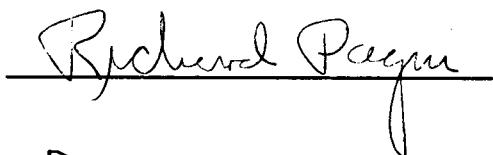


To the Graduate Council:

I am submitting herewith a thesis written by Marie E. Bates entitled "Dual Mechanism Bifunctional Polymers. Class III. Ion Exchange/Precipitation Resins." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.


Spiro D. Alexandratos, Major Professor

We have read this thesis
and recommend its acceptance:





Accepted for the Council:


Vice Provost
and Dean of The Graduate School

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a Master's degree at The University of Tennessee, Knoxville, I agree that the Library shall make it available to borrowers under rules of the Library. Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgment of the source is made.

Permission for extensive quotation from or reproduction of this thesis may be granted by my major professor, or in his absence, by the Head of Interlibrary Services when, in the opinion of either, the proposed use of the material is for scholarly purposes. Any copying or use of the material in this thesis for financial gain shall not be allowed without my written permission.

Signature Marie E. Bato

Date January 25, 1988

DUAL MECHANISM BIFUNCTIONAL POLYMERS. CLASS III.
ION EXCHANGE/PRECIPITATION RESINS

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Marie E. Bates

March 1988

To my parents, Hugh and Shelba Bates.

ACKNOWLEDGMENTS

I would like to thank Dr. S. D. Alexandratos for his excellent guidance and the Department of Energy for financial support during this course of study.

ABSTRACT

A third class of dual mechanism bifunctional polymers which operate by mechanisms of ion exchange and precipitation have been developed for specific metal ion recovery. A divinylbenzene crosslinked poly(vinylbenzyl chloride) copolymer is functionalized with a phosphonic acid ion exchange group and a quaternary amine group containing a counterion capable of precipitation with a targeted metal ion. Selectivity in metal ion extraction can be attained through varying the alkyl groups of the amine and/or the counterion. Bifunctional phosphonic acid/trimethylamine and phosphonic acid/tributylamine resins containing, for example, Cl^- , SCN^- , IO_3^- , and SO_4^{2-} counterions, have been synthesized. The performance of these resins in the extraction of various metal ions, such as Ag^+ , Hg^{2+} , Pb^{2+} , Ni^{2+} , and Zn^{2+} , has been investigated and compared with that of corresponding monofunctional phosphonic acid and quaternary amine resins. The extraction of Ag^+ by the bifunctional phosphonic acid/tributylamine resin with the thiocyanate counterion appears to be the first example of synergism in metal ion extraction by polymer--supported reagents.

A bifunctional phosphonic acid/dimethylamine resin has also been synthesized and its ability to extract Ag^+ and Hg^{2+} investigated. This resin can operate by ion exchange and coordination mechanisms and belongs to the second class of dual mechanism bifunctional polymers.

TABLE OF CONTENTS

CHAPTER	PAGE
INTRODUCTION	1
I. CLASS III RESINS	9
Synthesis and Characterization	9
Metal Ion Extraction Studies with Resins after KSCN, KIO ₃ , and HCl Elutions	16
Metal Ion Extraction Studies with Resins after H ₂ SO ₄ Elution	28
Metal Ion Extraction Studies with Resins after H ₃ PO ₄ Elution	40
Metal Ion Extraction Studies with Resins after Na ₂ S Elution	46
Concluding Remarks and Future Directions	56
II. CLASS II RESINS	59
Synthesis and Characterization	59
Silver and Mercury(II) Ion Extraction Studies	63
III. EXPERIMENTAL	70
Copolymer Synthesis	70
Phosphonic Acid Resin Synthesis	71
Trimethylamine Resin Synthesis	71
Tributylamine Resin Synthesis	72
Dimethylamine Resin Synthesis	72
Dimethylethylamine Resin Synthesis	72
Triethylamine Resin Synthesis	73

CHAPTER	PAGE
III. (Continued)	
Phosphonic Acid/Trimethylamine Resin Synthesis	73
Phosphonic Acid/Tributylamine Resin Synthesis	73
Phosphonic Acid/Dimethylamine Resin Synthesis	74
Procedure for % Solid Weight of a Functionalized Resin . .	74
Determination of the Acid Capacity via Titration with NaOH	74
Determination of the Acid Capacity via Titration with KOH in Dioxane	75
Phosphorus Elemental Analysis	75
Chlorine Elemental Analysis	76
Iodine Analysis for Oxidizable P-H Bonds	78
Silver Oxidation Analysis	78
Determination of the Total Anion Exchange Capacity (TAEC) .	79
Determination of the Salt Splitting Anion Exchange Capacity (SSAC)	79
Sulfide Analysis	80
Resin Elutions to Attain Appropriate Counterion on the Amine Sites	80
Metal Ion Extraction Studies	81
LIST OF REFERENCES	83
APPENDICES	86
APPENDIX A. PHOSPHINIC ACID RESIN AS A REDOX REAGENT IN ORGANIC REACTIONS	87

CHAPTER	PAGE
APPENDIX B. PHOSPHINIC ACID RESIN AS AN ACID CATALYST IN ORGANIC	
REACTIONS	94
VITA	97

LIST OF TABLES

TABLE	PAGE
I. Capacities of Phosphonic Acid Resins as a Function of Temperature and Catalyst	12
II. Percent Ag^+ , Hg^{2+} , and Pb^{2+} Absorbed by Resins After KSCN Elution	18
III. Percent Ag^+ , Hg^{2+} , and Pb^{2+} Absorbed by Resins After KIO_3 Elution	19
IV. Percent Ag^+ and Pb^{2+} Absorbed by Resins After HCl Elution	20
V. Calculated Percent Absorption Values for the Bifunctional Resins	23
VI. Percent Metal Ion Absorbed by a Mixed PA Resin and TBA Resin Bed	26
VII. Percent Ca^{2+} , Sr^{2+} , and Ba^{2+} Absorbed by Resins After H_2SO_4 Elution	29
VIII. R_i Study for the Absorption of Ca^{2+} at a 1 h Contact Time .	31
IX. R_i Study for the Absorption of Ba^{2+}	32
X. Calculated Ba^{2+} Percent Values for the Bifunctional PA/TMA Resin	36
XI. Percent Ba^{2+} Absorbed by a Mixed PA Resin and TMA Resin Bed	37
XII. Percent Ba^{2+} Absorbed in the Presence of Various Aqueous Anions	38
XIII. Percent Hg^{2+} Absorbed by Resins After H_2SO_4 Elution . . .	40

TABLE	PAGE
XIV. Percent Ca^{2+} , Sr^{2+} , and Ba^{2+} Absorbed by Resins After H_3PO_4 Elution	42
XV. Percent Zn^{2+} Absorbed in the Presence of Various Aqueous Anions	43
XVI. Hg^{2+} Absorption by Resins After H_3PO_4 Elution at Various R_i 's	45
XVII. Percent Metal Ion Absorbed with Resins After H_3PO_4 Elution	47
XVIII. Percent Ag^+ , Hg^{2+} , and Cd^{2+} Absorbed by Resins After Na_2S Elution	48
XIX. Percent Ni^{2+} and Cr^{3+} Absorbed by Resins After Na_2S Elution	50
XX. Percent Ni^{2+} and Cr^{3+} Absorbed by Resins After HCl and HNO_3 Elutions	53
XXI. Amination Conditions and Resulting Capacities of the Bifunctional PA/DMA Resins	62
XXII. Reaction of the Phosphinic Acid Resin with Dimethylsulfoxide	89
XXIII. Reaction of the Phosphinic Acid Resin with Crotonaldehyde, Triphenylphosphine Oxide, and Cinnamaldehyde	91

LIST OF FIGURES

FIGURE	PAGE
1. Class I Resins	6
2. Class II Resins	6
3. Class III Resins	6
4. Phosphonic Acid Resin Synthesis	10
5. Bifunctional Phosphonic Acid/Trimethylamine Resin Synthesis .	14
6. Bifunctional Phosphonic Acid/Tributylamine Resin Synthesis . .	15
7. % L vs. R_i for Ca^{2+} Absorption	33
8. % L vs. R_i for 1 h Ba^{2+} Absorption	33
9. % L vs. R_i for 3 h Ba^{2+} Absorption	34
10. % L vs. R_i for Hg^{2+} Absorption	45
11. Bifunctional Phosphonic Acid/Dimethylamine Resin Synthesis . .	59
12. Dimethylamine Resin Synthesis	62
13. % L vs. R_i Curves for Ag^+ Absorption with Resins after HCl Elution	64
14. % L vs. R_i Curves for Hg^{2+} Absorption with Resins after HCl Elution	65
15. % L vs. R_i Curves for Ag^+ Absorption with Resins after NaOH Elution	67
16. % L vs. R_i Curves for Hg^{2+} Absorption with Resins after NaOH Elution	68
17. % Reaction vs. Reaction Time for the Resins in Their Hydrated Form	95
18. % Reaction vs. Reaction Time for the Resins with the Waters of Hydration Removed	95

INTRODUCTION

Research involving chemical reagents bound to solid polymer supports has become increasingly widespread over the past years. In the area of biochemistry, polymer--supported reagents are used in the synthesis of peptides, oligosaccharides, and oligonucleotides.¹ Also a large amount of research exists in the area of polymer--supported enzymes as biological catalysts.² Polymer--supported oxidizing agents, reducing agents, photosensitizers, Wittig reagents, phase transfer catalysts, transition metal catalysts, inorganic acid, base, or metal ion catalysts and protective groups have been investigated for their usefulness in organic synthesis.^{3,4,5} Organic chemists have also used polymer--supported reagents as traps for reactive intermediates in mechanistic studies.⁴ The oldest utilization of polymer--supported reagents is with the synthetic ion exchange resins. The original and presently largest single application of such resins is in the purification and demineralization of water.⁶ In analytical and inorganic chemistry polymer--supported ion exchangers are commonly employed in chromatographic methods for the separation and preconcentration of metal ions.⁷

The growing need for the separation and recovery of specific metal ions from dilute aqueous solutions has resulted in a large effort toward synthesizing highly selective ion exchange resins. The separation and recovery of radioactive metal ions has become increasingly important in the nuclear industry.⁸ In the field of hydrometallurgy, the extraction of low abundance metals from their ores is becoming more economical for both environmental and political reasons.⁹ At present, solvent

extraction (or liquid--liquid extraction) is the sole means for metal ion recovery on the industrial scale. The solvent extraction process usually consists of two stages: extraction of metal ions (either metal cations or anionic or neutral metal complexes) from an aqueous solution by contact with an extractant in an organic solvent, and stripping of the loaded solvent by an aqueous solution resulting in a concentrated solution of the targeted metal species. Another stage often employed is the scrubbing of the loaded organic solvent for removal of undesired metals and impurities prior to the stripping of the desired metal. The major problem with the solvent extraction process is the loss of solvent which occurs mainly through entrainment into the aqueous phase during phase separation, but also occurs to a slight and unavoidable extent through solubility in the aqueous phase. Poor coalescence of the two immiscible layers increases solvent loss through entrainment as can the formation of a solid crud at the aqueous and organic interface. The fact that minimization of solvent loss requires extra expense has resulted in little effort to eliminate this problem. Since the contaminated water, which contains not only the organic components but also complexed metal ions, is eventually returned to the rivers and lakes, environmental concerns are increasing and will undoubtedly lead to stricter waste management controls.¹⁰

The use of ion exchange resins in the extraction of metal ions eliminates the problems associated with solvent extraction since the solid phase contains both the extractant and the solvent and can easily be separated from the aqueous solution. Ion exchange resins can also be used in the treatment of very dilute solutions in which solvent

extraction is not feasible. Another attractive feature with solid ion exchangers is that they can be employed easily in a continuous process. By successive elutions of the resins in a packed column the metal ion can be extracted, recovered, and the resins regenerated. The initial large scale application of synthetic resins would be an expensive process, but with growing environmental concerns and their probable employment as a cleanup step in solvent extraction, this is becoming less of a drawback.^{7,11} The major disadvantages with ion exchange resins in comparison to liquid extractants are their lower selectivities and slower extraction rates.

The best known ion exchange resin is the sulfonic acid resin which consists of sulfonic acid groups covalently bound to a polystyrene/divinylbenzene copolymer matrix. The fact that it is a strong acid ion exchanger makes its use as a general cation complexing agent quite popular, but at the same time, greatly reduces its use for selective recovery. The weaker carboxylic acid resin exhibits greater selectivity in metal ion recovery, but is only applicable at a relatively high pH since otherwise the carboxylate groups remain protonated.¹² In order to obtain resins with selectivities comparable to those found in solvent extraction, various liquid extractants have been covalently bound to solid polymer supports. The synthesis of quite a large number of chelating and coordinating ion exchange resins and their subsequent metal ion selectivities have recently been reviewed by Sahni and Reedijk.¹³ Chelating resins containing covalently bonded substituted hydroxyoximes and hydroxyquinolines have been synthesized and investigated for their ability to extract copper for which the monomeric liquid extractants are

commercially used.^{10,13} The most popular chelating ion exchange resin is the iminodiacetic acid resin which is used in the separation of nickel from cobalt.^{6,8} Picolylamine resins are being studied for their ability to extract copper in the presence of iron and also in the extraction of nickel from a cobalt electrolyte.⁸

Two of the most commonly employed types of liquid extractants are the organophosphorus acids and esters of which the best known are di(2--ethylhexyl)phosphoric acid (D2EHPA) and tri--n--butylphosphate (TBP). Incorporation of these extractants into polymer matrices (usually a polystyrene/divinylbenzene copolymer) has resulted in what are known as solvent impregnated resins. These resins are prepared either by the absorption of the extractant into the copolymer or by the addition of the extractant as a diluent in the polymerization reaction resulting in the Levextrel resin.⁹ Resins impregnated with D2EHPA, TBP, tertiary amines, and hydroxyoximes have been investigated in the extraction of uranium, zinc, gold, copper, nickel, iron, cobalt, etc.⁹ More recently, solvent impregnated resins containing a synergistic mixture of the extractants D2EHPA and trioctylphosphine oxide have been studied in the recovery of uranium.⁸ The application of solvent impregnated resins eliminates the problems of solvent entrainment, crud formation, and poor coalescence which accompany solvent extraction, but loss of extractant due to solubility in the aqueous phase remains a significant problem here since it affects the resins' lifetimes.

The selectivity of all ion exchange resins is affected to a certain extent by several factors: the acid or base strength of the fixed exchanger groups, the valence, solvated size, and polarizability of the

targeted counterion, the possible interaction of the polymer support with the counterions (London forces), and specific interactions between the ion exchange group and the targeted species such as complex formation which is employed with the chelating resins.¹² Other methods of increasing selectivity in metal ion extraction involve combining the ion exchange reaction with an additional reaction. This has recently been referred to as reactive ion exchange and is defined to encompass any possible metal extraction process in which the ion exchange reaction is accompanied, preceded, or followed by another reaction such as oxidation, reduction, precipitation, chelation, complex formation, or neutralization to name a few.⁷ An extensive discussion of the subject of reactive ion exchange is presented by Janauer.⁷

In the laboratory of Professor S. D. Alexandratos, phosphorus based ion exchange resins, known as dual mechanism bifunctional polymers, are being designed and developed for selective metal ion extraction. At present, three general classes of resins exhibiting reactive ion exchange through redox, coordination, and precipitation reactions have been prepared. Figures 1, 2, and 3 contain representative resins from the three classes. The resins utilize either a polystyrene/divinylbenzene copolymer or a poly(vinylbenzyl chloride)/divinylbenzene copolymer support. The selectivity of the resins in metal ion extraction has been and is presently being investigated. The name **dual mechanism bifunctional polymer** results from the fact that each resin contains two functional groups and is capable of metal ion extraction by two different mechanisms.

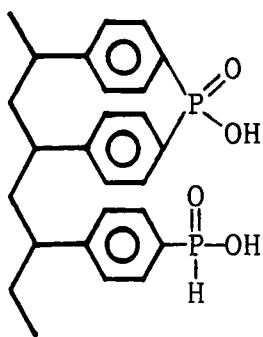
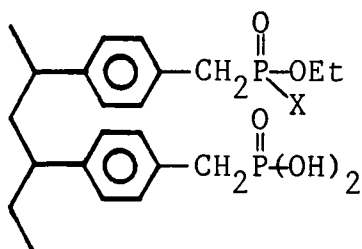


Figure 1. Class I resins.



$X = \text{OH}, \text{OEt}$

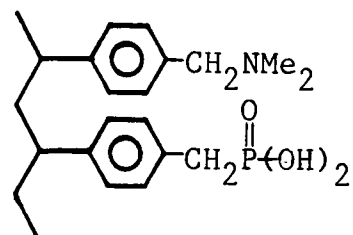
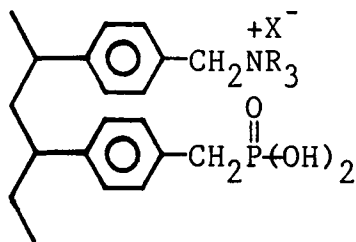


Figure 2. Class II resins.



$R = \text{Me}, \text{Et}, \text{Bu}$

$X = \text{Associated Anion}$

Figure 3. Class III resins.

The Class I resins are synthesized with primary and secondary phosphinic acid functional groups or primary phosphinic acid and secondary phosphine oxide groups.¹⁴ As expected, due to its intermediate acid strength the phosphinic acid resin exhibits a greater selectivity in the extraction of various metal ions including uranium, plutonium, and americium in the presence of sodium ions than the corresponding sulfonic and carboxylic acid resins. This higher selectivity is observed in the extraction of the metal ions from 4 M HNO_3 solutions due to coordination through the phosphoryl oxygen.¹⁵ In the presence of metals with the appropriate reduction potentials the phosphinic acid resin also operates by a redox mechanism. Silver and mercury(II) ions are reduced to their metallic states by the oxidizable P-H bond.¹⁶ As a result of this dual mechanism extraction process the Class I polymers fall into the class of ion exchange/redox resins.

The Class II dual mechanism bifunctional polymers are ion exchange/coordination resins and consist of a phosphonic acid functional group and another group capable of metal ion coordination such as a phosphonate ester or a tertiary amine. The fact that the acid groups create a hydrophilic environment within the resin increases the accessibility of the neutral coordinating ligands to the metal ion which allows for additional selectivity to occur through complexation. Synergism has been observed in liquid--liquid extraction systems containing a mixture of an alkylphosphoric acid (e.g. D2EHPA) and a neutral phosphonate ester or amine such as TBP¹⁷ or tri--n--octylamine.¹⁸ The synergistic effect is attributed to the fact that upon complexation the neutral ligands are capable of replacing the waters of hydration around the metal ion, thus

rendering the complex more compatible with the organic phase. This suggests that the same type of synergistic behavior could occur with a solid extractant in which the two ligands are immobilized on the same polymer backbone although at present this has not been observed with the Class II resins. The synthesis and characterization of the phosphonic acid/tertiary amine resin are presented in this thesis along with subsequent metal ion extraction studies. In its protonated form with the chloride counterion, the phosphonic acid/amine resin resulted in the precipitation of AgCl in the extraction of silver ions. The possibility of a resin exhibiting metal ion specificity through a precipitation mechanism led to the synthesis of the Class III ion exchange/precipitation resins. Examples of reactive ion exchange, in which a metal loaded cation exchange resin or an anion exchange resin loaded with an anionic complex of the targeted metal are eluted with a precipitating agent, are discussed by Janauer.¹⁰ The Class III resins consist of a quaternary amine group which contains a counterion capable of precipitation with the targeted metal ion. By increasing the size of the quaternary amine alkyl group and employing a somewhat organophilic counterion, precipitation within the resin can be achieved. The synthesis of and initial metal ion studies with the Class III resins is also presented in this thesis, and their mechanism of action is developed.

