To the Graduate Council:

I am submitting herewith a thesis written by David L. Wilson II entitled "Synthesis and Characterization of Novel Metal Ion Extractants." 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:

William T Buell

Richard Paegn

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 of Science 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 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 David L Wilson

Date 7-23-85

SYNTHESIS AND CHARACTERIZATION OF NOVEL METAL ION EXTRACTANTS

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

David L. Wilson II

August 1985

To mom, dad and my wife, Teresa, your love and sacrifice made this possible.

ACKNOWLEDGMENTS

In the course of this research, three people assisted me generously. In particular I am indebted to Professor S. D. Alexandratos (The University of Tennessee, Knoxville), as well as W. J. McDowell and G. N. Case (Chemistry Division, Oak Ridge National Laboratory) for their advice and encouragement.

ABSTRACT

Three methods for cation-exchange were investigated: ion-exchange resins, liquid/liquid extraction and polymer absorbed extractants (PAE). For ion-exchange resins, the cation-exchange capabilities of a novel bifunctional phosphinic acid resin were investigated for Zn(II), Sr(II), Na(I), K(I) and Eu(III) relative to sulfonic, carboxylic and phosphonic acid resins. The extent of extraction was measured as a function of the initial ratio (R_i) of the metal ions to the total acid capacity of the resin and the amount of acid sites which underwent ion-exchange (% loading). The phosphinic resin exhibited better selectivity than the sulfonic resin for all metals except those in Group IA. Also investigated were the kinetics of the extraction of $Zn(NO_3)_2$ at a $R_i = 1$ for the phosphinic, sulfonic and carboxylic resins. Phosphinic and sulfonic resins were found to have similar rates of zinc extraction if a macroreticular (MR) phosphinic resin was employed. The zinc loadings of the resins were also shown to be independent of the counter-ion (nitrate, chloride and sulfate), while sulfonic resins showed a substantial decrease in chloride and sulfate medium. The phosphinic resins were also found to operate by a redox mechanism with Hg(II), Ag(I) and Cu(II) but not with Fe(III). The loading of Au(III) with the phosphinic, sulfonic and carboxylic resins was also investigated.

The synthesis and purification problems of three di-C_8 phosphinic acid liquid extractants were investigated and an outline for the synthesis of five additional extractants is discussed.

The retention and extraction properties of PAEs impregnated with di(2-ethylhexyl) phosphoric acid (DEHP) were investigated as a function of bead type (gel and MR), pH, ionic strength and composition of the polymer matrix. The ion-exchange capabilities of PAEs were measured with zinc and compared to 1M DEHP/toluene solution.

PREFACE

"Then Moses led Israel onward from the Red Sea, and they went three days in the wilderness and found no water. When they came to Marah, they could not drink the water of Marah because it was bitter: therefore it was named Marah. And the people murmured against Moses saying 'What shall we drink?' and he cried to the LORD; and the LORD showed him a tree, and he threw it into the water, and the water became sweet."

Exodus 15:22

TABLE OF CONTENTS

CHAPTER PAGE

LIST OF TABLES

TABLE PAGE

PART II

TABLE PAGE

PART III

INTRODUCTION

The recovery of metals from an aqueous system via a cation exchange process can be accomplished by three methods: (1) Liquid/liquid extraction, (2) polymer absorbed extractants, and (3) cation-exchange resins. Each technique is unique in its utility and properties, as will be discussed below.

Liquid/liquid extraction is a binary system. The organic phase, which contains the extractant, is placed in contact with the aqueous phase. The two phases are agitated and once extraction is complete, the phases are allowed to separate. Fresh aqueous phase is introduced and the cycle repeated. The cycle continues until the extraction capabilities of the organic phase are exhausted. The advantages of such a system are as follows:

1. There are many types of liquid extractants ranging from neutral (tributyl phosphate) to the acidic [di(2-ethylhexyl) phosphoric acid].

2. Each type of extractant by virtue of its polarity has certain selective properties towards different types of metals. For example, tributyl phosphate is a well known extractant for actinides while di(2-ethylhexyl) phosphoric acid is a well known extractant for transition metals. However, liquid/liquid extraction has the one major disadvantage of extractant entrainment into the aqueous phase. This problem can result in the loss of extractant with time thus increasing the cost of the extraction process.

Polymer absorbed extractants, which entail the entrapment of extractant within a cross-linked polymer matrix, offer the same selective properties as liquid/liquid extraction but with the added advantage of placing the ion-exchange material in a column and eluting with the metal containing solution. However, the disadvantage of such a system is the loss of the extractant with time from the polymer matrix through solubility. The loss of the extractant decreases the ion-exchange capacity of the material and also increases the overall cost of the process.

The answer to the problem of extractant loss through entrainment and solubility is to covalently bind the ion-exchange site on a polymer support. The ion-exchange resin can be placed in a column and eluted with the metal containing solution. Unfortunately, the choice of commercially available ion-exchange resins is rather limited and those that are available often lack the selectivity and versatility of liquid/liquid extractants.

The purpose of this thesis is to investigate the three major areas of ion-exchange: ion-exchange resins (Part I), liquid/liquid extraction (Part II) and polymer absorbed extractants (Part III) with novel ideas for the selective and enhanced recovery of metals from aqueous systems.

PART I

DUAL MECHANISM BIFUNCTIONAL ION-EXCHANGE RESINS

CHAPTER I

INTRODUCTION

In 1848, Thompson reported that upon the treatment of soil with either ammonium sulfate or ammonium carbonate, most of the ammonia was absorbed and lime was released.[1] For the next 85 years, scientists explored the utility and limitations of the ion-exchange phenomenon in clays, soils and silicates.[2] In 1935, Adams and Holmes reported the first synthetic cation exchanger, a phenol-formaldehyde condensation resin.[3] This discovery led to one of the first commercially available synthetic ion-exchange resins, a phenol-based sulfonic acid exchanger.[4-6] This resin was made in bulk and had to be ground and sieved to give a particle of optimum size.[4-6] These resins, although an improvement over existing systems, e.g., clays, were reported to be of low capacity (2.2mequiv/g) and high attrition rates.[4-6]

In 1945, the discovery of the first styrenic sulfonic acid ion-exchange resin by D'Alelio led to the replacement of the phenolics.[7] These new resins were reported to be higher in capacity (5.0mequiv/g) and of much greater attrition resistance.[4-7] Since then, many improvements, applications and types of ion-exchange resins (Table I) have been discovered.[2,4-6] Today, ion-exchange resins have found use in such diverse areas as catalysis, sugar refinement and water treatment.[2,4-6]

TABLE I

TYPES OF COMMERCIALLY AVAILABLE CATION-EXCHANGE RESINS

Name	Manufacturer	Polymer Support	Acid Group	Capacity mequiv/g
Amberlite IR-120	Rohm & Haas	Styrene	Sulfonic	4.6
Amberlite IRC-50	Rohm & Haas	Acrylic	Carboxylic	10.2
Nalcite X-219[a]	Natl. Aluminate	Styrene	Phosphonic	8.8
PM-52[b]	Natl. Aluminate	Styrene	Phosphinic	4.5

[a]No longer available.

[b]Experimental resin, never marketed.

Our study centers on the development and systematic study of novel ion-exchange resins with emphasis on chemical stability and selectivity.

CHAPTER II

RESULTS AND DISCUSSION

Requirements for a Polymer Support

The requirements for a polymer support for an ion-exchange resin are rather strict: (1) The support must be resistant to degradation by acid, base and oxygen; (2) The support must have a high attrition resistance to maximize its life expectancy; (3) The resin should have high capacity to minimize the resin bed volume; (4) The resin should allow for rapid exchange kinetics.

Polystyrene was the polymer of choice for our study of ion-exchange resins. The advantages are: (1) Polystyrene is resistant to degradation under normal conditions; (2) Various aromatic substitution reactions give high capacity resins; (3) Styrene is an inexpensive industrial monomer.

Attrition Resistance vs. Diffusion Properties

To achieve high attrition resistance properties, polystyrene can be cross-linked with divinylbenzene (DVB). However, a highly cross-linked matrix has poor diffusion properties and therefore, a proper balance of attrition resistance and diffusion must be maintained. Kunin[2] and Wiley[8] have reported that the best results are obtained when 8-10% DVB cross-linked resins are used. This level of cross-linking offers good attrition resistance and good diffusion properties. Therefore, we chose 10% DVB cross-linked beads for comparative analyses.

Copolymerization

The copolymerization of styrene-DVB (SDVB) copolymer can be performed by bulk polymerization and suspension polymerization. Of the two types, bulk polymerization is the simplest to perform but is the most difficult to control due to the heat of polymerization which is generated. The problem becomes particularly acute at high viscosities where localized pockets of heat can lead to the degradation of the polymer or, in the most severe case, an explosion.[9] The product obtained is a cross-linked mass which must be ground and sieved to obtain a polymer of optimum size. Although uniform in size, the copolymer is not uniform in shape or surface area. As a result, the best that can be attained is an average shape and surface area.

