beads for Cu(II) and Pb(II); the macroporous beads are best with Eu(III) and the gel beads best with Fe(III). When these studies are repeated in solutions of higher acidity/ionic strength (1 N nitric acid without and with 0.4 N sodium nitrate), the phosphonic acid foam gives greater distribution coefficients for each of the metal ions, relative to the beads. When a 20% DVB phosphonic acid foam is used for metal ion studies in 1 N nitric acid, also with a 30 min contact time, the distribution coefficients decrease slightly, relative to the 2.5% DVB foam, for each of the metal ions, but remain larger than those for the beads under identical conditions.

The use of the phosphonic/sulfonic acid polymers gives comparable distribution coefficients between the beads and the 2.5% DVB foam for Fe(III), Cu(II), and Pb(II) at a 30 min contact time in 1 N nitric acid, with the values increasing for the beads relative to the non-sulfonated samples. The values for the foam did not change significantly with Cu(II) and Pb(II) relative to the non-sulfonated foam, indicating that the ligands are accessible without the need of increased non-selective ion exchange at 30 min contact times. When the contact time is lengthened to 24 h with the phosphonic/sulfonic acid polymers, the foam does show a slight increase in the amount of metal ion complexed, while the values for the beads remain approximately the same, indicating that the foam had not completely reached equilibrium in 30 min.

When diphosphonic acid ligands are immobilized, 20% DVB foam can complex more Eu(III) than the macroporous resin in 1 N nitric acid. The gel beads outperform both, perhaps due to its higher level of functionalization. The 2.5% DVB foam complexes 100% of both Eu(III) and Fe(III) and 87.89% of Ag(I) at 24 h in 1 N nitric acid.

Studies with the relatively hydrophobic phosphonate esters indicate that foams can complex high levels of metal ions relative to beads.