CHAPTER I

CLASS III RESINS

Synthesis and Characterization

The Class III dual mechanism bifunctional polymers operate via ion exchange and precipitation mechanisms. Bifunctional phosphonic acid/quaternary amine resins could show enhanced selectivity in metal ion extraction through the precipitation of the metal ion with the counterion of the quaternary amine site. The selectivity of the resin may be adjusted by varying two factors: the quaternary amine and its counterion. Ion exchange with subsequent precipitation of a targeted metal ion within a polymer resin would be of utmost importance, since it would prevent the need for further separation processes. At present, resins containing phosphonic acid moieties and either trimethylamine or tributylamine groups have been synthesized and characterized. The counterion of choice can be obtained by simple elution of the resin with an acid or salt solution of the anion. The synthesis and characterization of phosphonic acid/quaternary amine resins, and initial metal ion extraction studies with the resins are presented.

Poly(vinylbenzyl chloride) (VBC) crosslinked with two weight percent divinylbenzene (DVB) in the form of gel beads was used as the polymer support unless otherwise noted. The VBC support was employed because it offers the same attractive features as polystyrene, such as ease of functionalization and physical and thermal stability, and at the same time avoids the highly toxic chloromethylation step necessary with the

polystyrene support prior to amination.¹⁹ The DVB monomer solution used in the copolymerization contained only 55.4% DVB due mainly to the presence of ethylvinylbenzene.¹⁹ As a result of this, one gram of a 2% crosslinked copolymer contains 0.96 g of VBC. This fact is taken into account in calculating theoretical capacities as will be seen later.

The bifunctional phosphonic acid/quaternary amine resins are prepared by amination of a partially functionalized phosphonic acid resin. In order to obtain a bifunctional resin containing relatively equal amounts of phosphonic acid groups and amine groups, a 50% functionalized phosphonic acid resin was needed. Before preparing the bifunctional resin, the synthesis of the phosphonic acid resin was studied and optimal conditions for partial functionalization determined. As outlined in Figure 4, the phosphonic acid resin is prepared by contacting the VBC copolymer with an excess of PCl_3 in the presence of AlCl_3 catalyst with a subsequent water quench. The functionalized resin is characterized for total acid capacity by a NaOH titration and total phosphorus capacity and chlorine capacity by corresponding elemental analyses. Resins prepared under various reaction conditions and the resulting total acid, phosphorus, and chlorine capacities are listed in

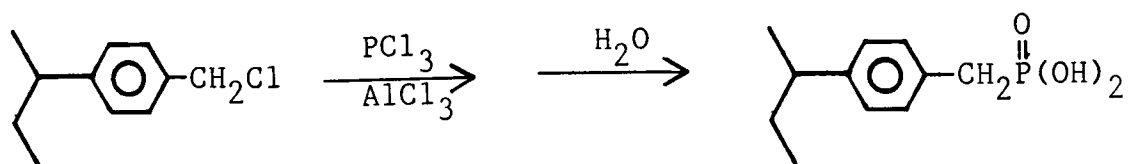


Figure 4. Phosphonic acid resin synthesis.

Table I. All reactions were carried out at the specified temperature for four hours except for the last entry which had a reaction time of twenty hours. The catalyst concentrations are expressed in mol AlCl_3 /mol VBC groups. The degree of functionalization was found to depend on the AlCl_3 catalyst concentration and the reaction temperature.

The fact that the total acid capacity does not equal twice the phosphorus capacity as expected for a phosphonic acid resin appears to be due to an accessibility problem, i.e., the NaOH neutralization does not go to 100% completion. In the presence of a swelling solvent (dioxane), a KOH analysis resulted in an acid capacity of 5.15 mequiv/g for a resin with a phosphorus capacity of 2.68 mequiv/g, whereas the aqueous NaOH analysis gave a value of only 3.90 mequiv/g. Inaccessibility is associated with the resin's hydrophobicity and becomes less of a problem with the more highly functionalized resins. The possibility of the acid capacity being reduced to less than twice the P capacity by the presence of primary phosphinic acid moieties has been dismissed since silver and iodine oxidation analyses indicate the absence of the phosphinic's P-H bonds.

The resin obtained with 1.22 mol of AlCl_3 at reflux (73°C) results in an acid capacity greater than twice the P capacity. This suggests that there is no accessibility problem with the NaOH and the acid sites of this resin. In fact, the P capacity appears to be slightly low since its value along with the Cl capacity accounts for only 87.4% of the resin, whereas half the acid capacity plus the Cl capacity account for 91.1% of the resin. These values are obtained by the following calculations in which VBPA represents vinylbenzyl phosphonic acid.

Table I
Capacities of Phosphonic Acid Resins as a
Function of Temperature and Catalyst

Functionalization Conditions	Capacity (mequiv/(g dry resin))		
	Total OH	Total P	Total Cl
0.77 mol AlCl_3 /40°C ^a	4.22	2.83	3.10
0.77 mol AlCl_3 /60°C	5.59	3.16	2.39
0.77 mol AlCl_3 /73°C ^b	6.40	3.62	1.58
0 mol AlCl_3 /73°C	0.30	0.65	5.28
0.33 mol AlCl_3 /73°C ^c	1.20	1.04	3.55
1.22 mol AlCl_3 /73°C ^c	7.72	3.67	0.96
0 mol AlCl_3 /73°C ^c	0.31	0.72	5.21

^aThe capacities listed for these reaction conditions are averaged from five functionalizations. The standard deviations are 0.80, 0.17, and 0.45 for total OH, total P, and total Cl, respectively.

^bThe capacities listed for these reaction conditions are averaged from three functionalizations. The standard deviations are 0.21, 0.07, and 0.05 for total OH, total P, and total Cl, respectively.

^cThese resins are 5 % crosslinked VBC/DVB gel copolymers.

$$\begin{aligned}
 & (3.67 \text{ mequiv P/g resin})(0.19815 \text{ g VBPA/mequiv P}) + \\
 & (0.96 \text{ mequiv Cl/g resin})(0.15262 \text{ g VBC/mequiv Cl}) \\
 & = 0.874 \text{ g VBPA and VBC /g resin} \\
 & (0.874 \text{ g/l g resin}) \times 100 = 87.4\%
 \end{aligned}$$

The same type of calculation using half the acid capacity as the P capacity results in the 91.1% value. The fact that 100% of the resin cannot be accounted for could be due to the formation of methylene bridges between neighboring VBC groups. Also, the resins contain inactive species (DVB and ethylvinlybenzene) which contribute to the weight of the resin but are not accounted for in the above calculation. The fact that this resin is 80% functionalized based on the P capacity (84% based on the acid capacity) could make it hydrophilic enough for complete reaction with the aqueous NaOH. On the other hand, the 2% gel phosphonic acid resin obtained at reflux with 0.77 mol AlCl_3 is 75% functionalized and the acid capacity is significantly less than two times the P capacity.

In order to obtain a bifunctional resin with approximately equal amounts of phosphonic acid and quaternary amine groups, the reaction conditions of 0.77 mol AlCl_3 at 40°C were chosen for the partial functionalization of the phosphonic acid resin. At these reaction conditions 60% functionalization occurs with the 2% gel copolymer leaving approximately 3 mequiv Cl/g for further reaction with the amine. Theoretically, complete conversion of the VBC groups to phosphonic acid sites would result in a P capacity of 4.86 mequiv/g. This theoretical value is calculated as follows noting that the molecular weight of the

vinylbenzyl phosphonic acid group is 198.15 g/mol.

$$\begin{aligned}
 &1 \text{ equiv}/198.15 \text{ g} \times 1000 \text{ mequiv/equiv} \\
 &= 5.047 \text{ mequiv/g} \\
 &5.047 \text{ mequiv/g} \times 0.963 \text{ g reactive copolymer/g resin} \\
 &= 4.860 \text{ mequiv/g resin}
 \end{aligned}$$

Figures 5 and 6 summarize the syntheses of the bifunctional phosphonic acid/trimethylamine (PA/TMA) resin and the bifunctional phosphonic acid/tributylamine (PA/TBA) resin, respectively. The phosphonic acid resin is converted to its sodium salt prior to amination in order to minimize protonation of the amine. The bifunctional resins are analyzed for new acid, P, and Cl capacities and also for the total anion exchange capacity. It should be noted that the Cl capacity obtained with the resins after elution with HCl reflects the presence of the Cl^- counterion of the amine along with any unreacted VBC groups. The bifunctional PA/TMA resin is prepared by contacting the partially functionalized phosphonic acid (PA) resin with reagent grade 25 weight %

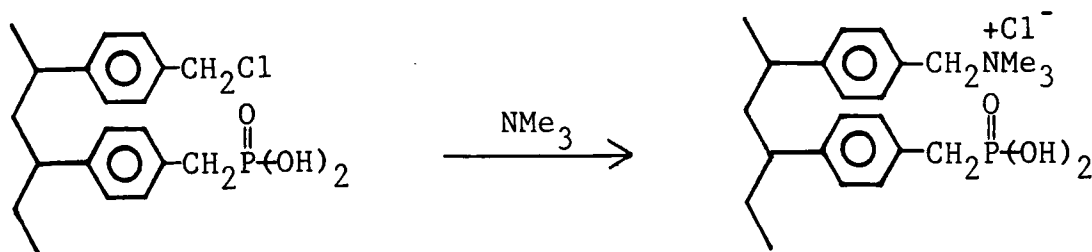


Figure 5. Bifunctional phosphonic acid/trimethylamine resin synthesis.

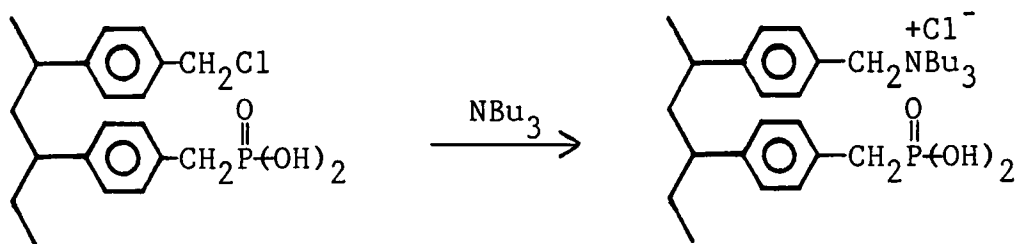


Figure 6. Bifunctional phosphonic acid/tributylamine resin synthesis.

trimethylamine at reflux (approximately 42°C) for 4 h. Three resins synthesized under these conditions resulted in an average TAEC of 2.44 ± 0.19 mequiv/g and an average P capacity of 2.00 ± 0.19 mequiv/g, which accounts for 91.3% of the resin. The synthesis of the bifunctional PA/TBA resin is carried out by refluxing (approximately 90°C) the partially functionalized PA resin in a 75 weight % solution of tributylamine in dioxane for 18 h. Characterization of three PA/TBA resins prepared under such conditions resulted in an average TAEC of 1.48 ± 0.02 mequiv/g and an average P capacity of 1.64 ± 0.35 mequiv/g, accounting for 82.6% of the resin. Both of the above values for the percent of the resin accounted for are based only on the TAEC's and P capacities of the resins and do not take into account the small unreactive mass of the resin or unreacted VBC groups.

Monofunctional quaternary amine resins were also prepared and used in the metal ion extraction studies. A trimethylamine (TMA) resin was obtained by aminating the VBC/DVB copolymer under the exact conditions as in the synthesis of the bifunctional PA/TMA resin. Two resins prepared in this manner resulted in identical TAEC's of 4.33 mequiv/g, indicating 95.1% reaction. The monofunctional tributylamine (TBA) resin

is prepared by refluxing the copolymer in a 37 weight % solution of TBA in dioxane for 18 h. Two resins prepared under these conditions had TAEC's of 1.84 mequiv/g and 1.85 mequiv/g which is 64.7% of the theoretical maximum yield. Monofunctional dimethylethylamine (DMEA) and triethylamine (TEA) resins were also synthesized in order to investigate further the effect of varying the amine group in metal ion extractions. Initially, the VBC/DVB copolymer was contacted with 25 weight % solutions of the amines in water for 10.5 h at reflux. As the reactions proceeded, extra water was added to the DMEA reaction mixture to maintain adequate fluidity, and ethanol was added to the TEA mixture to increase the solubility of the amine in the water. Analysis of the resins resulted in TAEC's of 4.17 mequiv/g for the DMEA resin and 3.58 mequiv/g for the TEA resin. These values represent 97.7% and 94.2% reaction yields, respectively.

Metal Ion Extraction Studies with Resins after KSCN, KIO₃, and HCl Elutions

The effects of changing the quaternary amine group on the resin and its counterion have been investigated in the extraction of silver, mercury(II), and lead(II) from aqueous nitrate salt solutions. The following resins were used in the study: a PA resin, a TMA resin, a bifunctional PA/TMA resin, a DMEA resin, a TEA resin, a TBA resin, and a bifunctional PA/TBA resin. The quaternary amine counterions (resin anions) SCN⁻, IO₃⁻, and Cl⁻ were obtained by eluting the resins with KSCN, KIO₃, and HCl, respectively. Prior to elution with KSCN and KIO₃, the resins were in their chloride form (Cl⁻ counterion). By comparing

the results of chlorine elemental analyses of the resins before and after the elutions and taking into account the relative weights of the anions, it appears that approximately 90 to 100% anion exchange occurred in all cases except for the conversion of the TMA resin to the SCN^- form in which case approximately 80% exchange occurred. In order to have an experimental control with which to compare the bifunctional resins, the phosphonic acid resin was also eluted with KSCN , KIO_3 , and HCl .

The individual metal ion extraction studies were set up at an R_i of one, where R_i is the initial ratio of milliequivalents of aqueous metal ions to milliequivalents of phosphorus and amine sites on the resin. The results of the studies are given in Tables II, III, and IV.

It is interesting to note that the pure amine resins seem to behave oppositely depending on the counterion. With the resins in their thiocyanate form, precipitation occurs to a much greater extent with the TMA and DMEA resins, whereas in their iodate form more precipitation occurs with the TBA resin.

The results with the resins in their thiocyanate form can be explained on the basis of the organophilicity of the thiocyanate anion. The anion's preference for the more highly organic environment of the TBA resin relative to that of the TMA resin is supported by the fact that the precipitation of AgSCN occurred and remained inside both the TBA and PA/TBA resins. Upon precipitation these resins became white and swollen in appearance, and no solid could be seen in the aqueous solution. In contrast, with the other amine resins the aqueous solution became cloudy, and solid AgSCN settled to the bottom of the vial. As a result of the precipitate forming and remaining within the resin along

Table II
Percent Ag^+ , Hg^{2+} , and Pb^{2+} Absorbed by
Resins After KSCN Elution

Aqueous Solution	Contact Time	Resin					DMEA	TEA
		PA	TMA	PA/ TMA	TBA	PA/ TBA		
AgNO_3	5 min	43.4	37.4	43.7	1.7	32.5		
	1 h	44.0	85.3	68.4	4.6	40.3	89.5	66.0
	24 h	52.9	98.3	71.8	41.5	67.6		
$\text{Hg}(\text{NO}_3)_2$	5 min	41.8	84.1	60.2	12.7	38.6		
	1 h	70.7	96.3	74.9	28.8	64.7	94.7	94.9
	24 h	91.6	98.8	88.5	67.0	91.1		
$\text{Pb}(\text{NO}_3)_2$	5 min	68.9	0	32.6	0	41.3		
	1 h	66.9	0	34.0	0	43.8	0	0
	24 h	66.7	0	35.6	0	44.1		

Table III
Percent Ag^+ , Hg^{2+} , and Pb^{2+} Absorbed by
Resins After KIO_3 Elution

Aqueous Solution	Contact Time	Resin					DMEA	TEA
		PA	TMA	PA/ TMA	TBA	PA/ TBA		
AgNO_3	5 min	40.7	20.8	30.8	11.2	43.0		
	1 h	41.3	25.5	44.4	24.4	55.3	28.8	39.5
	24 h	43.3	65.8	54.0	54.6	61.7		
$\text{Hg}(\text{NO}_3)_2$	5 min	19.4	68.1	67.5	43.2	47.3		
	1 h	87.6	65.1	79.6	74.6	86.4	58.0	74.6
	24 h	96.7	65.2	87.0	86.4	96.7		
$\text{Pb}(\text{NO}_3)_2$	5 min	61.5	21.8	48.4	7.8	68.0		
	1 h	61.9	60.7	65.6	29.3	70.5	64.0	70.7
	24 h	62.2	64.9	62.5	82.3	72.1		

Table IV
Percent Ag^+ and Pb^{2+} Absorbed by
Resins After HCl Elution

Aqueous Solution	Contact Time	Resin				
		PA	TMA	PA/ TMA	TBA	PA/ TBA
AgNO_3	5 min	31.1	89.5	67.6	17.3	57.7
	1 h	30.7	98.8	68.4	76.1	60.8
	24 h	31.6	98.5	69.6	98.7	60.6
$\text{Pb}(\text{NO}_3)_2$	5 min	52.2	0	32.9	0	40.2
	1 h	60.3	0	32.7	0	44.1

with the presence of the bulky butyl groups, the resin pores become clogged. Once this occurs, the thiocyanate ions in the inner part of the resin are no longer accessible to the remaining aqueous Ag^+ ions. Resin pore clogging does not occur with the TBA resin in the precipitation of AgCl , and 98.8% Ag^+ extraction occurs (Table IV). In this case the white AgCl solid was observed in the aqueous solution. The results in Table II suggest that pore clogging also occurs with the TEA resin but to a lesser extent. An important difference between the various amine resins is that with the smaller amines, especially TMA and DMEA, a large amount of bead fragmentation occurs during the functionalization of the polymer backbone, whereas with TBA no fragmentation is observed. The result of bead fragmentation is an increase in the accessibility of the resin's reactive sites which in this case could result in an increase in AgSCN precipitation.