Suspension polymerization, on the other hand, offers two major advantages over bulk: (1) better heat control and (2) better particle size control. The better heat control is due to the fact that the polymerization is carried out in water which absorbs and dissipates the excess heat. In addition, the size of the copolymer beads can be regulated by the experimental conditions. If done properly, the product obtained is uniformly shaped, spherical beads (0.5mm diameter) that are easily isolated, washed and dried.[9]

Two types of beads can be obtained by using suspension polymerization, gel and macroreticular (MR) beads. Gel beads have a smooth, continuous polymeric surface (surface area $<0.1 m^2/g$). MR beads on the other hand have a much greater surface area (100-$300 m^2/g$) due to the presence of pores within the bead (100-1000Å).[10]

Since suspension polymerization offers these advantages, it was chosen as the technique for the copolymerization of SDVB. For comparison, both types of beads (gel and MR) were investigated. Only the -20+40 mesh cut was utilized for this study.

Selectivity of Ion-Exchange Resins

One of the most important aspects of metal recovery today is the selective and quantitative removal of certain metals from aqueous industrial waste steams. For example, toxic metals such as mercury and lead in waste streams, must be removed to below 1ppm before being discharged.[11] Also, other valuable catalyst metals such as platinum and gold, need to be recovered with as much selectivity as possible in order to enhance the recovery process.

The selectivity of one ion over another in an ion-exchange process is controlled by a combination of electrostatic attractions and ionic hydration volume.[2,4-6] As a result, the ion-pair which has the largest free energy of formation will form to the greatest extent.[2,4-6]

Selectivity has also been found to be inversely proportional to the hydration volume of the resin-bound anion. The order of hydration volume is: sulfonic > phosphonic > carboxylic.[2,4-6] Theoretically, carboxylic resins should have the highest selectivity of all ion-exchange resins. However, carboxylic resins have a very high affinity for protons (7kcal/mole)[12] and as a result make poor extractants at an acidic pH.

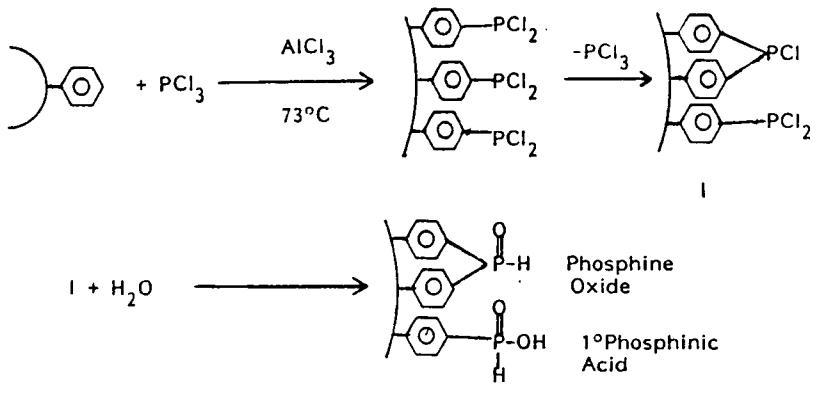
Sulfonic resins are very acidic (pK_a 2.8×10^{-3}) and can be applied at any pH (0-14), but show little selectivity due to their high

acidity.[2,4-6,13] The intermediate acid, phosphonic acid, also has a wide pH range of application, but being less acidic (pK_{a1} 1.83, pK_{a2} 7.07) is more selective.[2,4-6,14] With liquid extractants, phosphorus containing ligands have been shown to be highly selective towards transition metals, actinides and lanthanides.[15] Thus for our study, we concentrated on phosphorus containing ion-exchange resins. In order to make comparisons, sulfonic and carboxylic resins were studied as well.

Bifunctional Phosphine Oxide/Phosphinic Acid Ion-Exchange Resins

In liquid/liquid extraction, it has been reported that the combination of two ligands, a phosphine oxide and phosphinic acid resulted in the synergistic extraction of the metal into the organic phase to a greater extent than that of either extractant used alone.[16] An ion-exchange resin with similar functional groups would be expected to display a similar effect. The synthetic scheme for the synthesis of such a resin in outlined in Equation 1.

Equation 1:



If heat is applied during the course of the functionalization a disproportionation reaction occurs to give a chloro-diphenyl phosphine, which upon hydrolysis, becomes the diphenyl phosphine oxide. The disproportionation reaction, if not 100% would leave some of the dichloro-phenyl phosphine. This group upon hydrolysis, would yield the phosphinic acid. Therefore, by controlling experimental conditions, a bifunctional phosphine oxide/phosphinic acid ion-exchange resin could be obtained.

The literature precedents for such a reaction are as follows:

Equation 2:

$$2PhPCl_2 + AlCl_3 \longrightarrow Ph_2Cl + PCl_3 \qquad \text{(Ref. 17)}$$

Equation 3:

$$PhH + 3PCl_3 \xrightarrow{AlCl_3} \underset{59\%}{PhPCl_2} + \underset{40\%}{Ph_2Cl} \qquad \text{(Ref. 18)}$$

Equation 4:

$$ArH + PCl_3 \xrightarrow{AlCl_3} ArPCl_2 + Ar_2PCl \qquad \text{(Ref. 19)}$$

$$Ar_2PCl + H_2O \longrightarrow Ar_2\overset{O}{\overset{\|}{P}}\text{-H} \quad \text{If Ar is sterically hindered}$$

Based on these literature precedents, an experiment was performed and the beads analyzed. The results indicated a resin that was monoacidic that consisted of 60% phosphine oxide and 40% phosphinic acid (v.i.).

Hydrolytic Stability of the Phosphine Oxide

After functionalization and hydrolysis, the beads must be washed to remove the aluminum (from the catalyst) that was left inside the

beads. This process, known as conditioning, consisted of the elution of the resin with 1L/10g resin of the following solutions: water, 4wt% NaOH, water, 4wt% HCl and water. During the conditioning process, the evolution of hydrogen gas was observed during the contact with base. Subsequent analysis of the resin showed that in base, the phosphine oxide was oxidized to the phosphinic acid.

A titration curve of the resin showed that the resin was mono-acidic with no apparent difference in the acidities of the two acids present. With this information, we concluded that the phosphine oxide resin cannot be used in base and that the primary acid was stable in base and acid under the conditions employed. The conditioned resin consisted of two different acidic functions capable of ion-exchange and therefore we decided to investigate its ion-exchange properties.

Analysis of the Phosphinic Acid Resin

The following procedures were used to analyze the phosphinic acid resins:

1. The measurement of the cation exchange capacity (CEC) with 4wt% sodium nitrate. This was accomplished by placing 5g of resin in a column and eluting the resin with 1L of a 4wt% sodium nitrate solution at a rate of 1L/h. The effluent was collected, an aliquot taken and titrated with base for the protons of the resin which underwent ion-exchange.

2. The measurement of the total acid capacity with base (TAC). TAC was measured by contacting the resin (1g) with excess base and back titrating a 50mL aliquot with acid.

3. The measurement of the elemental phosphorus content (EPC). EPC was measured by the digestion of 0.02g of resin in perchloric acid and analyzing the solution spectrometrically.

4. The measurement of the primary acid concentration (PAC). PAC was measured by the oxidation/reduction reaction with iodine and the primary acid (Equation 5). The resin (0.5g) was contacted with excess iodine followed by a back titration with thiosulfate. Table II outlines the typical analyses obtained with the phosphinic acid resins.

Equation 5:

TABLE II

PHOSPHINIC ACID RESIN PROPERTIES

Run Number[a] DW-01-	Type	Cross-Link Level %DVB	CEC[b]	TAC[b]	PAC[b]	EPC[b]	% Solids[c]
242A	Gel	2	1.89	5.39	1.57	5.48	43.8
242B	Gel	10	1.02	3.39	1.92	3.08	73.8
204E	Gel	15	0.75	2.97	1.51	3.05	75.9
204A	MR	2	1.25	4.72	2.00	4.89	44.1
204C	MR	10	1.18	4.68	2.16	4.76	31.8
204D	MR	15	1.03	3.95	1.97	4.18	32.5

[a]Run number code: DW = David Wilson; -01 = book number; -242 = page number; A = reaction.

[b]All measurements are expressed in mequiv/g.

[c]% Solids is the ratio of the dry weight of the resin to the wet weight.

If the resin were pure 1° acid, the TAC, PAC and EPC would be equal; given that they are not, bifunctionality must exist.

Along with the conclusion that bifunctionality does exist, three additional conclusions can be drawn: (1) Gel resins show a decrease in capacity and water content with increased cross-linking; (2) MR resins show only a minor effect of cross-link level on the capacity and water content; and (3) MR resins at a higher cross-link level have a higher water content than gel resins.

Theoretical Capacities of Bifunctional Phosphinic Acid Resins

To better understand the composition of the bifunctional phosphinic resin, calculations of theoretical capacities were made with the following assumptions:

1. A phenyl ring can have only one phosphorus bonded to it.

2. The DVB used was of technical grade consisting of 55.4% DVB and 44.6% ethyl vinyl benzene (EVB). Assume that both, DVB and EVB are inert to functionalization.