The results for the extraction of mercury(II) by the resins in their thiocyanate form suggest that most of the cation is precipitated, but in fact no solid was observed with any of the resins. The $\text{Hg}(\text{SCN})_2$ complex is soluble at low concentrations and, though no precipitation occurs, complexation does occur. This same type of behavior was observed in the extraction of Hg^{2+} by the resins in their Cl^- form. These results are not included in Table IV because according to the analysis of the aqueous solutions approximately 100% extraction occurs, and based on solubility data HgCl_2 should be quite soluble at the experimental concentrations. As above, a soluble Hg^{2+} complex forms, and as a result the Hg^{2+} ions are invisible to the Volhard titration used for the analysis of the aqueous solution.²⁰

The behavior of the resins in their iodate form (Table III) is not as easily explained. In this case there appears to be a competition between the quaternary amine groups and the aqueous cation for the iodate anion. The TMA and DMEA resins seem to hold the iodate more tightly than the TBA and TEA resins. A possible explanation for this is that the large iodate cannot get very close to the positively charged nitrogen centers of the tributylamine groups due to their bulkiness, and as a result, weak ionic bonds exist, which are easily overcome by the precipitate formation. On the other hand, the iodate can come into much closer contact with the trimethylamine groups and as a result form stronger ionic bonds.

Both the TMA and TBA resins extract approximately 100% of the Ag^+ in their Cl^- forms. The hydrophobic nature of the TBA resin results in a longer time for complete AgCl precipitation. The fact that the TBA resin is slower than the TMA resin in all of the extraction studies can partly be attributed to its hydrophobicity.

The results of the bifunctional resins are best viewed in light of Table V which contains calculated percent absorbed values based on the experimental results of the individual phosphonic acid and quaternary amine resins. These calculated values may be somewhat lower than the experimentally observed results: for the monofunctional resins, the R_i is equal to one, whereas for the bifunctional resins, the overall R_i is equal to one but with respect to the individual phosphorus and amine sites approximately 1.7 to 2.4. An increase in the R_i could result in the equilibrium shifting in the direction of ion exchange and/or precipitation. Comparison of the calculated and experimental values for the

Table V
Calculated Percent Absorption Values
for the Bifunctional Resins

Resin Anion		SCN ⁻		IO ₃ ⁻		Cl ⁻	
Aqueous Solution	Contact Time	Resin					
		PA/ TMA	PA/ TBA	PA/ TMA	PA/ TBA	PA/ TMA	PA/ TBA
AgNO ₃	5 min	42	25	28	28	65	23
	1 h	68	26	30	34	72	50
	24 h	79	47	54	48	70	62
Hg(NO ₃) ₂	5 min	49	29	48	30		
	1 h	82	51	65	83		
	24 h	94	80	79	95		
Pb(NO ₃) ₂	5 min	28	36	38	37	21	29
	1 h	28	38	60	47	25	33
	24 h	28	36	65	62		

extraction of Pb^{2+} by the bifunctional resins after KSCN and HCl elution illustrates the extent to which the R_1 difference can affect the ion exchange reaction ($\text{Pb}(\text{SCN})_2$ and PbCl_2 are soluble). These results indicate that the protonated form of the phosphonic acid is more highly affected than the potassium salt. On the other hand, the R_1 difference does not seem to affect the performance of the bifunctional PA/TMA resin. Actually the experimental results of the PA/TMA resin are accurately predicted by the calculated values which indicates that these two functional groups operate as well independently as when they are on the same resin support.

In comparing the values in Table V with the corresponding experimental results, it appears that the overall effect of having the phosphonic acid and tributylamine groups on the same resin is to increase the rate at which metal ion extraction occurs. This rate increase can be attributed to the hydrophilicity of the bifunctional resin allowing more precipitation to occur initially. At 5 min and 1 h contact times the PA/TBA resin (regardless of the counterion) extracts more metal ions than expected, but at equilibrium (24 h) the experimental results can basically be predicted based on the calculated values with a few exceptions. A significant difference is observed between the calculated and experimental values for the extraction of Ag^+ by the PA/TBA resin in its thiocyanate form. Experimentally the resin extracts 21% more Ag^+ than expected based on the two mechanisms operating independently. This suggests that when on the same polymer support the two functional groups operate synergistically in the extraction of Ag^+ . Such synergistic behavior would be observed if the initially ion exchanged Ag^+

precipitated with the counteranion followed by more Ag^+ being extracted through ion exchange. In order to observe the effect of the R_i difference in this case a mixed bed of PA resin and TBA resin each after elution with KSCN was contacted with AgNO_3 . The results for the extraction of Ag^+ at a contact time of 24 h is 1.5% less than the value calculated based on the individual resins, which indicates that in this case the R_i does not affect the results and at the same time supports the idea of a synergistic behavior with the bifunctional resin. Table VI contains the results from this study along with results from similar studies with the two resins after KIO_3 and HCl elutions. The mixed resin bed study allows for a direct observation of the effect the increase in R_i has on the ion exchange and precipitation mechanisms working independently on different resins.

In comparing the results in Table VI for the extraction of Pb^{2+} after the resins have been eluted with KIO_3 with the corresponding results in Table III (p. 19), it appears that the two mechanisms in the bifunctional resin operate independently. In both studies approximately the same amount of Pb^{2+} is extracted: at a contact time of 1 h 70.5% is extracted by the bifunctional resin and 78.7% by the mixed resin bed, and at 24 h 72.1% is extracted by the bifunctional resin and 80.6% by the mixed resin bed. These two studies also suggest that the amount of Pb^{2+} extracted at a contact time of 1 h is greatly affected by the R_i difference since in both cases 23 to 30% more Pb^{2+} is absorbed than expected. At 24 h the mixed resin bed extracts approximately 4.4% more Pb^{2+} than expected based on the results of the individual resin studies indicating a slight R_i effect at equilibrium which could contribute to the 10%

Table VI

Percent Metal Ion Absorbed by a Mixed
PA Resin and TBA Resin Bed

Aqueous Solution/ Resin Anion	Contact Time		
	5 min	1 h	24 h
$\text{AgNO}_3/\text{SCN}^-$	28.3	31.6	46.0
$\text{Pb}(\text{NO}_3)_2/\text{IO}_3^-$	37.6	78.7	80.6
$\text{AgNO}_3/\text{Cl}^-$	39.2	58.6	78.3

difference in the experimental and calculated values for the bifunctional resin.

The fact that the bifunctional PA/TBA resin in its iodate form extracts 14% more Ag^+ than expected from the calculated values could be a result of the R_1 difference, but it could also be a result of the calculated value being low. In comparing the results of the pure TBA and TMA resins in their iodate form (Table III, p.19) the 54.6% Ag^+ absorbed by the TBA resin at 24 h seems a little low. At contact times of 6h and 17h the resin extracts 30.2% and 47.7% Ag^+ , respectively, which suggests the possibility that at 24 h equilibrium has not yet been reached. If this is the case and since equilibrium seems to be attained by the bifunctional resin within 24 h, then the calculated value for the precipitation mechanism would be low causing the overall calculated value to be low.

In comparing the experimental and calculated values for the extraction of Ag^+ by the PA/TBA resin in its Cl^- form (Table IV, p.20)

along with the corresponding mixed resin bed results, it is observed that the ion exchange and precipitation mechanisms seem to be operating independently on the bifunctional resin. The fact that the bifunctional resin extracts more at a contact time of 5 minutes is probably due to its hydrophilicity allowing more precipitation to occur initially.

The effect of temperature on the extraction of Ag^+ was also investigated with the TBA resin, the PA/TBA resin, and a corresponding mixed resin bed, all of which were in their thiocyanate form. At 40°C and a 1 h contact time the TBA and PA/TBA resins extracted 12.8% and 54.7%, respectively. At 60°C and a 1 h contact time the TBA resin extracted 19.9%, the PA/TBA resin 70.8%, and the mixed PA resin and TBA resin bed extracted 42.3% of the Ag^+ . These results indicate that an increase in temperature increases the rate of extraction, and equilibrium is reached over a shorter period of time. At room temperature over a period of 24 h the PA/TBA resin extracts 67.6%, and the mixed resin bed extracts 46.0%. The amount of Ag^+ extracted by the TBA resin is also increased by the temperature increase, but pore clogging still occurs, and the precipitate remains in the resin.

The synergistic behavior of the bifunctional PA/TBA resin can be attributed to the enhancement of the precipitation reaction by the ion exchange mechanism. Since for all practical purposes precipitation is an irreversible process it cannot increase the final amount of metal ion extracted by ion exchange. Assuming that the percent of ion exchange occurring for both the PA resin and the bifunctional PA/TBA resin is constant then the ultimate performance of the bifunctional resin is limited by the ion exchange mechanism. This explains why a significant

synergistic behavior is only observed with the bifunctional resin when the amount of metal ion extracted by precipitation can be increased as in the case of Ag^+ extraction with the thiocyanate form of the resin. In the extraction of Ag^+ by the PA/TBA resin in its Cl^- form the precipitation of AgCl may not be enhanced since, according to the pure TBA resin results, it already occurs to 98.8% completion (Table IV, p.20). With the resins in their IO_3^- form, the amount of precipitate formation is large enough that if synergism is occurring with the bifunctional resin it will only slightly increase the amount of metal ion extracted over that expected from the mechanisms operating independently and as a result not be noticeable.

Metal Ion Extraction Studies with Resins after H_2SO_4 Elution

The sulfate form of a TMA resin, a bifunctional PA/TMA resin, a DMEA resin, a TEA resin, a TBA resin, and a bifunctional PA/TBA resin was obtained by eluting the resins in their chloride form with 1N H_2SO_4 . Titration of the sulfuric acid eluate for chloride indicated that approximately 100% anion exchange occurred. A hydroxide analyses of the resins showed no increase in the acid capacity which confirms the presence of the sulfate counterion instead of the bisulfate anion. The extraction of the alkaline earth metal ions Ca^{2+} , Sr^{2+} , and Ba^{2+} by these resins was investigated at an R_1 of 1.0. Table VII contains the results for the extraction of these cations from aqueous solutions of their nitrate salts. The PA resin used in these studies was also eluted with 1N H_2SO_4 .

The results in Table VII indicate that the amount of extraction by the PA resin is approximately the same for each of the metal ions. The

Table VII
Percent Ca^{2+} , Sr^{2+} , and Ba^{2+} Absorbed by
Resins After H_2SO_4 Elution

Aqueous Solution	Contact Time	Resin						DMEA	TEA
		PA	TMA	PA/ TMA	TBA	PA/ TBA			
$\text{Ca}(\text{NO}_3)_2$	1 h	26.4	0	13.0	0.8			1.9	1.2
$\text{Sr}(\text{NO}_3)_2$	1 h	21.8	35.3	29.1					
$\text{Ba}(\text{NO}_3)_2$	5 min	25.5	50.3	43.5	16.2	56.0			
	1 h	24.4	72.5	67.0	69.9	60.1	80.9	74.5	
	3 h	27.5	86.1	70.4					
	24 h	27.7	90.3	74.7	63.7	60.3	82.2	77.0	

fact that the ion exchange reaction is completed rather quickly is evident in the extraction of Ba^{2+} for which 25.5% is extracted at a contact time of 5 min and only 27.7% at 24 h. On the other hand, the precipitation reaction as seen with the pure amine resins takes at least an hour to complete. Since CaSO_4 is soluble, it is not extracted by the amine resins. The slight solubility of SrSO_4 results in the extraction of 35.3% Sr^{2+} . The insolubility of BaSO_4 results in 72.5% extraction after 1 h contact. The performance of the bifunctional PA/TMA resin in these studies is accurately predicted by the individual PA and TMA resins: at a contact time of 1 h extraction values of 11% Ca^{2+} , 26% Sr^{2+} , and 60% Ba^{2+} are expected based on the results of the monofunctional resins. These values, although slightly lower than the experimental results due to the R_i differences, indicate that the ion exchange

and precipitation mechanisms operate independently on this bifunctional resin. Similarly calculated values for the extraction of Ba^{2+} by the bifunctional PA/TBA resin at contact times of 5 min, 1 h, and 24 h are 21%, 44%, and 41%, respectively. These values are much lower than the experimentally observed results which suggests the possibility that the two mechanisms are operating synergistically, i.e. the ion exchange mechanism enhances extraction through precipitation.

The extraction of Ca^{2+} and Ba^{2+} was also investigated at R_i 's of 0.1, 0.5, and 1.5. Tables VIII and IX contain the results from these studies along with results at an R_i of 1.0. In addition to the percent absorbed (% Abs) values, the ratio of milliequivalents metal ions extracted to the milliequivalents of functional sites (milliequivalents of phosphorus and milliequivalents of amine sites) on the resin is given by the % Loading (% L) value. The results from these studies indicate that each resin approaches a constant % Loading value. This feature is more apparent with a plot of % L versus R_i as has been done in Figures 7, 8, and 9. The Ca^{2+} results illustrate a case in which only ion exchange is occurring. The ion exchange mechanism is much less affected by the R_i than the precipitation mechanism; an R_i increase from 0.5 to 1.5 results in an 11% increase in the amount of Ca^{2+} loaded by the PA resin and only a 6% increase in the amount of Ba^{2+} loaded. In contrast, the precipitation reaction approaches 100% completion as indicated by the fact that at an R_i of 0.5 the TMA resin loads 42.8% Ba^{2+} out of a maximum value of 50%, and at an R_i of 1.5 it reaches a value of 96.7% loaded. As a result of the low percent loading by the ion exchange resin, the performance of the bifunctional resin appears to be limited

Table VIII

R_i Study for the Absorption of Ca^{2+} at a 1 h Contact Time

R_i	Resin					
	PA		TMA		PA/TMA	
	% Abs	% L	% Abs	% L	% Abs	% L
0.1	100.0	9.9	0	0	27.4	2.6
0.5	47.1	23.8	0	0	26.9	13.7
1.0	26.4	26.1	0	0	12.9	14.5
1.5	23.1	34.3	0	0	13.0	19.5

Table IX
 R_i Study for the Absorption of Ba^{2+}

R_i	Contact Time	Resin					
		PA		TMA		PA/TMA	
		% Abs	% L	% Abs	% L	% Abs	% L
0.1	5 min	69.4	6.7	0	0	61.7	7.5
	1 h	95.7	9.8	23.4	2.3	94.2	9.5
	3 h	93.9	9.4	45.0	4.5	86.0	8.7
0.5	5 min	44.9	22.2	72.2	36.0	66.1	33.2
	1 h	46.8	23.0	83.0	41.7	88.3	44.1
	3 h	45.3	22.6	85.4	42.8	92.8	46.5
1.0	5 min	25.5	25.2	50.3	51.0	43.5	44.2
	1 h	25.5	25.3	72.5	70.8	67.0	69.2
	3 h	27.5	26.6	86.1	86.5	70.4	71.5
1.5	5 min	18.6	27.4	50.7	76.2	30.2	44.9
	1 h	18.7	28.2	47.6	74.0	44.8	68.0
	3 h	18.8	28.1	64.3	96.7	43.4	73.4

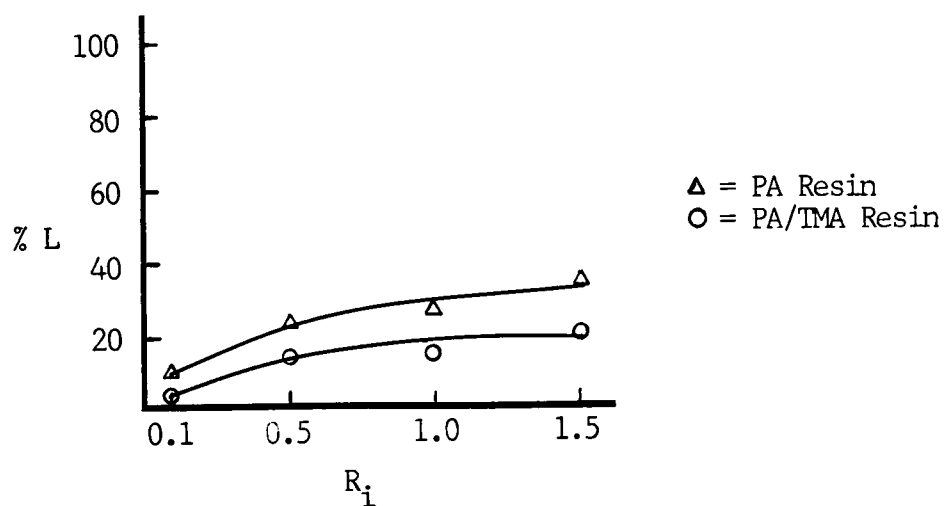


Figure 7. % L vs. R_i for Ca^{2+} extraction.

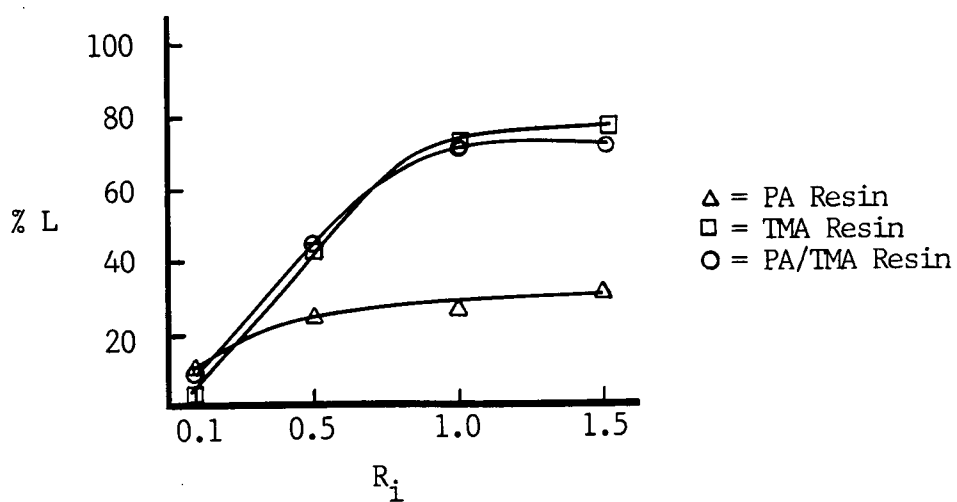


Figure 8. % L vs. R_i for 1 h Ba^{2+} extraction.

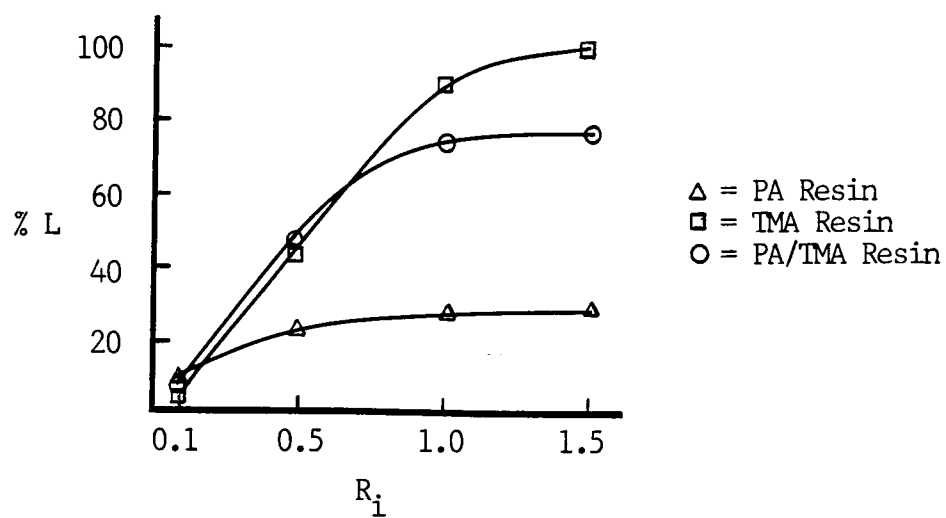


Figure 9. % L vs. R_i for 3 h Ba^{2+} absorption.

by this mechanism. At contact times of 1 h and 3 h the bifunctional PA/TMA resin loads a maximum of just over 70% Ba^{2+} at both an R_i of 1.0 and 1.5.

The performance of the TMA resin at an R_i of 0.1 is interesting due to the fact that it extracts only half as much Ba^{2+} than it actually could. It is possible that given more time the reaction would go to completion, although this does not seem likely since at the other R_i 's, especially 0.5, the precipitation occurs within a reasonable amount of time. It is also possible that with such a dilute aqueous solution the concentration of Ba^{2+} inside the resin is not great enough for complete precipitation to occur, or the amount of anion exchange between the nitrate and sulfate does not result in a large enough concentration of BaSO_4 in the aqueous solution for precipitation.

Table X contains calculated percent absorbed values which correspond to the bifunctional PA/TMA resin results in Table IX. These calculated values are based on the results of the individual PA and TMA resins at the same R_i as the bifunctional resin. The calculated values are much lower than the experimental results at the R_i 's of 0.1 and 0.5. This suggests that at these R_i 's either the ion exchange mechanism enhances the precipitation reaction or the increase in R_i with respect to the individual functional sites results in the greater amount of Ba^{2+} extracted. The fact that a mixed PA resin and TMA resin bed gives practically the same results as the bifunctional resin at an R_i of 0.5 (Table XI, p. 37) dismisses the possibility of the ion exchange mechanism enhancing the precipitation reaction in this case. For the bifunctional PA/TMA resin at an R_i of 0.5, the R_i with respect to the

Table X
Calculated Ba^{2+} Percent Values for the
Bifunctional PA/TMA Resin

R_i	Contact Time		
	5 min	1 h	3 h
0.1	22	49	65
0.5	60	66	67
1.0	40	60	62
1.5	38	36	43

ion exchange sites on the resin is approximately 1.2, and with respect to the anion exchange (precipitation) sites it is 0.8. By approximating the amount of Ba^{2+} the individual PA and TMA resins would load at these R_i 's from the graphs in Figures 8 and 9 (pp. 33 and 34), an expected value of 100% extraction is obtained for the bifunctional resin. The same type of treatment for the R_i of 0.1 studies also predicts that 100% extraction should occur with the bifunctional resin.

The experimental results and corresponding calculated values for a mixed PA resin and TMA resin bed study at R_i 's of 0.5 and 1.5 are given in Table XI. The calculated and experimental values differ only by 9% at an R_i of 0.5 and contact time of 5 min because the precipitation mechanism requires a longer time to reach completion as seen with the 3 h contact time results. The large difference in the values at the 3 h contact time is due to the fact that the R_i with respect to the individual resins is greater than 0.5 as mentioned above. At an R_i of 1.5 the

Table XI
Percent Ba^{2+} Absorbed by a Mixed
PA Resin and TMA Resin Bed

R_i	Contact Time	Experimental Value	Calculated Value
0.5	5 min	69.9	61
	3 h	92.6	69
1.5	5 min	24.8	38
	3 h	51.4	46

experimentally observed result at a contact of 5 min is significantly less than that predicted, but at 3 h the calculated and experimental values are in good agreement. This same type of behavior is observed with the bifunctional PA/TMA resin as seen in Tables IX (p. 32) and X (p. 36). A possible explanation for the results at the 5 min contact time is that the rate of extraction by precipitation is greatly reduced. Since the R_i with respect to the TMA resin in the mixed bed study is 2.5 and with respect to the trimethylamine sites on the bifunctional resin it is also 2.5, the initial formation of BaSO_4 precipitate could be large enough so as to clog the resin pores. The fact that the precipitate is observed in the aqueous solution indicates that pore clogging is not permanent, and as soon as the initial solid falls out of the resin further extraction is continued. This results in the expected amount of Ba^{2+} being extracted at greater contact times (1 h and 3 h for the bifunctional resin and 3 h for the mixed resin bed).

The effect of changing the aqueous anion was also investigated in the extraction of Ba^{2+} by the PA, TMA, and bifunctional PA/TMA resins after elution with H_2SO_4 . The perchlorate, monohydrogen phosphate, acetate, iodide, and nitrate anions were studied at a contact time of 1 h and R_i of 1.0 except in the case of the perchlorate anion for which the R_i was 0.7. The results from this study are presented in Table XII. The calculated values predicted by the individual PA and TMA resins are included in parentheses for the bifunctional resin. The values in Table XII indicate that the aqueous anion affects both the precipitation and ion exchange mechanisms. The significant increase in the amount of Ba^{2+} extracted by the PA resin in the presence of HPO_4^{2-} and $\text{C}_2\text{H}_3\text{O}_2^-$ is explained by the fact that these are anions of basic salts, and as a result, remove the proton from the ion exchange sites allowing for more Ba^{2+} to be extracted. The results for the TMA resin indicate the extent

Table XII
Percent Ba^{2+} Absorbed in the Presence of
Various Aqueous Anions

Aqueous Anion	Resin		
	PA	TMA	PA/TMA
ClO_4^-	32.8	83.1	72.4 (54)
HPO_4^{2-}	87.2	100.0	100.0 (84)
$\text{C}_2\text{H}_3\text{O}_2^-$	64.0	46.6	55.0 (56)
I^-	28.3	66.8	61.5 (51)
NO_3^-	24.4	82.1	67.0 (60)

to which the various aqueous anions exchange with the sulfate anion of the resin. The fact that 100% extraction occurs with the aqueous HPO_4^{2-} indicates that this anion prefers the resin environment much more than the SO_4^{2-} . As will be seen later, this same type of behavior is observed in the extraction of zinc(II) in which the aqueous SO_4^{2-} does not replace the resin HPO_4^{2-} (or H_2PO_4^-) counterion and as a result no zinc is precipitated. The bifunctional resin basically extracts the amount of Ba^{2+} predicted by the two mechanisms operating independently. The fact that the bifunctional resin does not show an R_i effect with the acetate anion could be due to a decrease in the amount of acetate anions available for anion exchange after cation exchange occurs. In other words, with the Ba^{2+} and proton exchange a certain amount of acetic acid will form decreasing the amount of free acetate ions.

The ability of the resins in their SO_4^{2-} form to extract Hg^{2+} from a solution of its nitrate salt was determined at an R_i of 1.2 and a 1 h contact time. The effect of increasing the ionic strength of the aqueous solution was also investigated by performing the extraction in 4M NaNO_3 at R_i 's of 1.4 and 2.0. The results in terms of percent Hg^{2+} absorbed (% Abs) and loaded (% L) are given in Table XIII. It is interesting to note that in the presence of NaNO_3 the ion exchange reaction indicates an R_i dependence. The amount of Hg^{2+} loaded by the PA resin in the presence of Na^+ is greatly increased by increasing the R_i from 1.4 to 2.0. The amount of Hg^{2+} extracted by the precipitation reaction is decreased by the presence of the NaNO_3 and does not increase with an increase in Hg^{2+} concentration. The results of the bifunctional resin are as expected based on the performance of the individual PA and TMA

Table XIII

Percent Hg^{2+} Absorbed by Resins
After H_2SO_4 Elution

Aqueous Solution	R_i	Resin					
		PA		TMA		PA/TMA	
		% Abs	% L	% Abs	% L	% Abs	% L
$\text{Hg}(\text{NO}_3)_2$	1.2	82.0	97.1	78.8	94.4	76.6	92.9
$\text{Hg}(\text{NO}_3)_2/$	1.4	38.3	54.1	16.1	22.9	27.4	38.2
4M NaNO_3	2.0	38.8	84.6	8.0	17.1	22.8	47.5

resins. It appears that in the presence of NaNO_3 the performance of the bifunctional resin is a result of an increase in the amount of metal ion extracted by the ion exchange mechanism due to an R_i increase.

Metal Ion Extraction Studies with Resins after H_3PO_4 Elution

Metal studies were also performed with the PA, TMA, and bifunctional PA/TMA resins after elution with 1N H_3PO_4 . Analysis of the eluate indicated that complete anion exchange occurred. A phosphorus elemental analysis on a nitric acid eluate of the TMA resin resulted in a value of 3.59 mequiv P/g resin. This suggests the presence of the H_2PO_4^- anion on the resin, since 100% anion exchange with this anion should result in a P capacity of 3.35 mequiv/g. The result of a hydroxide analysis gave a value much lower than expected for the presence of this anion though; a value of 6.7 mequiv/g is expected based on the P capacity, but

experimentally an acid capacity of only 3.49 mequiv/g was obtained. At the same time, an acid capacity of only 2.05 mequiv/g is expected if the counterion is HPO_4^{2-} . Although possible, a mixture of these two anions does not seem likely based on the P elemental analysis, since the presence of the monohydrogen phosphate anion would only result in lowering the P capacity.

Table XIV contains the results for the extraction of Ca^{2+} , Sr^{2+} , and Ba^{2+} with these resins. The values in parentheses are calculated from the corresponding PA and TMA resins' results. The extractions were carried out in the absence and presence of 4M NaNO_3 at an R_i of 1 and a contact time of 1 h. A number of interesting points can be noted. The fact that the results with the bifunctional resin are in agreement with the calculated values supports the validity of the monofunctional results. The value of 8.5% Ca^{2+} extracted by the PA/TMA resin is lower than expected which could indicate that this value is experimentally low, or an experimentally high result was obtained for the PA or TMA resin. It is not clear why the extraction of Ba^{2+} by the PA resin is not affected by the presence of the Na^+ ion when the extraction of Ca^{2+} and Sr^{2+} are greatly reduced. The results with the TMA resin indicate that the increased ionic strength is required for precipitation to occur. This could result from an increase in the amount of anion exchange occurring or from a decrease in the solubility of the precipitating salt.

The extraction of Zn^{2+} by the resins after H_3PO_4 elution was investigated in the presence of various aqueous anions. A dimethylethylamine (DMEA) resin and a triethylamine (TEA) were also used in this study which was carried out at an R_i of 1 and a contact time of 1 h. The

Table XIV
Percent Ca^{2+} , Sr^{2+} , and Ba^{2+} Absorbed by
Resins After H_3PO_4 Elution

Aqueous Solution	Resin		
	PA	TMA	PA/TMA
$\text{Ca}(\text{NO}_3)_2$	22.5	0.6	10.9 (8.7)
$\text{Sr}(\text{NO}_3)_2$	22.1	0.4	10.2 (8.0)
$\text{Ba}(\text{NO}_3)_2$	23.4	0.0	11.5 (8.4)
$\text{Ca}(\text{NO}_3)_2/4\text{M NaNO}_3$	5.9	17.0	8.5 (12)
$\text{Sr}(\text{NO}_3)_2/4\text{M NaNO}_3$	0	2.3	2.6 (1.5)
$\text{Ba}(\text{NO}_3)_2/4\text{M NaNO}_3$	25.1	24.8	24.5 (22)

results of the study are given in Table XV. Several similarities between the results in this table and those in Table XII (p. 38) are observed. As expected the acetate anion increases the amount of extraction with the PA resin by removing the proton from the acid sites. In both studies the perchlorate anion also slightly increases the amount of ion exchange over that which occurs in the presence of the nitrate anion. In comparing the results for the extraction of Ba^{2+} and Zn^{2+} by the pure amine resins two main points can be made. The first is that the phosphate anion, regardless of whether it is the monohydrogen or dihydrogen anion, seems to have a greater affinity for the resin than the sulfate anion. This is concluded from the fact that 100% extraction occurs in the precipitation of BaSO_4 which indicates complete anion exchange of the monohydrogen phosphate anion with the resin sulfate counterion. In

Table XV
Percent Zn^{2+} Absorbed in the Presence of
Various Aqueous Anions

Aqueous Anion	Resin				
	PA	TMA	PA/TMA	DMEA	TEA
ClO_4^-	41.3	13.1	25.8	21.9	16.8
SO_4^{2-}	35.5	0.0	23.3	2.4	0.0
$\text{C}_2\text{H}_3\text{O}_2^-$	87.9	43.2	49.8	50.0	49.1
NO_3^-	33.5	10.8	16.6	19.4	18.6

the opposite situation, wherein the aqueous sulfate anion must replace the dihydrogen phosphate ion on the resin, no extraction occurs suggesting no anion exchange. The second point of interest arises in comparing the results in the presence of the NO_3^- , ClO_4^- , and $\text{C}_2\text{H}_3\text{O}_2^-$ anions. An important difference between these anions is that the acetate will, to some extent, soak up protons and therefore act as a buffer. In the formation of $\text{Zn}_3(\text{PO}_4)_2$ from dihydrogen or monohydrogen phosphate ions, the pH will decrease and as a result the solubility of the precipitate will increase according to the equation $\text{Zn}_3(\text{PO}_4)_2 + 4 \text{H}^+ = 3 \text{Zn}^{2+} + 2 \text{H}_2\text{PO}_4^-$ which has a K_{sp} of $10^{7.06}$ at 298.15K.²¹ This explains why more precipitation occurs in the presence of a buffering anion. The performance of the bifunctional PA/TMA resin is as expected based on the results of the individual resins except in the presence of the acetate anion. In this case the calculated value predicts that 11 % more Zn^{2+} will be extracted

than actually is. This is a result of a pH decrease from both ion exchange and precipitation.

The extraction of Hg^{2+} was investigated with the PA, TMA, and bifunctional PA/TMA resins after elution with H_3PO_4 at R_i 's of 0.1, 0.5, 1.0, and 1.5 and at a contact time of 1 h. The percent Hg^{2+} absorbed (% Abs) and loaded (% L) by the resins is presented in Table XVI. The resins' performances as a function of the aqueous metal ion concentration is illustrated in Figure 10 with a plot of % L versus R_i . As seen with the PA resin the ion exchange reaction approaches 100% with increasing Hg^{2+} concentration. The amount of Hg^{2+} extracted with the TMA resin appears to depend on a maximum loading value of 63% to 69%. The fact that the precipitation reaction does not go to 100% completion could be a result of a pH change as precipitation occurs. For example, if the precipitating salt is $\text{Hg}_3(\text{PO}_4)_2$ and forms from the reaction $3 \text{Hg}^{2+} + 2 \text{H}_2\text{PO}_4^- = \text{Hg}_3(\text{PO}_4)_2 + 4 \text{H}^+$ then the pH will decrease as precipitation occurs. As seen in the extraction of Zn^{2+} the decrease in pH could increase the salt's solubility. This pH effect is also observed with the bifunctional resin. Values calculated based on the results of the individual PA and TMA resins for the % metal absorbed by the bifunctional PA/TMA resin if the two mechanisms operated independently are 89%, 96%, 78%, and 52% for the R_i 's of 0.1, 0.5, 1.0, and 1.5, respectively. At R_i 's of 1.0 and 1.5, the experimental results are much less than expected which is due to both the ion exchange and precipitation reactions decreasing the pH. It should be noted that a pH change could also influence the amount of Hg^{2+} extracted by ion exchange although this does not seem likely since such an effect is not noticed with the PA resin.

Table XVI
 Hg^{2+} Absorption by Resins After H_3PO_4
 Elution at Various R_i 's

R_i	Resin					
	PA		TMA		PA/TMA	
	% Abs	% L	% Abs	% L	% Abs	% L
0.1	90.5	9.4	82.5	8.5	94.0	9.8
0.5	97.7	47.9	97.0	48.3	89.4	44.5
1.0	85.4	85.6	71.2	69.2	55.8	55.0
1.5	65.8	95.2	42.9	62.5	37.4	54.8

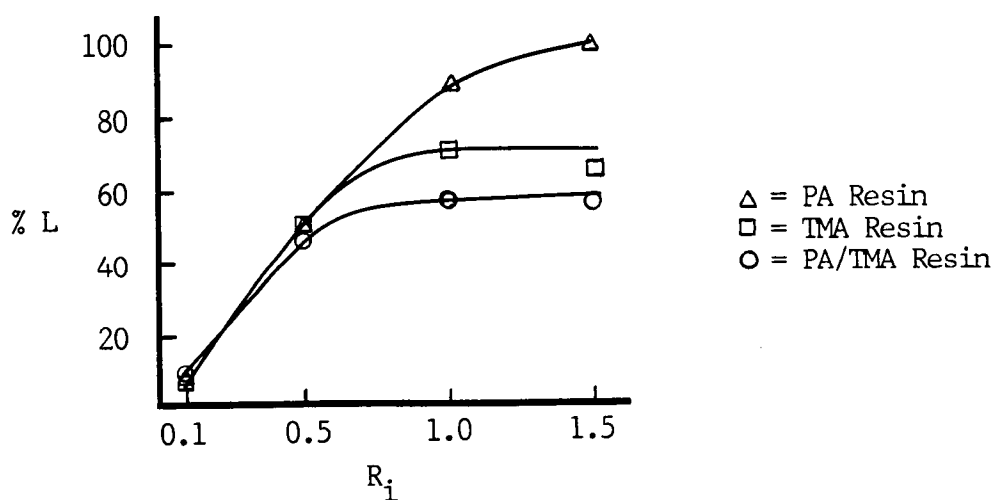


Figure 10. %L vs. R_i for Hg^{2+} absorption.