3. The functionalization goes to 100% completion. With these assumptions, the following calculations were performed.

Moles of Acid

(moles of styrene)(mole fraction of 1°) = moles of 1° Acid

(moles of styrene)(mole fraction of 2° Acid)/2 = moles of 2° Acid

Weights of Acid

(mole of 1° Acid) (M.W. 1° Acid) = g 1° Acid

(Mole of 2° Acid) (M.W. 2° Acid) = g 2° Acid

(g 1° Acid) + (g 2° Acid) + (g DVB) + (g EVB) = Total Weight

Weight Fraction of Acids

(g 1° Acid)/Total Weight = wt fraction 1° Acid = X

(g 2° Acid)/Total Weight = wt fraction 2° Acid = Y

Average Molecular Weight

(wt fraction 1° Acid) (M.W. 1° Acid)

+ (wt fraction 2° Acid) (M.W. 2° Acid)

= Average Molecular Weight

Capacity of Resin

1g of resin would contain X g of 1° Acid and Y g of 2° Acid

((X + Y)/Average M.W.) (1000) = Capacity (mequiv/g)

Table III outlines the theoretical capacities obtained with these assumptions and calculations.

TABLE III

CALCULATED THEORETICAL CAPACITIES FOR THE MODEL BIFUNCTIONAL PHOSPHINIC ACID RESIN BASED ON 100% REACTION

% 1° Acid	% 2° Acid	2% DVB Capacity mequiv/g	10% DVB Capacity mequiv/g
100	0	5.81	5.23
80	20	5.18	4.63
60	40	4.66	4.15
50	50	4.44	3.94
40	60	4.24	3.76
20	80	3.89	3.44
0	100	3.60	3.16

Table IV compares some of the resins we have synthezied to the calculated model values.

TABLE IV

COMPARISON OF EXPERIMENTAL PHOSPHINIC ACID CAPACITIES TO MODEL CALCULATIONS

Resin Number	Type	Cross-Link Level %DVB	% 1° Acid	% 2° Acid	Exp. Cap. mequiv/g	Cal. Cap. mequiv/g
DW-01-164A	Gel	2	37	63	4.97	4.14
DW-02-050A	Gel	2	38	62	5.10	4.17
DW-02-050B	Gel	2	40	60	5.07	4.24
DW-01-264B	Gel	10	46	54	3.90	3.88
DW-02-050C	Gel	10	60	40	3.53	4.15
DW-02-068C	Gel	10	55	45	3.54	4.04
DW-01-204A	MR	2	43	57	4.72	4.30
DW-01-204C	MR	10	46	54	4.68	3.87

From the data in Table IV, we can conclude that the 2% DVB gels and MR resins have more than one phosphorus atom bonded to some of the phenyl rings. In addition, the 10% DVB gels do not go to 100% functionalization.

Phosphonic Acid Resin Synthesis

An additional phosphorus containing resin was synthesized by the oxidation of the 1° acid sites of the phosphinic resin with 20% H_2O_2. The resin, a bifunctional phosphonic/phosphinic acid resin, was titrated and found to be diacidic with the first proton of the phosphonic acid being equivalent in acid strength to the proton of the remaining 2° phosphinic acid. Table V outlines the results obtained with the peroxide oxidation of the phosphinic acid resin.

As can be seen from the data in Table V, the resin does contain secondary sites since the TAC is not twice the EPC. Other

TABLE V

PROPERTIES OF PHOSPHONIC ACID GEL ION-EXCHANGE RESINS

Resin Number	Cross-Link Level %DVB	TAC mequiv/g	EPC mequiv/g	% Solids
DW-02-051A	2	7.04	4.54	41.1
DW-02-051B	10	5.66	3.25	60.9

experiments involving the oxidation of the phosphinic resin with peroxide will be discussed later in Part I.

Sulfonic Acid Ion-Exchange Resins

The sulfonic acid ion-exchange resin was made by the electrophilic aromatic substitution reaction of polystyrene and concentrated sulfuric acid. Table VI outlines the most common types of commercially available sulfonic resins in comparison to those we synthesized.

TABLE VI

SULFONIC ACID ION-EXCHANGE RESINS PROPERTIES

Resin Number	Type	Cross-Link Level %DVB	TAC mequiv/g	CEC mequiv/g	% Solids
DW-01-31D	Gel	2	5.00	5.00	17.3
DW-01-31A	Gel	10	4.76	4.90	50.8
DW-01-31B	Gel	15	3.16	3.11	59.6
DW-01-31C	Gel	30	0.30	0.28	79.2
DW-02-148	MR	10	4.81	----	23.9
Amberlite IR-120A	Gel	8	4.6	----	48
Duolite C-20	Gel	8	4.6	----	----
Dowex 50-8	Gel	8	4.6	----	48

From the data in Table VI, three conclusions can be drawn: (1) The higher cross-linked gel beads are lower in capacity; (2) The higher cross-linked gel beads are lower in water content; (3) The MR resins are similar in capacity to the gel beads but have a much greater water content.

Carboxylic Ion-Exchange Resins

The most common commercially available carboxylic resins are made by the copolymerization of acrylic acid with DVB.[2,4] Our interest with carboxylic resins is with one containing a poly(vinyl benzoic acid) unit because of our interest with styrenic supported ion-exchange groups. To make such a resin, we developed a synthesis which involved the oxidation of poly(vinyl benzyl chloride) with concentrated nitric acid. The synthesis gave a resin of very high capacity but also nitrated 58% of the rings. A titration curve of the resin showed it to be monoacidic with no difference between the two types of acid present, poly(vinyl benzoic acid) and poly(vinyl nitro-benzoic acid). Table VII outlines the results obtained with different cross-linked beads.

As was observed with the phosphinic and sulfonic resins, the capacity and water content of the carboxylic resin is dependent on the cross-link level of the bead. In addition, the MR resins do absorb significantly more water than the gel resins.

Ion-Exchange: Definition of Terms

The experiments, with exception of the CEC, were carried out with the aid of gamma emitting radioactive isotopes of the metal being

TABLE VII

POLY(VINYL BENZOIC ACID) RESIN PROPERTIES

Run Number	Type	Cross-Link Level %DVB	TAC mequiv/g	% Solids
DW-01-083				
B	MR	5	5.25	22.7
C	MR	10	4.83	26.3
D	MR	15	4.03	30.2
DW-01-091				
A	Gel	2	6.55	11.3
B	Gel	5	5.73	35.3
C	Gel	10	5.51	53.9
D	Gel	15	5.33	60.0

studied (see experimental section for list of isotopes). Every sample tested for a given series of experiments contained the same amount of radiotracer. After a specific period of time, depending on the experiment, 1mL of aqueous solution was removed and counted. All results for each series of experiments were based on an aqueous blank count which contained an identical concentration of solution and tracer, but without the resin being present.

The initial ratio (R_i) is the ratio of the mequiv of metal present initially to the mequiv of acid sites present.

The % loading is the percent of acid sites occupied on the ion-exchange resin for a given R_i. Examples:

At a R_i of 0.1, the maximum % loading attainable is 10%.

At a R_i of 1.0, the maximum % loading attainable is 100%.

As was observed in Tables II (p. 12), VI and VII, the MR resins absorb significantly more water than do gel resins. During extraction experiments, the metal can be absorbed into the pores without being ion-exchanged. As a result, the MR resins have an artificially high level of absorption requiring that an MR dilution factor be taken into account when reporting % loadings. All MR ion-exchange data to be reported will include the MR dilution correction factor (see experimental section for calculations).

Ion-Exchange with Alkali Metals: Sodium and Potassium

Table VIII compares the CEC data of the phosphinic, phosphonic, sulfonic and carboxylic resins.

The sulfonic resins appear to have the highest loadings of sodium. In addition, there is no cross-link level dependence on the CEC of the sulfonic resin. Phosphinic and phosphonic resins have similar loadings of sodium if the less acidic second proton of the phosphonic resin is discounted. Carboxylic resins have the lowest loadings of sodium, due to the fact that the carboxylic resins are not very acidic.

Tables IX and X compare the ion-exchange capabilities of the resins in a 1:1 potassium/sodium solution and with different R_i of potassium in a 4M $NaNO_3$ background.

At a 1:1 molar ratio of potassium/sodium, the phosphinic and sulfonic resins show a greater affinity towards potassium. However, if a large excess of sodium is present, the loadings of potassium are greatly reduced for all ion-exchange resins. Based on the data in

TABLE VIII

COMPARISON OF CEC OF THE ION-EXCHANGE RESINS FOR 4wt% $NaNO_3$

Type	Cross-Link Level %DVB	TAC mequiv/g	CEC mequiv/g	% Loading
Phosphinic[a]	2	4.92	1.70	34
	10	3.90	1.30	33
	15	2.99	0.79	26
Phosphonic[b]	2	7.04	1.98	28
	10	5.66	1.30	23
Sulfonic[c]	2	5.00	5.00	100
	10	4.80	4.90	100
	15	3.11	3.16	100
	30	0.28	0.30	100
Carboxylic[d]	5	5.25	0.81	15
	10	4.83	0.54	11
	15	4.03	0.34	8

[a]Run number DW-01-264.