The extraction of several other metal ions from aqueous solutions of their nitrate salts was observed with the resins after H_3PO_4 elution. The various metal ions and the results from the studies (performed at an R_1 of one) are listed in Table XVII. A significant amount of precipitation occurs only with Pb^{2+} , Ag^+ , and Hg^{2+} . The reason more Ag^+ is extracted at a contact time of 5 min than at 1 h with the PA and PA/TMA resins is not clear, but the fact that it occurs with both resins supports the validity of the results. The greater amount of Hg^{2+} precipitated in 5 min compared to that precipitated in 1 h with the TMA resin could be due to an initial complexation of the cation followed by precipitation at which point the pH begins to decrease. The bifunctional PA/TMA resin extracts approximately 6% less Ag^+ and approximately 20% less Hg^{2+} than expected based on the performance of the individual resins. As mentioned above, this could be the result of a pH change. In the extraction of Pb^{2+} the results with the bifunctional resin are slightly greater than the calculated values indicating the formation of a precipitate that is stable at the pH of the aqueous solution. This is supported by the fact that the two reactions $\text{PbHPO}_4 + \text{H}^+ = \text{Pb}^{2+} + \text{H}_2\text{PO}_4^-$ and $\text{Pb}_3(\text{PO}_4)_2 + 4 \text{H}^+ = 3 \text{Pb}^{2+} + 2 \text{H}_2\text{PO}_4^-$ have solubility product constants of $10^{-2.65}$ and $10^{-4.43}$, respectively.²¹

Metal Ion Extraction Studies with Resins after Na_2S Elution

The extraction of Ag^+ , Hg^{2+} , and Cd^{2+} was observed with the monofunctional TMA and TBA resins in their sulfide form obtained by elution with Na_2S . The resins were contacted with aqueous nitrate salt solutions of these cations at R_1 's between 1.0 and 1.5 for 17 h. Table XVIII

Table XVII
Percent Metal Ion Absorbed with Resins
After H_3PO_4 Elution

Metal Ion	Contact Time	Resin		
		PA	TMA	PA/TMA
Hg^{2+}	5 min	60.2	86.1	54.2
	1 h	85.4	71.2	55.8
Pb^{2+}	5 min	54.9	84.1	80.0
	1 h	59.9	88.5	78.5
Ag^+	5 min	41.1	24.2	29.9
	1 h	29.7	23.1	20.6
Cd^{2+}	5 min	34.9	3.6	24.7
	1 h	37.2	5.6	22.3
Mg^{2+}	5 min	27.9	2.9	21.5
	1 h	27.9	2.4	18.7
Co^{2+}	5 min	26.1	0	16.7
	1 h	24.6	0	13.9
Cu^{2+}	1 h	26.2	0	12.8
Ni^{2+}	1 h	5.8	0	9.6
Fe^{3+}	1 h	0.1	0.4	0.8

Table XVIII
Percent Ag^+ , Hg^{2+} , and Cd^{2+} Absorbed by
Resins After Na_2S Elution

Aqueous Solution Resin	AgNO_3		$\text{Hg}(\text{NO}_3)_2$		$\text{Cd}(\text{NO}_3)_2$	
	TMA	TBA	TMA	TBA	TMA	TBA
R_i	1.10	1.14	1.27	1.45	1.12	1.11
% Abs	76.9	31.0	76.5	36.1	31.2	27.6

contains the percent metal ion absorbed by the resins and also the corresponding R_i values. Two slightly different methods were employed to try to determine the amount of S^{2-} initially on the resins. Analyses of the Na_2S eluate for the amount of S^{2-} absorbed by the resins resulted in a value of 129.6% change for the TBA resin, and elutions of two different samples of the same TMA resin resulted in an average value of 103.2% exchange. The % exchange values represent the mequiv S^{2-} lost from the eluate (or absorbed by the resin) per total mequiv anion exchange sites in the resin sample. Another method employed to determine the amount of S^{2-} on the resins is similar to the TAEC analysis. A sample of the resin in its S^{2-} form was eluted with NaNO_3 and the eluate analyzed for the amount of sulfide displaced by the nitrate. This type of analysis resulted in a value of 14.5 % S^{2-} recovered for a TBA resin and a value of 137.5% for the TMA resin. These % S^{2-} recovered values are based on the assumption that 100% anion exchange occurred during the Na_2S elution. Also, a different TBA resin was used in this analysis than was used in the previous analysis. If the results

from both of the above analyses are valid (including the assumption of 100% anion exchange in the latter) then it appears that the nitrate anion does not displace the sulfide anion from the TBA resin, and that the NaS^- anion is also present on the resin resulting in the % exchange values of greater than 100. The results for the extraction of Ag^+ and Hg^{2+} support the idea that the S^{2-} anion has a greater affinity for the TBA resin than for the TMA resin since much more metal ion was absorbed by the latter. It is unclear as to why the TMA resin absorbed only 31.2% of the Cd^{2+} but approximately 77% of the Ag^+ and Hg^{2+} .

The extraction of Ni^{2+} and Cr^{3+} was also investigated with the PA, TMA, PA/TMA, TBA, and PA/TBA resins after elutions with Na_2S , HCl , and HNO_3 . Table XIX contains the results for the extraction of the two metal ions from solutions of their nitrate salts. The studies were carried out at R_i 's of one unless noted otherwise. The results indicate that very little NiS and no Cr_2S_3 is precipitated by the monofunctional resins. Actually, the results presented for the extraction of Ni^{2+} by these amine resins are slightly misleading since the reactions were set up at R_i 's of greater than one. As a result of this, the values of % Ni^{2+} loaded by the resins may be better for comparison with the other % Abs values. The TMA and TBA resins loaded 20.9% and 7.9%, respectively. Although % L values are affected by the R_i , these values indicate that a significant amount of precipitation does occur, especially with the TMA resin. It can be noted that at an R_i of exactly one the % Abs and % L values are identical. Two Ni^{2+} extraction studies carried out with a mixed PA resin and TMA resin bed at an R_i of one and a 1 h contact time resulted in % Ni^{2+} Abs values of 72.6% and 68.5%. These results

Table XIX
Percent Ni^{2+} and Cr^{3+} Absorbed by
Resins After Na_2S Elution

Aqueous Solution	Contact Time	Resin				
		PA	TMA	PA/ TMA	TBA	PA/ TBA
$\text{Ni}(\text{NO}_3)_2$	1 h			73.3		64.9
	17 h	87.2	11.6 ^a	80.0	4.7 ^b	74.4 ^c
	114 h			69.3		50.5
$\text{Cr}(\text{NO}_3)_3$	1 h			54.1		37.4
	17 h	99.8	0	68.8	0	42.9

^aThis study was carried out at an R_i of 1.80.

^bThis study was carried out at an R_i of 1.69.

^cThis study was carried out at an R_i of 0.87.

indicate that the precipitation and ion exchange mechanisms operate independently on the bifunctional PA/TMA resin since it extracts only 73.3% of the Ni^{2+} . It is not clear as to why both bifunctional resins extract a smaller percentage of Ni^{2+} at a prolonged contact time as observed in comparing the results at contact times of 114 h and 17 h. The results obtained with the bifunctional resins suggest that precipitation of Cr_2S_3 does occur to some extent. If only ion exchange were occurring then both bifunctional resins should extract similar amounts of Cr^{3+} since the resins contain relatively equal amounts of phosphonic acid groups. The fact that the performance of the monofunctional resins indicates no precipitation of Cr^{3+} but that of the bifunctional resins does, could be due to a pH difference in the two resins. This possibility has not been investigated.

A Ni^{2+} study was also conducted with the PA, TMA, PA/TMA, TBA, and PA/TBA resins after elution with NaCl. At an R_i of one and a contact time of 17 h the resins absorbed 96.9%, 0%, 62.8%, 0%, and 53.0% of the Ni^{2+} , respectively. Since NiCl_2 is soluble, the % Ni^{2+} absorbed by these resins is through ion exchange. Assuming that elution of the bifunctional resins with NaCl and Na_2S results in equal amounts of cation exchange between the Na^+ and H^+ of the phosphonic acid groups, the comparison of these results with those of the bifunctional resins after Na_2S elution can provide an estimation of the amount of Ni^{2+} absorbed via precipitation as NiS . The fact that after elution with Na_2S both the PA/TMA and PA/TBA resins absorb approximately 20% more Ni^{2+} than they do after elution with NaCl, suggests that this 20% represents the amount of Ni^{2+} extracted via precipitation.

Table XX contains the results for the extraction of Ni^{2+} and Cr^{3+} by the resins after elution with HCl and HNO_3 . The studies were carried out at R_1 's of one, and the Resin Form column represents the solution with which the resins were eluted prior to contact with the metal ion solutions. The nitrate and chloride salts of nickel(II) and chromium(III) are soluble, and as a result the monofunctional resins did not absorb any of the metal ions. The performance of the bifunctional resins is due to the metal ions exchanging with the phosphonic acid sites of the resin.

The extraction of Ni^{2+} was also observed in the presence of 0.1 M NaNO_3 with the PA resin and the bifunctional PA/TMA and PA/TBA resins after elution with Na_2S , HCl , and HNO_3 . The extractions were carried out at an R_1 of one and a 1 h contact time. The % Ni^{2+} Abs values obtained with the resins after Na_2S elution were 99.6%, 68.3%, and 54.5% for the PA resin, PA/TMA resin, and PA/TBA resin, respectively. Comparison of these results with the corresponding % Abs values in Table XIX indicates that the presence of NaNO_3 decreases the amount of Ni^{2+} extracted by the bifunctional resins by 5% to 10%. Actually, these differences in the % Abs values are due to a slight difference in the R_1 's in the two different studies. The difference in % Ni^{2+} loaded by the two resins with and without the presence of the NaNO_3 is only approximately 3% in both cases. This suggests that the increased ionic strength of the aqueous solution does not affect the performance of the resins. The % Ni^{2+} absorbed by the resins after elution with HCl and HNO_3 also does not indicate any effect due to the presence of the NaNO_3 .

Table XX
 Percent Ni^{2+} and Cr^{3+} Absorbed by Resins
 After HCl and HNO_3 Elutions

Resin Form	Aqueous Solution	Contact Time	Resin		
			PA	PA/ TMA	PA/ TBA
HCl	$\text{Ni}(\text{NO}_3)_2$	1 h	17.6	14.3	13.9
		17 h	21.9		
	$\text{Cr}(\text{NO}_3)_3$	1 h	31.1		
		17 h		17.3	18.7
HNO_3	$\text{Ni}(\text{NO}_3)_2$	1 h		7.7	12.0
	$\text{Cr}(\text{NO}_3)_3$	1 h		20.3	18.9

The extraction of Ni^{2+} from aqueous $\text{Ni}(\text{NO}_3)_2$ was studied with the bifunctional PA/TMA and PA/TBA resins after elution with Na_2S at R_i 's of 1.0 to 1.2 and at contact times ranging from 5 min to 17 h. The results are expressed in terms of the % Ni^{2+} loaded since this quantity is not greatly affected by the slight R_i difference. For example, with the TMA resin at an R_i of 1.2, 60.1% absorption occurs and 71.8% loading and at an R_i of 1.0, 69.4% absorption and 70.0% loading occur. The results for the PA/TMA resin and corresponding contact times were: 71.1% L at 5 min, 71.5% L at 10 min, 70.8% L at 20 min, 70.0% L at 30 min, 73.7% L at 1 h, 73.5% L at 2 h, 78.2% L at 3 h, 79.6% L at 4 h, 69.0% L at 8 h, and 72.3% L at 17 h. For the PA/TBA resin the % L values and corresponding contact times were: 57% L at 5 min, 57.6% L at 10 min, 58.7% L at 20 min, 55.7% L at 30 min, 65.1% L at 1 h, 65.0% L at 2 h, 65.8% L at 3 h, 64.9% L at 4 h, 60.4% L at 8 h, and 60.0% L at 17 h. The results with both resins show the same trends, i.e., an increase in the amount of Ni^{2+} extracted occurs at intermediate contact times and then a slight decrease occurs at longer contact times. The fact that the variations in the % L values are not significantly large suggests that they could be due to experimental error. After contact with the $\text{Ni}(\text{NO}_3)_2$ solution and determination of the % Ni^{2+} absorbed, the resins were analyzed in order to determine the amount of metal ion extracted by the individual mechanisms. The resins were contacted with NaOH as in the hydroxide analysis and acid and sulfide capacities determined. Assuming the hydroxide precipitates 100% of the ion exchanged Ni^{2+} and displaces all of the unreacted S^{2-} remaining on the quaternary amine sites, then a new acid capacity should represent mequiv ion exchanged $\text{Ni}^{2+}/\text{g} + \text{mequiv}$

unreacted S^{2-} /g. Analysis of the NaOH solution for the presence of S^{2-} allows for determination of the unreacted S^{2-} /g value. Comparison of these results with initial acid and sulfide capacities determined in the same manner with the resins prior to contact with the metal ion solutions should give approximate values for the amount of extraction occurring by the individual mechanisms. Also, the sum of the decrease in the acid capacity due to ion exchanged Ni^{2+} and the loss of S^{2-} should equal the amount of Ni^{2+} absorbed per gram of resin. Analysis of this type for the PA/TMA resin samples resulted in an average value accounting for 98.8%, ranging from 89% to 109%, of the Ni^{2+} absorbed by the samples. Based on the results, 12% of the Ni^{2+} absorbed was via the precipitation mechanism. The fact that the same type of analysis could not be made with the PA/TBA resin since the initial acid capacity determined for the resin was less than the sulfide capacity questions the validity of the method of analysis.

The effect of the ion exchanged Ni^{2+} on the hydroxide analysis was investigated with a monofunctional PA resin. A Ni^{2+} loaded resin containing 5.03 mequiv Ni^{2+} /g was analyzed with NaOH for a new acid capacity of 5.74 mequiv/g. The difference between this new capacity and the original acid capacity should equal 5.03 mequiv/g if the OH^- precipitated 100% of the loaded Ni^{2+} . Prior to contact with the $Ni(NO_3)_2$ solution the PA resin was in its Na^+ salt form and had an acid capacity of 1.22 mequiv/g, therefore the increase in acid capacity due to the presence of the ion exchanged Ni^{2+} was found to be 4.52 mequiv/g. This value accounts for 90% of the Ni^{2+} absorbed by the resin. Another analysis of the same type resulted in a value accounting for 82% of the extracted

Ni^{2+} . An attempt to determine the amount of Ni^{2+} remaining in the interstitial volume of the resin and thus being lost during washings of the resin prior to the hydroxide analysis resulted in a value of 0.06 mequiv Ni^{2+} /g. The fact that the total amount of Ni^{2+} absorbed by the resin cannot be accounted for could be due to clogging of the resin pores by the formation of $\text{Ni}(\text{OH})_2$.

Concluding Remarks and Future Directions

The results from the various metal ion extraction studies lead to several general conclusions. The use of the bifunctional PA/TMA resin does not offer any advantages over that of the individual monofunctional resins in the sense that by having the two functional groups on the same resin neither the rate of metal ion extraction nor the amount of metal ion absorbed is increased. In contrast to this, the bifunctional PA/TBA resin results in a significant increase in the extraction rate over that which is observed with a mixed resin bed containing the monofunctional PA and TBA resins. This rate increase can be attributed to an increase in the rate of metal ion extraction occurring through precipitation due to the increased hydrophilicity of the resin. In other words, a mixed resin bed containing the monofunctional resins requires a longer contact time with the metal ion solution for the maximum amount of extraction to occur, because the hydrophobicity of the TBA resin results in a slow rate of precipitation. An excellent example of this is found in the extraction of Ag^+ by the resins after elution with HCl.

Another interesting result observed with the bifunctional PA/TBA resin is that in a couple of cases the amount of metal ion extracted by the resin is significantly larger than that which is expected based on the performance of the individual monofunctional resins. The amount of Ba^{2+} extracted by the resin after elution with H_2SO_4 is approximately 16% to 20% greater than that which is expected. This increase in the amount of Ba^{2+} absorbed by the bifunctional resin could be a result of an R_i difference as has been discussed, or it could be the result of the phosphonic acid group and the tributylamine group operating synergistically when bound to the same polymer support. An R_i study or a mixed resin bed study with the monofunctional PA and TBA resins would determine whether or not the R_i difference results in the increased amount of Ba^{2+} absorbed by the bifunctional resin.

The extraction of Ag^+ by the bifunctional PA/TBA resin with the thiocyanate counterion indicates that in this case the two functional groups do operate synergistically given the fact that the amount of Ag^+ extracted by the resin is greater than the sum of Ag^+ extracted by the individual resins. This is concluded from the fact that the bifunctional resin extracts 20% more Ag^+ than that which is calculated for the two functional groups operating independently, and from the fact that it also extracts 20% more Ag^+ than a mixed resin bed containing the same number of phosphonic acid and tributylamine groups as that which is on the bifunctional resin. The maximum amount of Ag^+ extracted by the bifunctional resin at equilibrium (24 h) is equivalent to that which would be extracted if 100% of the thiocyanate anions were precipitated and approximately 50% of the phosphonic acid sites were loaded.

This fact suggests that the synergistic mechanism is such that the precipitation reaction continually displaces the ion exchange equilibrium in the direction of increasing the amount of Ag^+ extracted by ion exchange until complete precipitation occurs with the final amount of Ag^+ extraction being limited by the ion exchange reaction occurring to 50% completion. This is supported by the fact that the monofunctional PA resin also extracts only 50% of the Ag^+ at a 24 h contact time. It is possible that supporting the phosphonic acid and tributylamine groups on the same resin increases the accessibility of the tributylamine group's counterion and thus results in an increase in the amount of extraction occurring by the precipitation reaction. The fact that the bifunctional PA/TBA resin performs as well as the bifunctional PA/TMA resin in the extraction of Ag^+ and Pb^{2+} after elution with KIO_3 and also in the extraction of Ag^+ after elution with HCl suggests that accessibility is not a problem with the PA/TBA resin. In order to further investigate the extent to which accessibility effects the amount of extraction, metal ion studies with resins employing a macroporous polymer support should be performed.

CHAPTER II

CLASS II RESINS

Synthesis and Characterization

The Class II dual mechanism bifunctional polymers are capable of metal ion extraction through ion exchange and coordination mechanisms. The resins developed in this laboratory contain a phosphonic acid ion exchange site and either a phosphonate ester or a tertiary amine coordinating group. The synthesis and characterization of a bifunctional phosphonic acid/dimethylamine resin are presented. The resin's ability to extract silver and mercury(II) ions is also discussed.

Figure 11 summarizes the synthesis of the bifunctional phosphonic acid/dimethylamine resin. The phosphonic acid resin is converted to its sodium salt prior to amination in order to minimize protonation of the amine. A slight amount of 50% NaOH is also added to neutralize any HCl produced. The bifunctional resins are analyzed for new acid, P, and Cl capacities and also for the total anion exchange capacity (TAEC) or amine

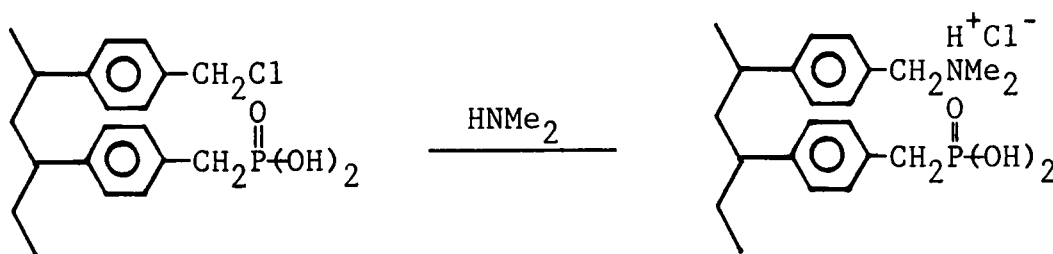
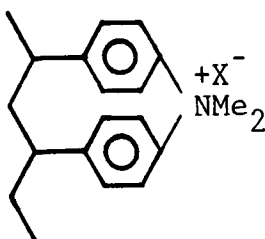


Figure 11. Bifunctional phosphonic acid/dimethylamine resin synthesis.

capacity. It should be noted that the Cl and acid capacities obtained with the resins after elution with HCl are affected by the tertiary amine group which is protonated and retains the Cl^- counterion. The resins were also analyzed for their salt splitting anion exchange capacity (SSAC) which is due to the presence of quaternary amine sites formed by secondary crosslinking from the amine. This type of crosslinking was



not observed with any of the bifunctional resins but was found to occur to a slight extent with the pure dimethylamine resins, which is discussed later.

Initial amination reactions were carried out at ratios of dimethylamine (DMA) to available VBC groups of 3:1, 10:1, 75:1, and 100:1, and constant volumes were maintained by the addition of water. The largest extent of reaction occurred with the 100:1 DMA to VBC ratio, and as a result all further aminations were carried out with the reagent grade 40 weight % DMA without dilution. Various reaction times and temperatures were investigated for the amination: 17 h at room temperature, 17 h at reflux (approximately 60°C), 16 h at room temperature with an additional 1 h heat up to reflux, 5 h at reflux, and 4 h at reflux. All of the reactions resulted in a significant amount of amination except for the

ones carried out at room temperature for 17 h, thus elevated temperature is necessary whether it is held for 17 h, 5 h, 4 h, or attained over a period of 1 h after 16 h at room temperature. A reaction carried out at room temperature for 16 h with an additional heat up to 40°C over a period of 1 h resulted in a larger amount of amination than that which is obtained at just room temperature but not as much as that which occurs at reflux. Table XXI contains the reaction conditions for the amination of three partially functionalized phosphonic acid (PA) resins, the P and Cl capacities of the original phosphonic acid resins, and the resulting P capacities and TAEC's of the bifunctional phosphonic acid/dimethylamine (PA/DMA) resins. The results in Table XXI indicate the reproducibility of the reaction in subsequent aminations of the same acid resin. The decrease in the P capacity in converting the phosphonic acid resin to the bifunctional resin is due to the weight change of the resin that results with the replacement of the Cl with the dimethylamine group. The larger the extent of amination that occurs, the greater the weight increase, and thus a greater decrease in the P capacity is observed as seen in the last two entries in Table XXI.

A pure dimethylamine resin was also synthesized as outlined in Figure 12 for use as a control in the metal ion extraction studies. In the synthesis of the monofunctional resin the reaction time appears to have a more important effect on the degree of functionalization than in the case of the bifunctional resin. Two resins prepared by a 17 h reflux in DMA resulted in TAEC's of 5.06 mequiv/g and 5.56 mequiv/g whereas with a 4 h reflux the resin obtained had a TAEC of 3.89 mequiv/g. The resin with a TAEC of 5.56 mequiv/g was subjected to a 4 h pre--swell in

Table XXI

Amination Conditions and Resulting Capacities of
the Bifunctional PA/DMA Resins

Amination Conditions	Capacities mequiv/(g dry resin)			
	PA		PA/DMA	
	Total P	Total Cl	Total P	TAEC
17 h/Reflux	3.16	2.39	2.61	1.65
5 h/Reflux	3.16	2.39	2.64	1.62
17 h/Reflux	2.96	2.68	2.66	1.89
5 h/Reflux	2.96	2.68	2.52	1.77
4 h/Reflux	2.48	3.00	1.59	2.45
4 h/Reflux	2.48	3.00	1.68	2.41

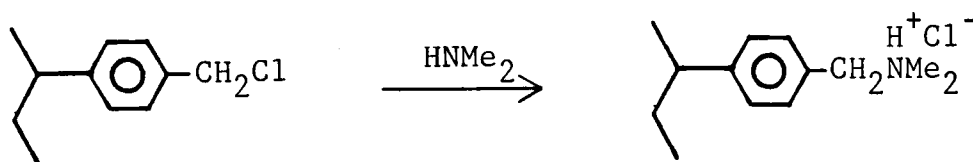


Figure 12. Dimethylamine resin synthesis.

ethylene dichloride prior to amination. The two resins synthesized at 17 h reflux also had SSAC's of 0.62 mequiv/g and 0.64 mequiv/g. The reason the monofunctional DMA resins form salt splitting anion exchange sites and the bifunctional resins do not is that with the former resin there are more VBC sites available for secondary crosslinking. In the bifunctional resin the number of adjacent VBC units is limited by the presence of the phosphonic acid groups, and in order to form quaternary amine sites the amine would have to displace the phosphorus which does not seem to occur.

Silver and Mercury(II) Ion Extraction Studies

The ability of the bifunctional PA/DMA resin to extract Ag^+ and Hg^{2+} was investigated at various R_i 's. Monofunctional PA and DMA resins, phosphonate ester resins, and a PA resin with a styrene support were also included in the studies. Before contact with the metal ion solutions the resins were eluted with HCl resulting in protonation of the acid and amine sites, and also producing Cl^- as the counterion of the protonated amine. The results from these studies are presented in Figures 13 and 14 as plots of the percent Ag^+ and Hg^{2+} loaded by the resins as a function of the R_i . The reason the R_i values are not the same for each resin is that the studies were initially set up based on the milliequivalents of acid sites on the resins (mequiv OH) but are presented here based on mequiv (P + TAEC). The results indicate that Hg^{2+} has a greater affinity for the PA resin than does Ag^+ . The reason that values of greater than 100 % loading are obtained in the extraction of Hg^{2+} is due to the fact that for each milliequivalent of P there are

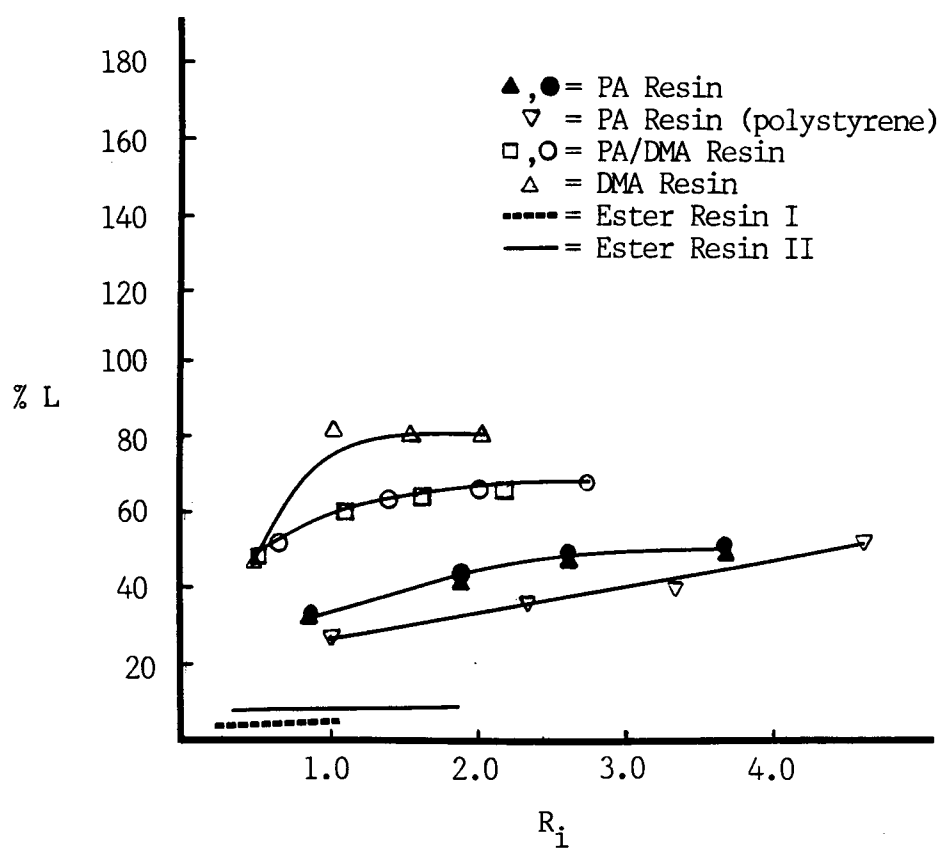


Figure 13. % L vs. R_i curves for Ag^+ absorption with resins after HCl elution.

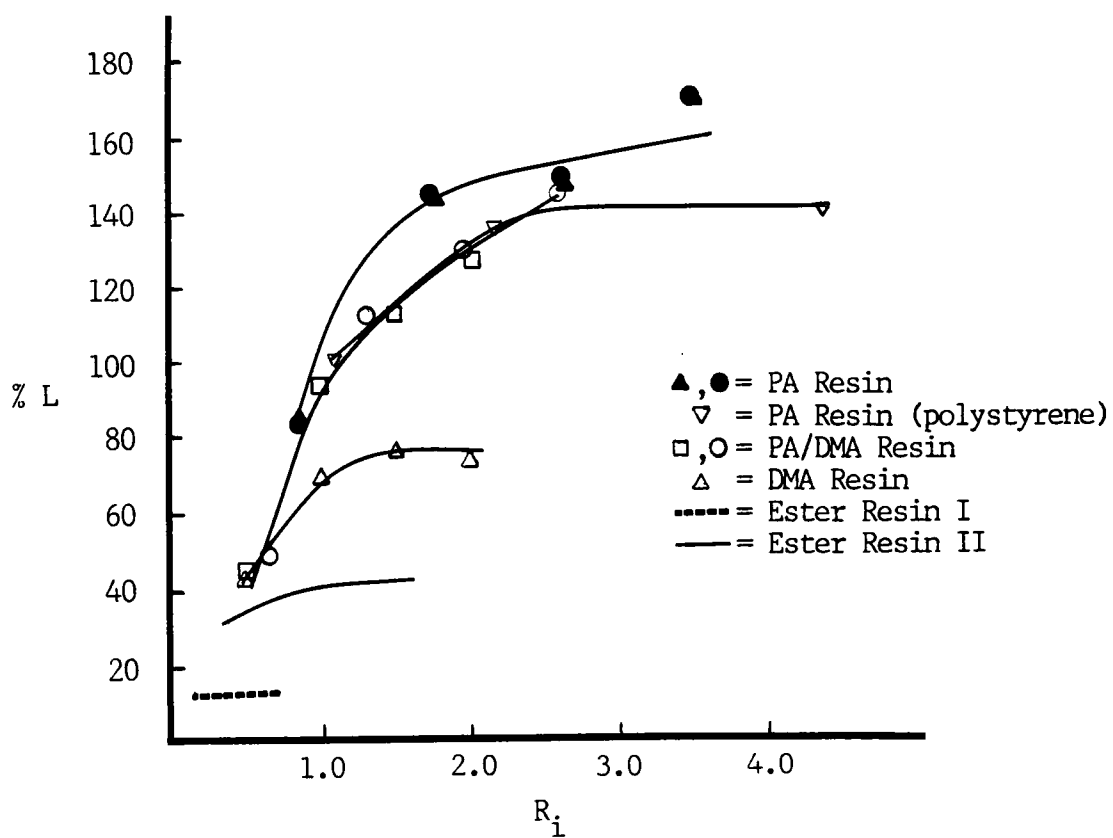


Figure 14. % L vs. R_i curves for Hg^{2+} absorption with resins after HCl elution.

two millequivalents of acid sites which can ion exchange with the mercury(II) ions. It is unclear as to why the VBC supported and the styrene supported PA resins perform so differently. The fact that the phosphonate ester resin I extracts much more Hg^{2+} than the other can be attributed to the larger acid capacity of this resin. It appears that neither metal ion is extracted to any significant degree through coordination with the ester group. The presence of solid AgCl in the aqueous solutions of the monofunctional DMA resin's and bifunctional PA/DMA resins' reaction vials indicates that the DMA groups are not operating via a coordination mechanism but through precipitation with the Cl^- counterion of the protonated amine. In order to observe the coordinative ability of the amine groups the free amine form of the resins was obtained by eluting the resins with NaOH.

Silver and mercury(II) ion extraction studies were performed with a PA resin (VBC support), a DMA resin, a phosphonate ester resin, and two bifunctional PA/DMA resins all of which had been eluted with NaOH followed by a water elution. The results from these studies are presented in Figures 15 and 16. As expected the amount of Ag^+ loaded by the DMA resin in its free base form is greatly reduced although the fact that the resin approaches 40 % L indicates that some coordination does occur. In the extraction of Hg^{2+} the amount of metal ion loaded by the DMA resin is also greatly reduced. This is a result of the fact that in its protonated form the chloride counterion of the amine resin forms a stable complex with the mercury(II) ion making it "invisible" to the titrimetric analysis employed²⁰, and thus giving the appearance that a significant amount of extraction occurs. The increased extraction of

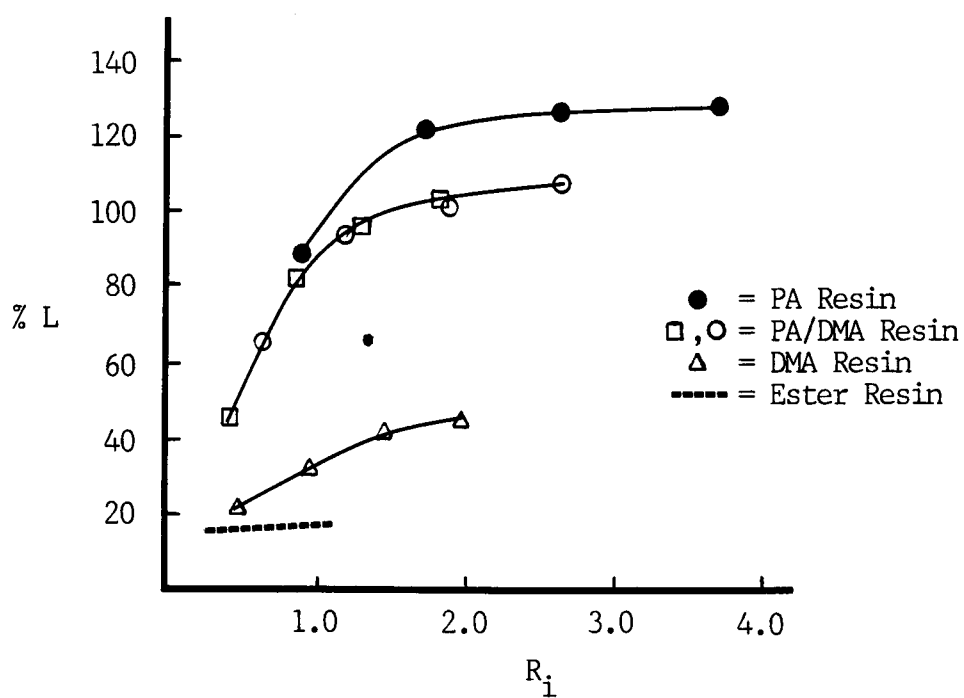


Figure 15. % L vs. R_i curves for Ag^+ absorption with resins after NaOH elution.

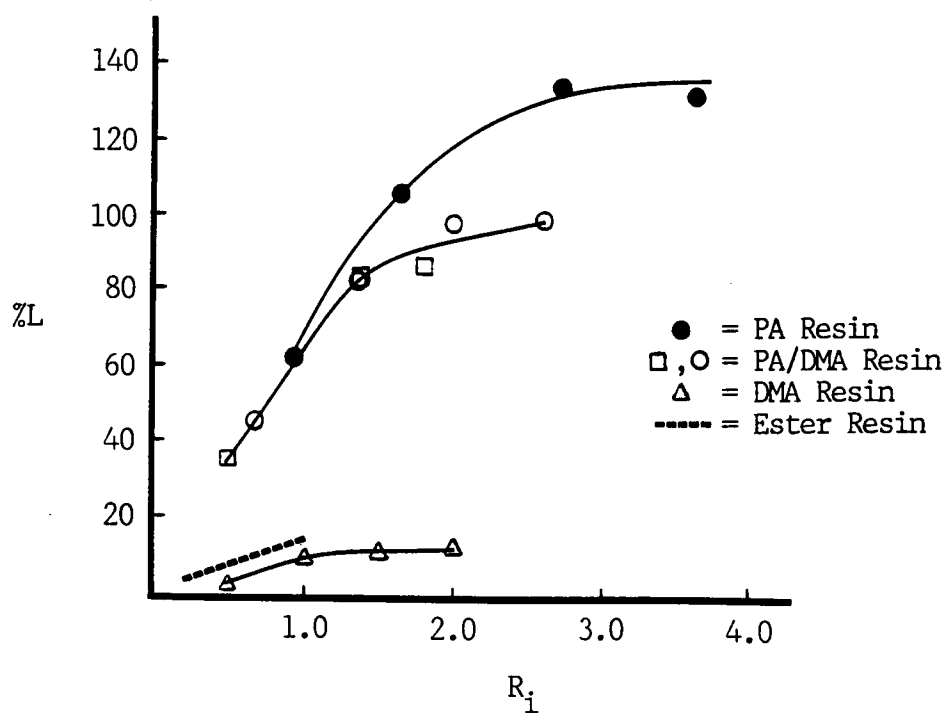


Figure 16. % L vs. R_i curves for Hg^{2+} absorption with resins after NaOH elution.

Ag^+ by the PA/DMA resins after NaOH elution is due to the presence of the Na^+ form of the PA sites increasing the amount of extraction through the ion exchange mechanism as indicated by the performance of the monofunctional PA resin. In the case of Hg^{2+} extraction, removal of the Cl^- counterion eliminates complexation of the metal ions and as a result appears to decrease the % Hg^+ loaded by the PA/DMA resin. The phosphonate ester resin used in this study can be compared with the ester resin II of the above studies.

The performance of the bifunctional PA/DMA resin can be analyzed in light of the results obtained with the monofunctional PA and DMA resins. It must be taken into account that the R_i with respect to the individual phosphonic acid groups or the individual amine groups of the bifunctional resin is much greater than the R_i with respect to the sum of these sites. For example, in the extraction of Ag^+ by a PA/DMA resin after elution with HCl at an R_i of 1.1 the R_i , with respect to the individual phosphonic acid groups is 1.9 and with respect to the dimethylamine sites is 2.6. At these R_i 's the monofunctional resins load approximately 42 % and 80 %, respectively, (assuming the DMA % L vs. R_i curve can be extrapolated to an R_i of 2.6). If the two different groups operate independently when bound to the same resin and load their respective amounts of Ag^+ then the bifunctional resin can be predicted to absorb 53 %. Experimentally, the resin was found to extract 55 % of the silver ions from the aqueous solution. This type of behavior was observed in each of the metal ion studies and indicates that no synergistic effect is obtained in the extraction of Ag^+ or Hg^{2+} by having these two functional groups in close proximity on the same resin.