[b]Run number DW-02-051.

[c]Run number DW-01-031.

[d]Run number DW-01-083.

TABLE IX

THE LOADINGS OF POTASSIUM AND SODIUM FROM A 1:1 MOLAR POTASSIUM/SODIUM SOLUTION[a]

Type[b]	Cross-Link Level %DVB	TAC mequiv/g	% K^+ Loading[c]	% Na^+ Loading
Phosphinic	2	4.93	22	0
	10	3.37	12	7
Sulfonic	10	3.57	83	17

[a]Solution used was 2N KNO_3 and 2N $NaNO_3$.

[b]Run number DW-01-213.

[c]% Loadings ±3%.

TABLE X

THE LOADINGS OF POTASSIUM AT DIFFERENT R_i WITH A 4M $NaNO_3$ BACKGROUND[a]

Type[b]	Cross-Link Level %DVB	TAC mequiv/g	% Load.[b] R_i = 0.1	% Load. R_i = 1	% Load. R_i = 1.5
Phosphinic	2	4.93	0.7	6	14
	10	3.37	0.1	4	3
Sulfonic	10	3.57	1	13	18
Carboxylic	10	5.00	0.6	6	10

[a]Run number DW-01-212.

[b]% Loadings ±3%.

Tables VIII-X, the sulfonic resin has the highest affinity for the alkali metals sodium and potassium, with the highest affinity for potassium.

Ion-Exchange with a Transition Metal: Zinc

The loading characteristics with Zn(II) of the sulfonic, carboxylic, phosphonic and phosphinic resins were measured as a function of cross-link level in a 4M $NaNO_3$ background. The results are outlined in Tables XI-XIII.

Sulfonic and carboxylic resins show a strong dependency on the amount of zinc extracted as a function of the cross-link level. Sulfonic resins show a 17% decrease (R_i = 1) in a five-fold increase in the cross-link level (2% to 10% DVB). Likewise, the carboxylic resins lose half of their loading capacity by increasing the cross-link level by a factor of two (R_i = 1, 5% to 10% DVB). Phosphonic resins show only a 5% loss (R_i = 1) for an increase by a factor of five in the cross-linking. Phosphinic resins, on the other hand, lose no significant amount of zinc at a R_i = 1 for the 2, 10 and 15% DVB resins. This is a major advantage for the phosphinic resins since a seven-fold increase in the cross-link level had no significant effect on the loading of the resin. Therefore, better attrition resistance can be obtained at the higher cross-link level with no effect on the loading of the resin.

Table XIV compares the loading capabilities of the 10% DVB ion-exchange resin at different R_i of zinc nitrate. The sulfonic resin, being more acidic, extracted more zinc from water than any resin tested (72%, R_i = 1). The phosphinic resin extracted 8% more zinc

TABLE XI

ZINC LOADINGS AS A FUNCTION OF CROSS-LINK LEVEL FOR GEL SULFONIC ACID ION-EXCHANGE RESINS WITH A 4M $NaNO_3$ BACKGROUND[a]

Cross-Link Level % DVB	TAC mequiv/g	% Load.[b] R_i = 0.1	% Load. R_i = 1	% Load. R_i = 1.5
2	5.00	4	41	58
10	4.75	2	24	29
15	3.16	2	18	22
30	0.30	1	5	7

[a]Run number DW-01-031.

[b]% Loadings ±3%.

TABLE XII

ZINC LOADINGS AS A FUNCTION OF CROSS-LINK LEVEL FOR MR CARBOXYLIC ACID ION-EXCHANGE RESINS WITH 4M $NaNO_3$ BACKGROUND[a]

Cross-Link Level % DVB	TAC mequiv/g	% Load.[b] R_i = 0.1	% Load. R_i = 1	% Load. R_i = 1.5
5	5.25	2	16	24
10	4.83	1	7	12
15	4.03	1	7	7
10(gel)[c]	5.00	1	4	5

[a]Run number DW-01-084.

[b]% Loadings ±3%.

[c]Run number DW-01-164.

TABLE XIII

ZINC LOADINGS AS A FUNCTION OF CROSS-LINK LEVEL FOR PHOSPHONIC AND PHOSPHINIC ACID ION-EXCHANGE RESINS WITH A 4M $NaNO_3$ BACKGROUND

Cross-Link Level % DVB	TAC mequiv/g	% Load.[a] R_i = 0.1	% Load. R_i = 1	% Load. R_i = 1.5
Phosphonic[b]				
2	7.04	3	21	27
10	5.66	3	16	22
Phosphinic[c]				
2	4.93	6	27	37
10	3.37	6	25	35
15[d]	1.85	5	24	29

[a] % Loadings ±3%.

[b] Run number DW-01-052.

[c] Run number DW-01-166.

[d] Run number DW-01-085.

TABLE XIV

THE LOADINGS OF 10% DVB GEL ION-EXCHANGE RESINS WITH ZINC NITRATE AT DIFFERENT R_i

Type	TAC mequiv/g	% Load.[a] R_i = .1	% Load. R_i = .3	% Load. R_i = .5	% Load. R_i = .7	% Load. R_i = 1	% Load. R_i = 1.3	% Load. R_i = 1.5
Phosphinic[b]	3.39	9	16	22	24	35	---	40
Phosphonic[c]	5.66	8	13	16	17	22	26	28
Sulfonic[b]	5.00	9	30	50	62	72	---	82
Carboxylic[b]	5.72	1	2	3	3	3	--	5
With 4M $NaNO_3$[c]								
Phosphinic[d]	3.37	6	13	17	19	25	---	35
Phosphinic[c]	5.66	3	7	13	15	21	25	27
Sulfonic[d]	3.57	2	5	11	12	17	22	25
Carboxylic[d]	5.00	0.4	2	3	4	4	5	5

[a] % Loading ±3%.

[b] Run number DW-02-12.

[c] Run number DW-02-52.

[d] Run number DW-01-164.

than the phosphonic resin. The carboxylic resin did not perform well, only extracting 3% of the zinc at a $R_i = 1$.

To test the selectivity of the resins, the experiment was repeated but in a 4M $NaNO_3$ background. The addition of sodium nitrate, decreased the loading of zinc by the sulfonic resin by 55% ($R_i = 1$), while the phosphinic and phosphonic resin decreased only slightly (10% and 1% respectively, $R_i = 1$). The carboxylic resin did not extract enough zinc to make any general conclusions.

In addition to investigating the loadings of zinc nitrate by the resins at different R_i, the loadings of zinc chloride and zinc sulfate were measured as well (Table XV). In the chloride case, the sulfonic resin extracted 72% of the zinc ($R_i = 1$), while the phosphinic resin extracted 32% ($R_i = 1$). However, as was observed with zinc nitrate, the zinc loadings of the sulfonic resin were greatly decreased with the addition of sodium, while only slightly affecting the phosphinic resin (68% and 14% decrease respectively, $R_i = 1$).

A similar trend was observed for zinc sulfate. In water, the sulfonic resin loaded 67% of the zinc ($R_i = 1$) vs. 27% for the phosphinic resin. The addition of sodium caused a decrease of 62% loading of zinc for the sulfonic resin, but no decrease in loading was observed for the phosphinic resin ($R_i = 1$).

The loadings of the carboxylic resin with zinc chloride and zinc sulfate, as before, were too low to make any general conclusions.

From the data in Tables XIV and XV, four general conclusions can be drawn for the extraction of zinc with the ion-exchange resins:

TABLE XV

THE LOADINGS OF 10% DVB GEL ION-EXCHANGE RESINS WITH ZINC CHLORIDE AND ZINC SULFATE AT DIFFERENT R_i

Type	TAC mequiv/g	% Load.[a] R_i = .1	% Load. R_i = .3	% Load. R_i = .5	% Load. R_i = .7	% Load. R_i = 1	% Load. R_i = 1.3	% Load. R_i = 1.5
$ZnCl_2$								
Phosphinic[b]	3.54	9	19	24	29	32	36	39
Sulfonic[c]	5.04	10	--	48	--	72	--	79
Carboxylic[c]	5.43	1	--	5	--	11	--	17
With 4M NaCl								
Phosphinic[b]	3.54	3	7	10	13	18	23	27
Sulfonic[d]	3.57	1	--	--	--	4	--	7
Carboxylic[d]	5.00	0.9	--	--	--	5	--	10
$ZnSO_4$								
Phosphinic[b]	3.54	9	19	20	24	27	28	33
Sulfonic[c]	5.00	10	--	48	--	67	--	74
Carboxylic[c]	5.72	1	--	5	--	11	--	15
With 4N Na_2SO_4								
Phosphinic[b]	3.54	6	14	20	24	27	28	33
Sulfonic[d]	3.57	0.6	--	--	--	5	--	7
Carboxylic[d]	5.00	0.1	--	--	--	1	--	1

[a] % Loadings ±3%.

[b] Run number DW-02-128.

[c] Run number DW-02-207.

[d] Run number DW-01-174.

1. For all cases investigated, the nitrate system gave the highest overall loadings of zinc.

2. For the extraction of zinc from aqueous solution, the sulfonic resin was superior.

3. The addition of sodium decreased substantially the amount of zinc loaded by the sulfonic resin, while not affecting the loadings of the phosphinic resin to any large degree.