CHAPTER III

EXPERIMENTAL

Copolymer Synthesis

The divinylbenzene crosslinked poly(vinylbenzyl chloride) polymer support is prepared by a suspension polymerization. The apparatus consists of a three--neck round bottom flask equipped with an overhead stirrer, a condenser, and a thermometer. Two hours prior to polymerization a N₂ purge of the system is begun and is continued throughout the reaction. The aqueous phase consists of a mixture of Pharmagel (0.96 g) in 100.1 mL of water heated to 50°C, combined with a mixture of poly(diallyldimethylammonium chloride) (23.8 g, Calgon Corp.) and boric acid (6.33 g) in 204.6 mL of water at a pH of 10.3. Upon addition of the aqueous phase to the reaction flask, the position of the stir blades is adjusted and the desired stir speed set. In the preparation of a 2% gel resin, the organic phase consists of 10.83 g divinylbenzene (Dow Chemical Co.), 286.17 g vinylbenzyl chloride (Rohm and Haas), and 3.00 g benzoyl peroxide initiator. The organic phase is added to the aqueous phase and the polymerization mixture is subjected to 2 min of stirring and a 1 min break, repeated three times, in order to ensure suspension of the organic phase as opposed to phase inversion. The reaction mixture is heated to 80°C in 7°/15 min increments and is held at 80°C for 10 h. The polymerization is completed by heating the mixture at 100°C for 2 h. After cooling to room temperature the copolymer beads

are washed four times 15 min each with pH 4 water, followed by four 15 min washes with pure water, and then dried at room temperature.

Phosphonic Acid Resin Synthesis

Ten grams of the VBC/DVB copolymer (0.63 mol) is added to a 250 mL three--neck round bottom flask equipped with an overhead stirrer, a condenser, and a thermometer. The copolymer is allowed to swell in 80 mL PCl_3 (Aldrich) for 1 h, after which 6.73 g AlCl_3 catalyst (0.49 mol) is added. The reaction mixture is then heated to reflux (73°C) over a period of 1 h and held at reflux for 4 h. The mixture is cooled to room temperature and the reaction quenched in ice water saturated with NaCl. The functionalized resins are washed with water until neutral, placed in a glass frit funnel, and conditioned with successive 1 L/ h elutions of H_2O , 1 N NaOH, H_2O , 1 N HCl, and H_2O .

Trimethylamine Resin Synthesis

Ten grams of the VBC/DVB copolymer and 167 mL of reagent grade 25 weight % trimethylamine (Aldrich) are added to a 250 mL three--neck round bottom flask equipped with an overhead stirrer, a condenser, and a thermometer. The reaction mixture is refluxed (approximately 42°C) for 4 h and then cooled to room temperature. The beads are washed with water, placed in a glass frit, and conditioned as above for the phosphonic acid resin.

Tributylamine Resin Synthesis

Ten grams of the VBC/DVB copolymer and 365 mL of a 37 weight % solution of tributylamine (Aldrich) in dioxane (Aldrich) are added to a 500 mL three--neck round bottom flask equipped with an overhead stirrer, a condenser, and a thermometer. The reaction mixture is refluxed for 18 h and then cooled to room temperature. The beads are washed with 95% ethanol, placed in a glass frit, and conditioned with successive 1 L/h elutions of 95% ethanol, H_2O , 1 N NaOH, H_2O , 1 N HCl, and H_2O .

Dimethylamine Resin Synthesis

A mixture of 10 g VBC/DVB copolymer, 80 mL reagent grade 40 weight % dimethylamine (Aldrich), and 0.5 g 50% NaOH is refluxed for 4 h in a 250 mL three--neck round bottom flask equipped with an overhead stirrer, a condenser, and a thermometer. After cooling to room temperature, the beads are washed with water, placed in a glass frit, and conditioned as above for the phosphonic acid resin.

Dimethylethylamine Resin Synthesis

A mixture of 10 g VBC/DVB copolymer, 141 mL H_2O , and 50 mL N,N--dimethylethylamine (Aldrich), is refluxed ($53^{\circ}C$) for 10.5 h in a 250 mL three--neck round bottom flask equipped with an overhead stirrer, a condenser, and a thermometer. After cooling to room temperature the beads are washed with water, placed in a glass frit, and conditioned as above for the phosphonic acid resin.

Triethylamine Resin Synthesis

A mixture of 10 g VBC/DVB copolymer, 192 mL H₂O, 130 mL 95% ethanol, and 89 mL triethylamine (Aldrich) is refluxed for 10.5 h in a 500 mL three--neck round bottom flask equipped with an overhead stirrer, a condenser, and a thermometer. After cooling to room temperature the beads are washed with 95% ethanol, placed in a glass frit, and conditioned as above for the tributylamine resin.

Phosphonic Acid/Trimethylamine Resin Synthesis

A partially functionalized phosphonic acid resin is obtained as described above with the exception that a 40°C reaction temperature is employed. The functionalized phosphonic acid resin (10 g dry weight) is changed to its sodium salt form by elution with 1 L of NaOH over a period of 1 h. Amination with trimethylamine and conditioning of the final resin are carried out exactly as in the synthesis of the monofunctional trimethylamine resin.

Phosphonic Acid/Tributylamine Resin Synthesis

The sodium salt form of a partially functionalized phosphonic acid resin (10 g dry weight) is placed in a 500 mL three--neck round bottom flask and refluxed for 18 h with 365 mL of a 37 weight % solution of tributylamine (Aldrich) in dioxane. The beads are washed with 95% ethanol, placed in a glass frit, and conditioned as outlined for the monofunctional tributylamine resin.

Phosphonic Acid/Dimethylamine Resin Synthesis

Amination of the sodium salt form of a partially functionalized phosphonic acid resin (10 g dry weight) is obtained according to the synthesis of the monofunctional dimethylamine resin. Conditioning of the bifunctional resin is also as specified in the synthesis of the monofunctional resin.

Procedure for % Solid Weight of a Functionalized Resin

The conditioned resin is placed in a Buchner funnel and aspirated at 720 mm Hg for 5 min. An accurately weighed sample (approximately 1.25 g) of the suction dried resin is then placed in an oven at 110°C for 16 h. The weight of the oven dried sample divided by the weight of the suction dried sample multiplied by 100 results in the % solid value for the resin. Since the suction dried (hydrated) form of the resin is commonly used, the % solid value is necessary to determine the actual dry weight of the resin.

Determination of the Acid Capacity via Titration with NaOH

An accurately weighed 1.0 to 1.5 g sample of the suction dried resin is placed in a 250 mL ground glass Erlenmeyer flask and stirred for 17 h with 200.0 mL standard 0.1 N NaOH in 5 weight % NaCl. A 50 mL aliquot of the NaOH solution is titrated with 0.1 to 0.15 N H₂SO₄ using phenolphthalein as the indicator. The acid capacity of the resin is calculated as follows:

acid capacity =

$$[(200 \text{ ml NaOH})(N \text{ NaOH}) - 4(\text{Vol. H}_2\text{SO}_4 \text{ titrant})(N \text{ H}_2\text{SO}_4)]/\text{g dry resin}$$

The NaOH solution is standardized against primary standard potassium hydrogen phthalate and subsequently used to standardize the H_2SO_4 solution.

Determination of the Acid Capacity via Titration with KOH in Dioxane

This analysis is performed exactly as the NaOH analysis described above with the exception that a standard solution of KOH in 81% dioxane in water is employed rather than aqueous NaOH.

Phosphorus Elemental Analysis

An accurately weighed oven dried resin sample (approximately 20 mg) is placed in a 125 mL Erlenmeyer flask with 5 mL of concentrated HNO_3 and 10 mL of 70 to 72% HClO_4 . This mixture is heated on a hot plate until complete dissolution of the beads is attained. After cooling the solution is quantitatively transferred to a 100 mL volumetric flask and diluted to the mark with distilled water. A 5 mL aliquot of this solution is placed in a 50 mL volumetric flask to which is added in the following order 3.5 mL 70 to 72% HClO_4 , 4.5 mL amidol solution, and 3.5 mL molybdate solution. A blank solution is also prepared containing everything except a resin sample. The solutions are diluted with distilled water to the 50 mL mark and allowed to develop for 30 min. The amidol solution contains 1 g of 2,4--diaminophenol dihydrochloride (Aldrich), 10 g of Na_2SO_3 , 2.7 g of concentrated H_2SO_4 , and 90 g of H_2O . The molybdate solution is prepared by dissolving 4.4 g of ammonium molybdate(VI) tetrahydrate in 50 mL H_2O . The absorbance of the

developed solution is measured at 700 nm on a Bausch and Lomb Spectronic 21 Spectrophotometer. The percent and capacity of P in the resin are calculated with the following equations, in which the slope is obtained from a Beer's law plot prepared using a series of KH_2PO_4 standards, and 30.974 is the atomic weight of phosphorus:

$$\% \text{ P} = \text{Abs.}/(\text{slope})(\text{g dry resin})$$

$$\text{P capacity} = (\text{Abs.})(10)/(\text{slope})(\text{g dry resin})(30.974)$$

The factor of 10 in the equation for the P capacity is equal to the dilution factor of 1000 ml (obtained from 100 mL x 50 mL/ 5 mL) divided by the slope, which is in units of $(\text{mg}/100\text{mL})^{-1}$. An example calculation for the P capacity of a phosphonic acid resin, for which an absorbance of 0.193 is obtained from a 20.1 mg sample of the resin, is presented with all units included (slope = $1.3170 (\text{mg}/100 \text{ mL})^{-1}$):

$$\begin{aligned} & (0.193)(1000 \text{ mL})/(1.3170 (100 \text{ mL}/\text{mg}))(0.0201 \text{ g})(30.974 \text{ mg/mequiv}) \\ & = 2.354 \text{ mequiv/g} \end{aligned}$$

Chlorine Elemental Analysis

The chlorine elemental analysis involves decomposition of the resin sample by a sodium fusion. An accurately weighed oven dried resin sample (0.3 to 0.4 g) is placed in a pyrex 15 x 160 test tube, to which 2 to 3 g sodium metal and 1 mL xylene are added. A second test tube containing approximately 1 g sodium metal is also prepared. The two test tubes are connected by a 7 mm transfer tube equipped with a #1 rubber stopper in a

manner such that all the gases produced during the sodium fusion bubble through the molten sodium of the second test tube. The sodium in the second test tube is melted with a Bunsen burner before inserting the transfer tube. Another Bunsen burner is used to slowly melt the sodium in the first test tube and decompose the resin. At this point, the test tubes are heated strongly for 15 min to ensure complete resin decomposition. After cooling to room temperature, all glassware is quantitatively broken into a 250 mL beaker containing approximately 100 mL methanol. The methanol is completely evaporated by heating on a hot plate. The remaining solid is dissolved with water and quantitatively transferred with filtering into a 250 mL volumetric flask. A 50 mL aliquot of this solution is placed in a 125 mL Erlenmeyer flask, acidified with concentrated HNO_3 to a methyl orange endpoint (red), and neutralized with 0.3 N NaOH (a yellow endpoint). A Mohr titration is then performed to determine the amount of chloride present with standard 0.05 N AgNO_3 employing an aqueous 5 weight % K_2CrO_4 (2 mL) indicator. The chlorine capacity is calculated as follows:

$$\text{Cl capacity} = 5(\text{Vol. AgNO}_3)(\text{N AgNO}_3)/\text{g dry resin}$$

A sample containing nitrogen (amine resins) must be boiled for 15 min after acidification since the presence of CN^- interferes with the titration for Cl^- .

Iodine Analysis for Oxidizable P-H Bonds

The iodine analysis consists of oxidation of the resin's P-H bonds with a KI_3 solution, reduction of the excess I_2 with a sodium thiosulfate solution, and a subsequent back titration of the excess thiosulfate with the KI_3 solution. A 0.2 N KI_3 solution is prepared by dissolving 25.4 g iodine (Aldrich) and 80 g iodate--free KI (Aldrich) in 1 L H_2O . The sodium thiosulfate solution consists of 25 g $\text{Na}_2\text{S}_2\text{O}_3$ (0.1 mol) and 0.2 g Na_2CO_3 (as a preservative) in 1 L H_2O and is standardized against primary standard KIO_3 . The iodine solution is then standardized with the standard sodium thiosulfate.

An accurately weighed suction dried resin sample (equivalent to approximately 0.5 g dry resin) is placed in a 250 mL brown bottle and contacted with 50 mL KI_3 solution and 2 mL pyridine for 22 h. A 50 mL aliquot of the thiosulfate solution is added and the solution shaken until the beads become clear (not to exceed 2.5 h). Addition of 2 mL toluene may be necessary to attain complete reaction of the thiosulfate with the iodine absorbed in the resin. An aliquot of the solution is then titrated with the KI_3 solution. The capacity of oxidizable P-H bonds is calculated as follows:

$$\text{P-H capacity} =$$

$$[(\text{Vol. KI}_3)(\text{N KI}_3) - (\text{Vol. sample solution})(\text{N Na}_2\text{S}_2\text{O}_3)] / (2)(\text{g dry resin})$$

Silver Oxidation Analysis

This method of analysis involves oxidation of the P-H bonds with Ag^+ followed by the determination of a new % solid and acid capacity for the

resin. A sample of suction dried beads (equivalent to approximately 4 g dry resin) is placed in a 100 mL bottle and contacted with approximately 10 g AgNO_3 and 100 mL H_2O for 17 h. The resin sample is then transferred to a glass frit, eluted with 1 L 4 N HNO_3 over a period of 2 h, followed by elution with 2 L H_2O also over a 2 h time period. A new % solid and acid capacity are determined as described above. The increase in acid capacity represents the P-H capacity of the resin.

Determination of the Total Anion Exchange Capacity (TAEC)

An accurately weighed suction dried resin sample (10 to 15 g) is placed in a glass frit and eluted with 1 L 4 weight % NaNO_3 . The eluate is collected in a 1 L volumetric flask, and the amount of Cl^- displaced by NO_3^- is determined by titrating a 100 mL aliquot as described in the Cl elemental analysis procedure. The amine capacity (TAEC) is calculated according to the equation

$$\text{TAEC} = (10)(\text{Vol. AgNO}_3)(N \text{ AgNO}_3)/\text{g dry resin}$$

Determination of the Salt Splitting Anion Exchange Capacity (SSAC)

An accurately weighed suction dried resin sample (10 to 15 g) is placed in a glass frit, eluted with 1 L 1 N NaOH , 1 L H_2O , and 1 L 4 weight % NaNO_3 , each elution occurring over a 1 h time period. The NaNO_3 eluate is collected in a 1 L volumetric flask. A 100 mL aliquot of the eluate is then titrated with standard 0.1 N H_2SO_4 . The SSAC is

equivalent to the mequiv OH^- displaced by the NO_3^- per dry gram of resin and is calculated accordingly:

$$\text{SSAC} = (10)(\text{Vol. H}_2\text{SO}_4)(N \text{ H}_2\text{SO}_4)/\text{g dry resin}$$

Sulfide Analysis

This analysis involves the oxidation of S^{2-} by I_2 and a subsequent titration of the iodine solution with sodium thiosulfate.²² An aliquot of the sulfide containing solution is contacted with an excess of a standard KI_3 solution (Iodine Oxidation Analysis, p.76). The solution is then acidified with approximately 1 N HCl and the remaining iodine titrated with a standard $\text{Na}_2\text{S}_2\text{O}_3$ solution.

Resin Elutions to Attain Appropriate Counterion on the Amine Sites

In order to obtain the Cl^- , SO_4^{2-} , and H_2PO_4^- (or HPO_4^{2-}) counterions, the suction dried resins are placed in a glass frit and eluted with a liter of the corresponding acid (1 N) over a period of 1 h followed with a 1 L/h water elution. If the resin is already in its Cl^- form from previous conditioning, it is not necessary to elute it again with HCl.

The SCN^- and IO_3^- counterions are obtained by elutions with aqueous solutions of the potassium salts. The SCN^- form of the resin is obtained by a 1 L /h elution with 1 N KSCN followed by a 1 L/h H_2O elution. Due to its insolubility, a 1 N aqueous solution of KIO_3 cannot be prepared. As a result of this, two 1 L/h elutions of the resins with a saturated

solution of the salt (approximately 0.2 N) are employed with a subsequent 1 L/h H_2O elution.

The S^{2-} counterion is obtained by a 1 L/h elution of the resins with aqueous 1 N Na_2S followed by a 1 L/h H_2O elution.

In all cases the quantity of resin eluted should not be greater than 10 g dry resin weight. Prior to use in the metal ion studies, the resins are suction dried and a new % solid value determined.

Metal Ion Extraction Studies

A quantity of suction dried resin containing a total of 1 mequiv of reactive sites (P capacity plus TAEC) is placed in a 100 mL bottle and contacted with 100 mL of a standard metal ion solution. The values presented are for an R_i of one; other R_i 's are obtained either by varying the amount of resin or the concentration and/or volume of the metal ion solution. The reactive sites of the resin are defined as the number of phosphonic acid and amine groups on the resin. The % metal ion absorbed by the resins is determined by analyzing the aqueous solution for the amount of metal ion lost during contact with the resin.

The Volhard method is used for the analysis of Ag^+ and Hg^{2+} .²³ An aliquot (10 to 25 mL) of the aqueous solution is placed in a 125 mL Erlenmeyer flask to which is added 5 mL 6 N HNO_3 and 5 ml indicator (a saturated iron(III) ammonium sulfate solution in 6 N HNO_3) and titrated with a standard NH_4SCN solution. The NH_4SCN solution is standardized against a primary standard AgNO_3 solution.

EDTA titrations are performed for the analysis of Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , Zn^{2+} , and Cd^{2+} according to the procedures outlined by

Schwarzenbach.²⁴ Eriochromeblack T is the indicator used for the titration of Pb^{2+} , Cd^{2+} , Zn^{2+} and Mg^{2+} . The titrations of Sr^{2+} and Ba^{2+} are performed in the presence of a metalphthalein--naphthol green indicator, and the titration of Ca^{2+} is carried out in the presence of the indicator murexide.

The concentrations of the metal ions Co^{2+} , Cu^{2+} , Ni^{2+} , Fe^{3+} , and Cr^{3+} are determined spectrophotometrically with a Bausch and Lomb Spectronic 21 Spectrophotometer. The absorbances of Co^{2+} , Cu^{2+} , Ni^{2+} , and Cr^{3+} are measured directly at 515 nm, 820 nm, 392 nm, and 410 nm, respectively. The spectrophotometric determination of Fe^{3+} involves the complexation of Fe^{2+} with 1,10--phenanthroline.²³ Five mL of the Fe^{3+} solution is placed in a 100 mL volumetric flask and contacted with 1 mL of a hydroxylamine solution (reducing agent, 10 g dissolved in 100 mL water), 10 mL of a 1,10--phenanthroline solution (0.1 g dissolved in 100 mL water), and 8 mL of a sodium acetate solution (10 g dissolved in 100 mL water). After dilution to 100 mL with distilled water the solutions are allowed to develop for 15 min, and the absorption measured at 508 nm.