4. The changing of the zinc counter-ion had little effect in water. The addition of sodium chloride or sodium sulfate did decrease the loadings of the sulfonic resin with respect to the nitrate. The phosphinic resin on the other hand, was not affected to any great extent. Since the phosphinic resin loaded approximately the same amount of zinc in water and 4M $NaNO_3$, it does exhibit some selectivity towards divalent zinc with respect to monovalent sodium.

Kinetics of the Extraction with Zinc Nitrate

Phosphinic resins, unlike sulfonic and carboxylic resins, have no dependency on the cross-link level for zinc loading (Table XIII). As a result, it was postulated that a highly cross-linked phosphinic resin with better attrition resistance properties would have similar extraction properties relative to a low cross-linked resin. In addition, it was shown that the phosphinic resin was more selective towards zinc than to sodium relative to the sulfonic resin. However, both of these advantages could be negated by very slow rates of metal ion extraction. To measure the time required to achieve equilibrium with Zn(II), two sets of experiments were performed on the phosphinic, sulfonic

and carboxylic resins: (1) Zinc in water and (2) zinc in 4M $NaNO_3$. The results of the kinetic study are outlined in Table XVI.

From the data in Table XVI, three conclusions can be drawn:

1. In both sets of experiments (with and without sodium), the sulfonic resin attained equilibrium faster than both phosphinic resins (2 and 10% DVB).
2. The 2% DVB phosphinic resin attained equilibrium slightly faster than the 10% DVB resin in both water and sodium nitrate.
3. The addition of sodium slowed the kinetics slightly of both phosphinic acids (2 and 10% DVB), but had no effect on the sulfonic resin.

The carboxylic resins did not load enough zinc to make any general conclusions about the kinetics of extraction.

To see if the kinetics of the phosphinic acid resin could be improved, the same experiment was repeated with the MR beads. For comparison, MR sulfonic resins were analyzed as well. Table XVII outlines the kinetic results obtained with the MR sulfonic and phosphinic resins.

The results in Table XVII indicate that in both cases (with and without sodium), the MR phosphinic resin had a much improved equilibrium time (5min) over the gel resin (Table XVI). The sulfonic resin on the other hand, showed no improvement in equilibrium time in comparison to the gel resin. In addition, the MR phosphinic and sulfonic resin both attained equilibrium at the same time. Therefore, by using

TABLE XVI

THE KINETICS OF THE EXTRACTION OF ZINC NITRATE AT A $R_i = 1$

Type	TAC mequiv/g	% Load.[a] 5min	% Load. 10min	% Load. 15min	% Load. 30min	% Load. 45min	% Load. 1h	% Load. 2h	% Load. 3h
Water[b]									
Phosphinic									
2% DVB	4.90	16	21	27	29	30	31	32	31
10% DVB	3.54	14	22	25	26	30	30	30	30
Sulfonic									
10% DVB	5.04	70	72	72	--	73	72	71	72
Carboxylic									
10% DVB	5.43	5	4	4	5	5	5	4	6
With 4M $NaNO_3$									
Phosphinic									
2% DVB	4.93	17	15	20	24	26	28	29	29
10% DVB	3.37	12	13	13	14	17	23	26	26
Sulfonic									
10% DVB	3.57	17	17	17	19	19	19	19	19
Carboxylic									
10% DVB	5.00	2	2	3	3	3	4	5	5

[a] Loadings ±3%.

[b] Run number DW-02-196.

[c] Run number DW-01-172.

TABLE XVII

THE KINETICS OF THE EXTRACTION OF ZINC NITRATE AT R_i = 1 WITH 10% CROSS-LINKED PHOSPHINIC AND SULFONIC MR[i] ION-EXCHANGE RESINS

Type	TAC mequiv/g	% Load.[a] 1min	% Load. 5min	% Load. 10min	% Load. 15min	% Load. 1h
Phosphinic[b]	4.68	19	29	26	28	30
Sulfonic[c]	4.81	47	72	79	78	79
With 4M $NaNO_3$						
Phosphinic[d]	4.68	19	27	28	28	28
Sulfonic[e]	4.81	21	27	27	28	27

[a] % Loadings ±3%.

[b] Run number DW-02-197.

[c] Run number DW-02-198.

[d] Run number DW-02-127.

[e] Run number DW-02-166.

a MR phosphinic resin, one can attain similar kinetics as found with the sulfonic acid resin.

The Loading of an Alkaline Earth: Strontium

Table XVIII outlines the loadings of the ion-exchange resins with strontium nitrate at different R_i. As was observed with zinc nitrate (Table XIV, p. 25), the sulfonic resin had the highest loading of Sr(II) in water (79%, R_i = 1) and the addition of 4M $NaNO_3$ resulted in a substantial decrease of the loadings of Sr(II) by the sulfonic resin (53% decrease, R_i = 1). In this case, its loadings were higher than

TABLE XVIII

THE LOADINGS OF GEL ION-EXCHANGE RESINS WITH $Sr(NO_3)_2$[a]

Type	Cross-Link Level %DVB	TAC mequiv/g	% Load.[a] R_i = .1	% Load. R_i = .3	% Load. R_i = .5	% Load. R_i = .7	% Load. R_i = 1	% Load. R_i = 1.3	% Load. R_i = 1.5
Phosphinic	2	4.57	8	14	17	19	20	23	26
Phosphinic	10	3.39	8	12	13	16	17	17	19
Phosphonic	10	5.66	6	--	--	--	14	--	17
Sulfonic	10	5.00	10	30	49	66	79	82	88
Carboxylic	10	5.43	2	--	--	--	8	--	10
With 4M $NaNO_3$									
Phosphinic	2	4.85	2	7	9	13	18	24	29
Phosphinic	10	3.39	2	5	9	10	14	16	19
Phosphonic	10	5.66	0.6	--	--	--	4	--	10
Sulfonic	10	5.04	3	8	12	17	26	36	37
Carboxylic	10	5.43	0.5	--	--	--	5	--	7

[a]Run number DW-02-222.

[b]All loadings reported are ±3%.

those of the phosphinic resin (12% higher, $R_i = 1$). The phosphinic resins loadings of Sr(II) were lower than those of zinc and a loading dependency of strontium was observed as a function of the cross-link level. However, the addition of sodium had only a marginal effect on the loadings of the phosphinic resins. Again, as was observed with zinc, the phosphinic resin displayed some selectivity towards a divalent cation over sodium in comparison to the sulfonic resin.

The loadings of the phosphonic resin with Sr(II) were lower than the phosphinic resin in water and 4M $NaNO_3$. The loading difference between the resins was more pronounced with the addition of sodium, the phosphinic resin loading 10% more Sr(II) at a $R_i = 1$. The carboxylic resin, as in the case of zinc, did not extract enough Sr(II) to make any general conclusions.

The Extraction of Tracer Amounts of a Lanthanide: Europium

For tracer quantities, the concentration of the metal in solution is approximately 1ppm. At this low of a concentration, % loading of the resin is difficult to quantify accurately. Therefore, for this analysis, the distribution coefficient (D) will be employed for the discussion and comparison of the data. D is the ratio of the equilibrium concentration of the metal in the resin/g dry resin to the equilibrium concentration of the metal per milliliter of the aqueous phase. Table XIX outlines the extraction of trace amounts of Eu(III) in a 4M $NaNO_3$ background in terms of % Eu(III) absorbed and D.

TABLE XIX

THE DISTRIBUTION COEFFICIENTS FOR THE EXTRACTION OF EUROPIUM NITRATE BY THE ION-EXCHANGE RESINS WITH A 4M $NaNO_3$ BACKGROUND[a]

Type	Cross-Link Level %DVB	TAC mequiv/g	% Eu(III)[b] Absorbed	D
Phosphinic	2	4.91	98.0	95
Phosphinic	10	3.54	98.9	153
Phosphinic (MR)	10	4.68	99.7	1250
Sulfonic	10	5.04	29.1	0.9
Sulfonic (MR)	10	4.82	29.1	1.7
Carboxylic	10	5.43	40.0	1.3

[a]Run number DW-02-227.

[b]% Eu(III) Absorbed ±3%.

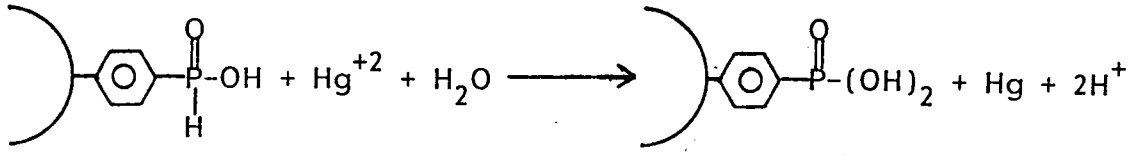
The data in Table XIX show that the phosphinic resins have a very high affinity for Eu(III) even in trace amounts with high sodium background concentrations. The sulfonic resins, on the other hand, have a much lower affinity for Eu(III) as do the carboxylic resins.