LIST OF REFERENCES

LIST OF REFERENCES

1. Hodge, P. Chemistry in Britain 1978, 14, 237.
2. "Immobilized Enzymes: Research and Development"; Chibata, I., Ed.; Kodansha Ltd.: Tokyo, 1978.
3. Kraus, M., Patchornik, A. Chemtech 1979, 118.
4. "Polymer--Supported Reactions in Organic Synthesis"; Hodge, P., Sherrington, D. C., Eds.; Wiley: London, 1980.
5. "Polymeric Reagents and Catalysts"; Ford, W. T., Ed.; American Chemical Society: Washington, DC, 1986.
6. Dorfner, K. "Ion Exchangers: Properties and Applications"; Ann Arbor Science: Ann Arbor, Michigan, 1972.
7. Janauer, G. E., Gibbons, R. E., Jr., William, W. E., in "Ion Exchange and Solvent Extraction"; Marinsky, J. A., Marcus, Y., Eds.; Marcel Dekker: New York, 1985; Vol. 9, Chapter 2.
8. "Ion Exchange Technology"; Naden, D., Streat, M., Eds.; Ellis Horwood Limited: Chichester, 1984.
9. Tavlarides, L. L., Bae, J. H., Lee, C. K. Sep. Sci. Technol. 1987, 22, 581.
10. Ritcey, G. M., Ashbrook, A. W. "Solvent Extraction: Principles and Applications to Process Metallurgy, Parts I and II"; Elsevier: New York, 1984.
11. Schulz, W. W. Proc. Int. Solvent Extr. Conf., Vol. I 1971, 174.
12. Helfferich, F. "Ion Exchange"; McGraw--Hill: New York, 1962.
13. Sahni, S. K., Reedijk, J. Coordination Chemistry Reviews 1984, 1.
14. Alexandratos, S. D., Strand, M. A., Quillen, D. R., Walder, A. J. Macromolecules 1985, 18, 829.
15. Alexandratos, S. D., Quillen, D. R., McDowell, W. J. Sep. Sci. Technol. 1987, 22, 983.
16. Alexandratos, S. D., Wilson, D. L. Macromolecules 1986, 19, 280.
17. De, A. K., Khopkar, S. M., Chalmers, R. A. "Solvent Extraction of Metals"; Van Nostrand Reinhold Company Ltd.: London, 1970.
18. Deptula, C. Proc. Int. Solvent Extr. Conf., Vol. I 1971, 638.

19. Barrett, J. H. U. S. Patent 3,843,566 1974.
20. "Treatise on Analytical Chemistry, Part II, Vol. 3"; Kolthoff, I. M., Elving, P. J., Eds.; Interscience Publishers: New York, 1961.
21. "Phosphate Minerals"; Nriagu, J. O., Moore, P. B., Eds.; Springer--Verlag: Berlin, 1984.
22. Charlot, G., Bezier, D. "Quantitative Inorganic Analysis"; Methuen and Co. Ltd.: London, 1957.
23. Day, R. A., Underwood, A. L. "Quantitative Analysis" Ed. 4; Prentice--Hall, Inc.: Englewood Cliffs, N.J., 1980.
24. Schwarzenbach, G., Flaschka, H. "Complexometric Titrations" (English Ed. 2, translated by H. M. N. H. Irving); Methuen and Co. Ltd.: London, 1969.

APPENDICES

APPENDIX A

PHOSPHINIC ACID RESIN AS A REDOX REAGENT IN ORGANIC REACTIONS

Discussion

The fact that the phosphinic acid resin operates by a redox mechanism in the selective extraction of some metal ions, e.g. silver and mercury(II), has led to the investigation of its utility as a reducing agent in organic reactions. Preliminary work in this area is discussed. All results are described in terms of the resin itself, i.e. the extent to which the phosphinic's P-H bonds are oxidized, and are obtained by determining a new acid capacity after the resin has been in contact with the organic reagent. An increase in the acid capacity is attributed to the oxidation of the P-H bond to a P-OH bond. The reaction solutions have not been analyzed for the formation of products or loss of reactants. Most of the reactions studied employed a phosphinic acid resin supported on a macroreticular (MR) polystyrene matrix crosslinked with 5% divinylbenzene. Macroreticular resins offer the advantage of larger pore sizes in comparison to gel resins and as a result do not require a swelling solvent. A disadvantage of MR resins is that due to the large pores, the resins are fairly fragile and a larger degree of crosslinking agent must be employed to increase the stability of the resin.

The organic reagents that have been investigated are dimethylsulfoxide, acetic acid, crotonaldehyde, tri--n--butylphosphate, triphenylphosphine oxide, cinnamaldehyde, phenol, allyl alcohol,

cinnamyl alcohol, and tri--octylphosphine oxide. The capacity of oxidizable P-H bonds was estimated as 3.0 mequiv/(g dry resin) based on previous oxidation analyses of the resins. The reactions with acetic acid, phenol, cinnamyl alcohol, and tri--octylphosphine oxide resulted in no increase in the acid capacity, thus indicating no reduction of these compounds occurred. Analysis of the resin after reaction with cinnamyl alcohol resulted in an extremely low acid capacity (3.02 mequiv/(g dry resin) compared to an initial capacity of 5.38 mequiv/(g dry resin)), which is due to experimental conditions. The cinnamyl alcohol reaction was performed at approximately 100°C employing heptane as the solvent. At room temperature the alcohol is insoluble in heptane and, although the resin was washed with dioxane prior to the KOH/dioxane acid capacity analysis, the presence of solid cinnamyl alcohol remaining in the resin's pores would result in incomplete reaction between the base and acid sites of the resin.

Various reactions of the phosphinic acid resin with dimethylsulfoxide (DMSO) indicate that the resin is oxidized, thus suggesting the reduction of the compound to dimethylsulfide. Table XXII contains the reaction conditions and results from analysis of the resin. The % P-H bonds oxidized is based on an initial value of 3.00 mequiv P-H/(g dry resin). All of the reactions were carried out at a constant volume of 50 mL. The first four reactions in Table XXII were performed with a 5% MR resin that had been heptane dried to remove the water inside the resin, whereas the last three reactions employed a 2% gel resin in its hydrated form. A distinct difference is observed between the first four reactions and the last three. In the presence of a large excess of DMSO

Table XXII
Reaction of the Phosphinic Acid Resin with
Dimethylsulfoxide

Solvent	Temp. (°C)/ Time	mequiv DMSO/ mequiv P-H	Acid Capacity Increase (mequiv/ g dry resin)	% P-H Bonds Oxidized
neat	Ref. ^a /47.5 h	175.5	3.02	100
neat	Ref./17 h	165.3	2.73	91
xylene	Ref./17 h	3.8	1.23	41
xylene	Ref./24 h	1.5	0.92	31
H ₂ O	Ref./23.3 h	68.3	0.26	4
neat	Ref./24 h		1.75	58
neat	100°C/24 h		1.41	47

^aReflux

the heptane dried 5% MR resin is completely oxidized, but the hydrated 2% gel is only approximately 50% oxidized. It is not clear as to whether the type of resin employed or the the different forms of the two resins (heptane dried or hydrated) is responsible for the results.

The results from the reactions with crotonaldehyde, triphenylphosphine oxide, and cinnamaldehyde are presented in Table XXIII. The heptane dried 5% MR phosphinic acid resin was employed in all of the reactions except for the cinnamaldehyde reaction with toluene as the solvent in which the heptane dried resin was first rinsed with toluene. The volume of the reaction solution was 50 mL in all cases. The results from the reactions of the phosphinic acid resin with crotonaldehyde are the opposite of what would be expected, since with an increasing ratio of oxidant to P-H bonds the % of oxidation of the bonds decreases. It should be noted that refluxing the resin in methanol alone results in an acid capacity increase corresponding to the oxidation of approximately 37.5% of the P-H bonds. Without further investigation of the liquid components these results cannot be explained. The triphenylphosphine oxide results indicate the importance of the solvent. The % oxidation of the P-H bonds in the presence of chlorobenzene is only half of that which occurs in the presence of benzene. No oxidation of the P-H bonds occurs in neat chlorobenzene. This type of control reaction has not been run with benzene. The results from the reactions of the resins with cinnamaldehyde employing methanol as the solvent are similar to those obtained from the crotonaldehyde reactions, i.e. the larger the ratio of mequiv oxidant to mequiv P-H bonds the smaller the amount of oxidation occurring. The fact that no oxidation occurs when heptane is

Table XXIII

Reaction of the Phosphinic Acid Resin with Crotonaldehyde,
Triphenylphosphine Oxide, and Cinnamaldehyde

Solvent	Temp. (°C)/ Time	mequiv Oxidant/ mequiv P-H Bonds	Acid Capacity Increase (mequiv/ g dry resin)	% P-H Bonds Oxidized
<u>Crotonaldehyde</u>				
methanol	R.T. ^a /60 h	2.9	0	0
methanol	Ref. ^b /24 h	3.0	2.12	70
methanol	Ref./24 h	5.5	1.86	62
methanol	Ref./24 h	15.9	1.23	41
<u>Triphenylphosphine Oxide</u>				
benzene	Ref./24 h	2.8	1.21	42
Cl-benzene ^c	Ref./24 h	1.7	0.62	21
Cl-benzene ^c	Ref./24 h	8.6	0.66	22
<u>Cinnamaldehyde</u>				
methanol	Ref./24 h	8.1	0.96	32
methanol	Ref./24 h	16.2	0.17	6
heptane	Ref./5.5 days	81.8	0	0
toluene	Ref./25 h	71.3	0	0

^aRoom Temperature

^bReflux

^cChlorobenzene

the solvent could be due to the fact that cinnamaldehyde is not soluble in heptane. On the other hand, the fact that no oxidation appears to occur in the presence of toluene suggests that cinnamaldehyde does not react with the resin. This suggests that in the presence of methanol, the solvent is responsible for the increase in the acid capacity. Basically, in order to have a better understanding of these types of reactions the liquid solution should be analyzed for the loss of reactant and formation of product.

Synthesis of the Macroreticular Copolymer Support

The divinylbenzene (DVB) crosslinked polystyrene polymer support is prepared by a suspension polymerization. The polymerization apparatus and the preparation of the aqueous phase are described in Chapter III, Copolymer Synthesis (p.68). In order to obtain a macroporous resin, the monomer solution must contain an inert organic diluent, around which polymerization occurs, and upon its removal leaves large pores. For the synthesis of the 5% MR resin, the organic phase consists of 13.54 g DVB (Dow Chemical Co.), 134.96 g styrene (Aldrich), 1.50 g benzoyl peroxide, and 150 g 4--methyl--2--pentanol. The polymerization and work up of the final copolymer beads is as described previously (Chpt.III, p.68) with the exception of a steam distillation in which the alcohol is removed, prior to the acid and water washes.

Phosphinic Acid Resin Synthesis

The synthesis of the phosphinic acid resin is basically the same as that outlined for the phosphonic acid resin (Chapter III, p.69), with

the exception that the starting copolymer is polystyrene/DVB instead of poly(vinylbenzyl chloride)/DVB. When a macroporous support is used the volume of PCl_3 is increased to 130 mL per 10 g copolymer.

Redox Reactions and Subsequent Resin Analysis

The reactions employ a 100 mL three-neck round bottom flask equipped with an overhead stirrer, a condenser, and a thermometer. The appropriate weight of resin and solid reactant is placed in the round bottom and 50 mL solvent added. With the liquid reagents (crotonaldehyde, tri-n-butylphosphate, cinnamaldehyde, and allyl alcohol), a 75 mL solution of the reagent and solvent of the appropriate concentration is prepared, and 50 mL is added to the resin sample in the reaction flask. For example, in order to obtain a 3:1 ratio of mequiv crotonaldehyde to mequiv P-H bonds, 50 mL of a 0.48 N solution of the reagent in methanol is added to a quantity of resin containing 8 mequiv P-H bonds. The reaction mixture is heated at the specified temperature for the desired amount of time. After cooling to room temperature, the resin is filtered from the solution, placed in a small vial with a Teflon lined cap, and washed a minimum of three times with 15 mL dioxane. A % solid weight and new acid capacity by a KOH/dioxane analysis are determined as outlined in Chapter III (pp.72 and 73).

APPENDIX B

PHOSPHINIC ACID RESIN AS AN ACID CATALYST IN ORGANIC REACTIONS

Discussion

The ability of the phosphinic acid resin to catalyze the esterification of ethanol and acetic acid has been investigated and compared with the performance of a sulfonic acid resin. Two sets of reactions were performed, one in which the resins were in their hydrated form and one in which the resins' waters of hydration had been removed by two rinses with dioxane followed by three rinses with ethanol. Since water is a product of the reaction, the removal of any excess water should result in a greater product yield. The reactions were set up in 25 mL and 50 mL ground glass Erlenmeyers equipped with a condenser and placed in an oil bath. Each reaction contained 20 mL of a solution, 11.5 N in acetic acid and 5.8 N in ethanol, and enough resin to provide 5 mequiv H^+ . The reactions were carried out at $45^\circ C$ for various periods of time. The % reaction was obtained by analyzing the solutions for the consumption of acetic acid by potentiometric titrations. The results of the study are presented in Figures 17 and 18 in terms of % reaction vs. reaction time.

The sulfonic acid resin has been used as a solid phase acid catalyst in many organic reactions but is limited to reaction temperatures of approximately $125^\circ C$.⁴ At higher temperatures deactivation of the resin begins to occur through the loss of SO_3 . Since deactivation of the phosphinic acid resin would involve the unfavorable formation of HPO_2 ,

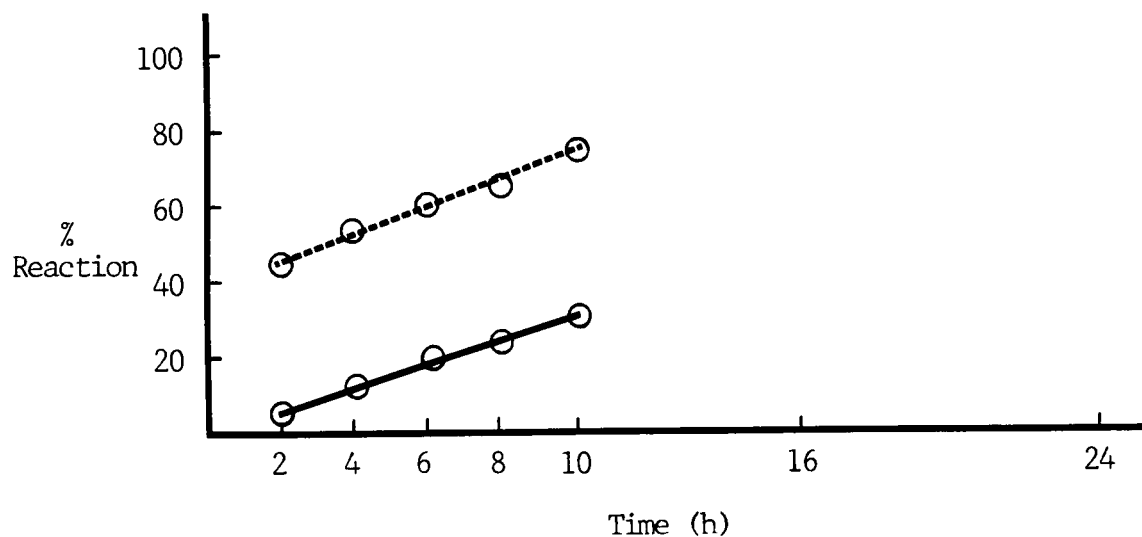


Figure 17. % Reaction vs. Reaction Time for the resins in their hydrated form. Sulfonic acid resin: ---- ; phosphinic acid resin: — .

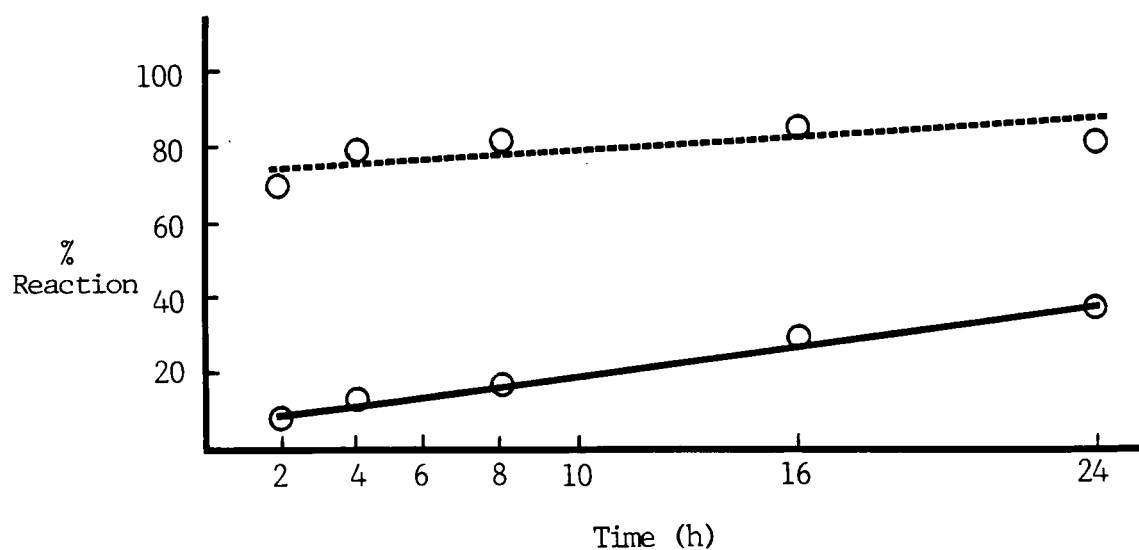


Figure 18. % Reaction vs. Reaction Time for the resins with the waters of hydration removed. Sulfonic acid resin: ---- ; phosphinic acid resin: — .

it is quite possible that the resin would remain stable and active at temperatures much higher than 125°C. The results from the above study indicate the ability of the resin to perform as a catalyst. Further studies with reactions requiring higher temperatures have not yet been investigated.

Sulfonic Acid Resin Synthesis

Ten grams of divinylbenzene crosslinked styrene gel copolymer beads are placed in a 250 mL three-neck round bottom flask equipped with an overhead stirrer, condenser, and thermometer. The beads are contacted with 21 g dichloroethane (a swelling solvent), 88.4 g concentrated H_2SO_4 , and 1.7 g H_2O . The reaction mixture is stirred at room temperature for 15 min, heated to 130°C over a period of 3 h, held at 130°C for 15 min, and then cooled to 110°C. The reaction is slowly quenched by the dropwise addition of 56.4 g H_2O with subsequent siphoning of the water from the reaction flask. This process is repeated until the reaction mixture maintains room temperature. At this point the resins are washed until neutral, placed in a glass frit, and conditioned with 1 L/h elutions of H_2O , 1 N NaOH, H_2O , 1 N HCl, and H_2O .

VITA

Marie Elizabeth Bates was born in Florence, Alabama on April 23, 1962. She attended elementary schools in Athens, Alabama and graduated in June 1980 from Gallatin Senior High School in Gallatin, Tennessee. After receiving her Bachelor of Science in Chemistry from the University of Tennessee in March 1985, she began study toward a Master of Science degree in polymer chemistry at the same university. This degree was awarded in March 1988.