Reductive Properties of Primary Phosphinic Acid: Introduction

During the study of another transition metal, Hg(II), it was observed that upon contact with mercuric nitrate, the phosphinic resin turned gray. It was also observed that if the resin was allowed to sit for several days following contact, metallic mercury pooled in the bottom of the bottle. Upon further investigation, it was found that the resin acid capacity had increased from 5.00 to 7.00mequiv/g. What had been discovered was a bifunctional dual mechanism ion-exchange/ redox polymer.

The redox reaction which occurred (Equation 6) had been observed with dialkyl phosphonates ($(RO)_2P(O)H$),[20] but had never been observed for phosphinic acids. To some extent, we had suspected that the 1° acid site could be used for a redox reaction (recall the iodine reduction, Equation 5). The reduction potentials for mercury(II) and iodine along with the oxidation potential for hypophosphorus acid are outlined in Equation 7. Based on these initial results with mercury, we undertook a comprehensive study of the redox properties of primary phosphinic acid resin with transition metals.

Equation 6:



Equation 7:

(a) $Hg^{+2} + 2e^- \longrightarrow Hg^0$ $E° = +0.851$

(b) $I_2 + 2e^- \longrightarrow 2I^-$ $E° = +0.535$

(c) $H_3PO_2 + H_2O \longrightarrow H_3PO_3 + 2H^+ + 2e^-$ $E° = +0.500$

Redox Properties of the Primary Phosphinic Acid with Mercury

The loadings of mercuric nitrate as a function of R_i are listed in Table XX for the phosphinic, phosphonic, sulfonic and carboxylic resins. The loadings of the mercury by the phosphinic resins exceed 100%. At even larger R_i (Table XXI), they exceed 200%. These seemingly impossible loadings are due to the combination of the redox

TABLE XX

THE LOADINGS OF THE ION-EXCHANGE RESINS WITH MERCURIC NITRATE AT DIFFERENT R_i

Type	TAC mequiv/g	% Load.[a] R_i = .1	% Load. R_i = .3	% Load. R_i = .5	% Load. R_i = .7	% Load. R_i = 1	% Load. R_i = 1.3	% Load. R_i = 1.5	
Phosphinic[b]									
2% DVB	5.10	10	30	50	70	90	100	126	136
10% DVB	3.53	10	30	50	70	90	99	123	132
Sulfonic[b]									
10% DVB	5.00	10	30	48	64	75	80	84	87
Carboxylic[c]									
10% DVB	5.43	6	--	--	--	--	31	--	45
Phosphinic[d]									
2% DVB	7.04	10	28	44	54	61	64	72	75
10% DVB	5.66	10	29	45	57	62	67	72	75
With 4M $NaNO_3$									
Phosphinic									
2% DVB[b]	5.10	10	30	50	57	62	69	82	91
10% DVB[e]	3.90	10	30	50	52	64	68	81	93
Sulfonic[b]									
10% DVB	5.00	3	8	13	18	23	26	32	37
Carboxylic[f]									
10% DVB	5.00	4	5	8	13	14	17	--	--
Phosphonic[d]									
2% DVB	7.04	8	21	34	44	51	53	62	69
10% DVB	5.66	9	23	33	42	50	52	65	67

[a] % Loadings ±3%.

[b] Run number DW-02-062: Maximum % Loading: 2% DVB 220%, 10% DVB 280%.

[c] Run number DW-02-207.

[d] Run number DW-02-054.

[e] Run number DW-01-276: Maximum % Loading: 240%.

[f] Run number DW-01-217.

TABLE XXI

THE LOADINGS OF THE PHOSPHINIC RESINS AT A R_i GREATER THAN 1.5[a]

Type	TAC mequiv/g	Maximum % Loading	% Load.[b] R_i = 2.0	% Load. R_i = 3.0	% Load. R_i = 4.0	% Load. R_i = 4.5
2% DVB	5.02	220	161	182	194	202
10% DVB	3.54	265	151	160	175	---
With 4M $NaNO_3$						
10% DVB	3.54	265	110	131	146	---

[a]Run number DW-02-123.

[b]% Loadings ±3%.

and ion-exchange mechanisms. If the mercury undergoes reduction, then a new acidic site is generated (Equation 6), which in turn can undergo ion-exchange. This cumulative effect can greatly increase the apparent loadings of the resin. For example, a phosphinic resin with a TAC of 5.0 and a PAC of 2.0 can extract 11.0mequiv/g of mercury for a loading of 220% (7.0mequiv/g ion-exchange, 4.0mequiv/g redox). The 2% DVB gel resin in Tables XX and XXI, has a total of 10.9mequiv/g of ion-exchange and redox capacity. Therefore, the maximum loading attainable would be approximately 220%. For the sake of comparison to the other resins which do not undergo redox (sulfonic, carboxylic and phosphonic), the % loading terminology shall still be employed but each table will include the maximum % loading attainable for the phosphinic resin examined.

The extraction capabilities of both low and high cross-linked phosphinic resins are similar and superior to those of the sulfonic

resin in aqueous solutions (with and without sodium background). Both phosphonic resins had identical loadings and loaded less Hg(II) than the sulfonic resins at $R_i = 1$ in water. The addition of sodium nitrate decreased the loadings of Hg(II) of the sulfonic resin by 55% ($R_i = 1$), but only decreased the phosphonic loadings by 15% ($R_i = 1$). The carboxylic resin, at a $R_i = 1$, loaded more Hg(II) than any other divalent cation investigated.

Kinetics: Redox vs. Ion-Exchange with Mercuric Nitrate

Based on the loading results with Hg(II) of the phosphinic resins (Tables XX and XXI), a kinetic study was performed with Hg(II) at a $R_i = 1$ to measure the rate of mercury oxidation as a function of time and the amount of mercury extracted. The results are outlined in Table XXII.

From the data in Table XXII, four conclusions can be drawn:

1. The rate of mercury extraction is faster than the rate of reduction.
2. The addition of sodium slows the extraction of Hg(II) and apparently slows the reduction process (100% oxidation: 2h(water), 4-17h(4M $NaNO_3$)).
3. In water after 100% oxidation of the resin, ion-exchange with Hg(II) continues.
4. The amount of Hg(II) reduced is a function of time and concentration of Hg(II) within the resin.

TABLE XXII

TIME VS. REDOX FOR 2% DVB PHOSPHINIC ACID RESINS WITH MERCURIC NITRATE AT A $R_i = 1$[a]

Time	% Load.[b]	Hg(II) Abs.[c] mequiv/g	1° Acid[c] Oxidized mequiv/g	% Hg(II) Reduced	% 1° Acid Sites Oxidized
30min	44	2.17	0.62	57.1	36.1
1h	59	2.89	1.03	71.3	60.0
1-1/2h	68	3.34	1.43	85.6	83.3
2h	73	3.56	1.74	97.8	100.0
2-1/2h	79	3.87	1.72	88.9	100.0
3h	83	4.07	1.64	80.6	95.6
4h	89	4.36	1.97	90.4	100.0
17h	99	4.88	1.63	66.8	95.0
With 4M $NaNO_3$					
30 min	33	1.62	0.30	37.0	17.5
1h	41	2.03	0.45	44.3	26.2
1-1/2h	56	2.76	0.66	47.8	38.5
2h	56	2.76	0.69	50.0	40.2
2-1/2h	61	3.01	0.98	65.1	57.1
3h	64	3.16	1.27	80.3	74.0
4h	66	3.24	1.45	89.5	84.5
17h	69	3.54	1.82	100.0	100.0

[a]Run number DW-02-192: Maximum Loading 205%.

[b]Loadings ±3%.

[c]Absorbance ±.05mequiv/g.

[d]Oxidation ±.05mequiv/g.

It is thus apparent that the reduction of Hg(II) by the resin is slowed in aqueous sodium not by a chemical process, but by a lower concentration of the metal in the resin.

Also performed was a kinetic study of the other ion-exchange resins (sulfonic and carboxylic acids) with mercuric nitrate (Table XXIII). Comparison of the kinetic data shows that the sulfonic resin as was observed with zinc (Table XV, p. 27), attains equilibrium faster than the phosphinic resins. In addition MR sulfonic and phosphinic resins were also investigated. As with zinc ions (Table XVI, p. 30), there is not a significant time difference between the gel and MR sulfonic resins to attain maximum loading. There appears however to be a difference between the MR and gel phosphinic resins. At short times, e.g. 5min to 2h, the MR resin has extracted significantly more Hg(II) than the gel. The gels eventually attain similar loadings at 4h (water) and the maximum loading within the same period of time (4-17h).

Redox Properties of the Phosphinic Resin with Silver

Based on the results with mercury ions described in the previous section, it was decided to investigate a metal with a slightly lower reduction potential and so we settled upon silver [E° = +0.7996 vs. +0.851 for Hg(II)]. Preliminary experiments with silver at different R_i of silver indicated that, like mercury, it too underwent reduction (Table XXIV).

As can be concluded from the data in Table XXIV, up to an R_i of 0.5 (excluding R_i = 0.1 due to experimental difficulties), there is 100%

TABLE XXIII

THE KINETICS OF THE EXTRACTION OF MERCURIC NITRATE AT A $R_i = 1$[a]

Type	TAC mequiv/g	% Load.[b] 5min	% Load. 15min	% Load. 30min	% Load. 1h	% Load. 2h	% Load. 3h	% Load. 4h	% Load. 17h
Phosphinic[c]									
2% DVB	4.91	29	--	44	59	73	83	89	99
10% DVB	3.54	--	46	47	56	74	83	90	100
10% DVB(MR)	4.68	62	73	77	79	83	85	89	98
Sulfonic									
10% DVB	5.04	72	72	72	75	75	74	74	75
10% DVB(MR)	4.81	69	73	77	79	81	81	--	--
Carboxylic									
10% DVB	5.43	30	34	35	--	34	36	--	36
With 4M $NaNO_3$									
Phosphinic									
2% DVB	4.91	19	31	33	41	56	64	66	69
10% DVB	3.54	24	31	40	43	54	63	70	68
10% DVB(MR)	4.81	59	69	72	--	73	76	78	--
Sulfonic									
10% DVB	5.04	14	18	18	22	23	23	--	25
10% DVB(MR)	4.81	24	25	27	29	30	30	--	--
Carboxylic									
10% DVB	5.43	13	18	15	13	14	17	--	--

[a]Run number DW-02-199.

[b]Loadings ±3%.

[c]Maximum % Loading: 2% DVB 205%, 10% DVB 265%, 10% DVB MR 238%.

TABLE XXIV

R_i VS. REDOX FOR 2% DVB PHOSPHINIC ACID RESINS WITH SILVER NITRATE[a]

R_i	% Loading[b]	Ag(I) Abs.[c] mequiv/g	1° Acid[d] Oxidized mequiv/g	% Ag(I) Reduced	% 1° Sites Oxidized
0.1	9	.47	0.17	72.0	8.5
0.3	28	1.46	0.77	100	38.5
0.5	46	2.12	1.12	100	56.0
0.7	68	3.43	1.60	94.1	80.0
1.0[e]	91	4.61	2.00	86.8	100
1.5	119	5.69	2.30	80.8	100

[a]Run number DW-02-072: Maximum Loading 220%.

[b]Loadings ±3%.

[c]Absorbance ±.05mequiv/g.

[d]Oxidation ±.05mequiv/g.

[e]Run number DW-02-036: Maximum Loading 215%.

reduction of Ag(I). At a higher R_i, the reduction process continues until the primary acid sites are consumed.

Also investigated were the loadings of silver nitrate with the sulfonic, phosphonic and carboxylic resins at different R_i. Table XXV outlines these results.

As was observed with mercury (Table XX, p. 36), the loadings of Ag(I) exceeded 100%. At even higher R_i, the loadings approached 200% (Table XXVI). The loadings although exceptional, are slightly lower than those found with mercury (10% lower at a $R_i = 1$ for 2% DVB resin). The loadings of phosphonic resins at both cross-link

TABLE XXV

THE LOADINGS OF THE ION-EXCHANGE RESINS AT DIFFERENT R_i OF SILVER NITRATE

Type	TAC mequiv/g	% Load.[a] R_i = .1	% Load. R_i = .3	% Load. R_i = .5	% Load. R_i = .7	% Load. R_i = 1	% Load. R_i = 1.3	% Load. R_i = 1.5
Phosphinic[b]								
2% DVB	4.62	9	28	46	63	90	114	126
10% DVB	3.39	9	27	44	61	84	102	112
Phosphinic[c]								
2% DVB	7.04	8	20	27	32	38	42	44
10% DVB	5.66	9	22	30	37	39	44	46
Sulfonic[d]								
10% DVB	4.99	10	28	45	59	73	85	89
Carboxylic[e]								
10% DVB	5.72	2	4	4	6	6	9	12
With 4M $NaNO_3$								
Phosphinic[f]								
2% DVB	5.10	7	21	37	50	68	90	97
10% DVB	3.53	6	19	34	46	63	79	84
Phosphonic[c]								
2% DVB	7.04	3	11	18	23	30	36	40
10% DVB	5.66	3	13	18	22	29	32	32
Sulfonic[d]								
10% DVB	4.99	4	9	14	19	27	30	34
Carboxylic[e]								
10% DVB	5.72	1	2	3	5	5	6	6

[a] Loading ±3%.

[b] Run number DW-02-19: Maximum Loading 2% DVB 183%, 10% DVB 270%.

[c] Run number DW-02-56.

[d] Run number DW-02-67.

[e] Run number DW-01-281.

[f] Run number DW-02-66: Maximum Loading 2% DVB 214%, 10% DVB 280%.

TABLE XXVI

THE LOADINGS OF THE PHOSPHINIC RESINS WITH SILVER NITRATE AT R_i GREATER THAN 1.5[a]

Type	TAC mequiv/g	Maximum % Loading	% Load.[b] R_i = 2.0	% Load. R_i = 2.5	% Load. R_i = 3.0	% Load. R_i = 4.0
2% DVB	5.00	223	137	133	166	183
10% DVB	3.54	265	125	135	143	155
With 4M $NaNO_3$						
2% DVB	5.00	223	106	120	130	141
10% DVB	3.54	265	88	105	---	130

[a]Run number DW-02-125.

[b]Loadings ±3%.

levels were identical, but lower than those observed with mercury. The sulfonic resin, as was observed with Zn(II), Sr(II) and Hg(II), did extremely well in water but the addition of sodium resulted in a substantial decrease in the loading of the metal (46% decrease, R_i = 1). The carboxylic resin did not extract enough silver to make any general conclusions.

Kinetics: Redox vs. Ion-Exchange with Silver Nitrate

Based on the phosphinic resin loading results with Ag(I) (Tables XXIV-XXVI), a kinetic study was performed with Ag(I) at a R_i = 1 to measure the rate of silver oxidation as a function of time and the amount of Ag(I) extracted. The results are outlined in Table XXVII.

TABLE XXVII

TIME VS. REDOX FOR 2% DVB PHOSPHINIC ACID RESINS WITH SILVER NITRATE AT A $R_i = 1$[a]

Time	% Load.[b]	Ag(I) Abs.[c] mequiv/g	1° Acid[d] Oxidized mequiv/g	% Ag(I) Reduced	% 1° Acid Sites Oxidized
1h	51	2.52	0.41	32.5	23.9
3h	69	3.37	1.36	80.7	79.2
5h	77	3.77	1.48	78.5	86.3
7h	78	3.84	1.42	79.2	88.6
8h	79	3.85	1.55	80.5	90.3
9h	79	3.88	1.71	88.1	100.0
12h	80	3.94	1.74	88.3	100.0
17h	83	4.08	1.74	85.3	100.0
24h	83	4.10	1.82	88.7	100.0
With 4M $NaNO_3$					
1h	27	1.34	0.23	34.3	13.4
3h	41	2.02	0.61	60.4	36.1
5h	46	2.24	0.79	70.5	46.0
7h	50	2.46	0.91	74.0	53.0
9h	54	2.66	1.04	78.2	59.4
12h	55	2.70	1.08	80.0	62.9
17h	59	2.87	1.13	78.9	65.9
24h	62	3.07	1.18	76.9	68.8

[a]Run number DW-02-19): Maximum Loading 205%.

[b]Loadings ±3%.

[c]Absorbance ±.05mequiv/g.

[d]Oxidation ±.05mequiv/g.

From the data in Table XXVII, four conclusions can be drawn:

1. The rate of silver extraction is faster than the rate of reduction. In addition, the rate of silver reduction is much slower than that of mercury (Table XXII, p. 39).

2. The addition of sodium slows the extraction of silver and apparently slows the reduction process [100% oxidation 9h (water), >24h (4M $NaNO_3$)].

3. In water, after 100% oxidation, the resin does not extract a significant amount of silver. With mercury, after 100% resin oxidation, the resin extracted 1.3mequiv/g additional mercury.

4. As was found with mercury, the amount of silver reduced is a function of time and concentration within the resin and not due to a chemical process.

Also performed was a kinetic study of the other ion-exchange resins (sulfonic and carboxylic) with silver nitrate (Table XXVIII).

The comparison of the kinetic data in Tables XXVII and XXVIII shows that the sulfonic resin attains equilibrium faster than the phosphinic resin. In general, for all metals examined thus far [Zn(II), Hg(II) and Ag(I)], the sulfonic resin attained equilibrium in approximately 5 min and had very similar loadings in water and sodium nitrate.

Oxidation of the Phosphinic Acid Resin with Copper Nitrate

Based on the slower rate of oxidation with silver, Cu(II) was investigated. Cu(II) has a reduction potential of +0.3402 which is less

TABLE XXVIII

THE KINETICS OF THE EXTRACTION OF SILVER NITRATE AT A R_i = 1 WITH SULFONIC AND CARBOXYLIC RESINS[a]

Type	TAC mequiv/g	% Load.[b] 5min	% Load. 10min	% Load. 30min	% Load. 45min	% Load. 1h
Sulfonic 10% DVB	5.04	74	75	74	73	74
Carboxylic 10% DVB	5.43	--	17	17	14	13
With 4M $NaNO_3$						
Sulfonic 10% DVB	5.04	20	22	24	24	25
Carboxylic 10% DVB	5.43	16	16	16	16	16

[a]Run number DW-02-205.

[b]Loading ±3%.

than half of the value of the reduction potential of mercury and silver (+0.851 and +0.7996, respectively). It was thought that if there were a correlation between reduction potential and the rate of oxidation of the resin, the time required for the copper oxidation of the resin would be much longer than that of mercury or silver. Table XXIX outlines the results of the copper oxidation of the resin with respect to time and concentration of copper in solution.

By comparing the kinetic redox data for Hg(II) and Ag(I) (Tables XXII, p. 39, and XXVII) with Table XXIX it is apparent that there is a correlation between the reduction potential and phosphinic acid oxidation. In water, at a R_i of 1, the time required for 100%

TABLE XXIX

THE RATE OF COPPER OXIDATION OF THE PHOSPHINIC RESIN AS A FUNCTION OF TIME AND INITIAL CONCENTRATION

$R_i = 1$[a]		With 4M $NaNO_3$	$R_i = 4$[b]	
Time	% 1° Acid[c] Oxidized	% 1° Acid Oxidized	Time	% 1° Acid Oxidized
12h	16.9	6.7	17h	36.2
1d	34.0	28.0	1d	40.4
3d	55.9	47.3	2d	65.1
4d	61.3	55.7	3d	88.4
5d	63.8	62.5	4d	95.6
7d	75.2	67.5		
9d	78.7	72.4		
10d	84.1	----		

[a]Run number DW-02-194.

[b]Run number DW-02-151.

[c]% Oxidized ±5%.

oxidation of the resin was 2h for Hg(II), 9h for Ag(I) and greater than 10d for Cu(II). However, the addition of sodium appears to have no significant affect on the oxidation of the resin with Cu(II) as was observed with Hg(II) and Ag(I). By increasing the initial ratio concentration by a factor of 4, the rate of oxidation with Cu(II) is almost doubled.

A different mesh cut bead (-40+60) was also utilized in the study of the Cu(II) oxidation of the resin. The smaller mesh cut bead was found to have similar redox properties as the standard -20+40 mesh cut bead. However, it was observed that after 24h contact with the Cu(II) solution, the smaller mesh cut resin had elemental copper present outside the resin. The standard mesh cut resin (-20+40) did

not exhibit this trait. Smaller mesh cut resins were also tried with silver nitrate and elemental silver was isolated.

Another transition metal of lower reduction potential, Sn(II) (E° = -.1364), was then investigated. After many experiments at long contact times (144h) and higher R_i (4), it was concluded that Sn(II) does not oxidize the phosphinic acid. Therefore, the lower limit for the redox reaction of the phosphinic acid is between Cu(II) and Sn(II) (+0.34 and -.1364).

The Oxidation of Phosphinic Acid with Hydrogen Peroxide

After the investigation of the effect of the metal's reduction potential on the kinetics we wanted to determine whether ion-exchange facilitates the redox process. To address this question, a kinetic study was performed with various concentrations of H_2O_2 (E° = +1.776) and resins of different 1° acid concentrations. The results are outlined in Table XXX.

From the data in Table XXX, two conclusions can be drawn:

1. The oxidation of the phosphinic acid resin appears to be much slower with hydrogen peroxide than with mercury or silver. Since the reduction potential of hydrogen peroxide is twice as large as those for either metal, it was concluded that ion-exchange facilitates the reduction process.

2. By comparing the increasing TAC values, there appears to be an apparent dependency on the rate of oxidation and the concentration of the peroxide in solution: 30wt% > 20wt% > 10wt%. However, if the

TABLE XXX

THE KINETIC STUDY OF THE ROOM TEMPERATURE OXIDATION OF PHOSPHINIC RESINS WITH DIFFERENT CONCENTRATIONS OF PRIMARY PHOSPHINIC ACID AND HYDROGEN PEROXIDE

	10wt% H_2O_2[a]		20wt% H_2O_2[b]		30wt% H_2O_2[c]	
Time	Increase[d] in TAC mequiv/g	% 1° Acid Oxidized	Increase in TAC mequiv/g	% 1° Acid Oxidized	Increase in TAC mequiv/g	% 1° Acid Oxidized
6h	0.03	1.2	0.41	25.5	0.19	6.9
17h	0.21	7.6	0.54	33.6	0.45	16.2
24h	0.48	17.3	0.69	42.7	0.75	26.8
48h	0.53	19.0	0.89	55.4	1.03	37.1
72h	0.82	29.3	1.13	70.1	1.41	50.5
96h	1.00	35.8	1.27	78.9	1.67	59.9
192h	1.14	41.1	1.77	100.0	2.25	81.0

[a]Run number DW-02-176: PAC value 2.78mequiv/g.

[b]Run number DW-02-162: PAC value 1.61mequiv/g.

[c]Run number DW-02-178: PAC value 2.78mequiv/g.

[d]Increase in TAC ±.05mequiv/g.

[e]% Oxidized ±5%.

difference in the primary acid concentration is taken into account, the 20 and 30wt% peroxide solutions have approximately the same rate of oxidation and both have a greater rate of oxidation than does the 10wt% solution.

Also investigated was the temperature dependency on the hydrogen peroxide oxidation of the phosphinic acid resin. Since 20 and 30wt% peroxide had similar oxidation properties at room temperature, it was elected to use the 20wt% peroxide. The temperature study was conducted as follows: The resin was allowed to stir for 1h at room temperature in an excess of 20% hydrogen peroxide and was heated up to temperature over a period of 4h. The temperature was held for 1h, cooled, and the resin analyzed. Table XXXI outlines the results.

TABLE XXXI

TEMPERATURE DEPENDENCY FOR THE OXIDATION OF A PHOSPHINIC ACID RESIN WITH 20wt% H_2O_2[a]

Temperature °C	Increase in TAC mequiv/g	Final TAC mequiv/g	Final % Solids
50	0.97	6.07	48.5
75	1.11	6.21	42.6
85	2.64	7.74	42.0
100	3.20	8.30	26.8

[a]Run number DW-02-160: Resin utilized was a 2% DVB gel with the following properties; TAC 5.10, PAC 1.61, % solids 54.8, EPC 4.92.

As can be seen from the data in Table XXXI, some secondary acids sites are being broken, giving a higher capacity. In addition, the % Solids decreases as the acid capacity increases. To test to see if the 2° acid sites are being oxidized, an additional experiment was performed with linear phosphinic acid. The resin is made from non-cross-linked polystyrene and during the functionalization, as secondary acid sites are formed, the non-DVB containing resin precipitates out of solution. The phosphinic acid polymer is water insoluble, but upon the treatment of the material with hydrogen peroxide at 100°C for 24h, the polymer dissolved, proving that the secondary sites were being broken up. Therefore, the maximum capacity obtainable for a phosphinic acid resin upon total oxidation of the resin (1° and 2° sites) would be approximately two times the EPC.

In an attempt to make a totally oxidized resin, the following experiments were performed: The resin was allowed to stir for 1h at room temperature in excess 20wt% H_2O_2 and then heated to 100°C over 4h. The temperature was maintained for a certain period of time, the reaction cooled, and the resin analyzed. Table XXXII outlines the results of the effect of time at 100°C for the peroxide oxidation of phosphinic acid resins.

As can be concluded from the data in Table XXXII, we were successful in making a totally oxidized phosphonic acid resin. Unfortunately, the solids of the resin (9-2%) made it very difficult to obtain accurate acid capacities. In addition, the resin was not in a bead form, but was more of a swollen jelly.

TABLE XXXII

THE EFFECT OF TIME AT 100°C FOR THE OXIDATION OF PHOSPHINIC ACID RESINS BY 20wt% H_2O_2[a]

Time at 100°C	Increase in TAC mequiv/g	Final TAC mequiv/g	% Solids
1h	1.94	6.96	35.1
3h	4.64	9.67	28.8
4h	6.26	11.28	8.9
5h	6.43	11.45	3.3
6h	6.88	11.90	2.4

[a]Run number DW-02-157: Resin utilized was a 2% DVB gel with the following properties; TAC 5.02, PAC 2.06, % Solids 52.7.

The rate of the peroxide oxidation of the resin can thus be increased by heating. The resin properties also can be controlled by the experimental conditions employed, yielding resins with different compositions of acidic sites: 1° phosphinic, 2° phosphinic and phosphonic.

The Loadings of the Ion-Exchange Resins with Gold

Au(III) has a very high reduction potential ($E^\circ = +1.42$) when compared to mercury and silver. As a result, it was predicted that the loadings of Au(III) would be higher with phosphinic resins since it would undergo the redox process. Table XXXIII outlines the extraction of $AuCl_3$ by the phosphinic, sulfonic and carboxylic resins as a function of R_i.

TABLE XXXIII

THE LOADINGS OF THE ION-EXCHANGE RESINS WITH $AuCl_3$ AT DIFFERENT R_i[a]

Type	TAC mequiv/g	% Load. R_i = .001	% Load. R_i = .01	% Load. R_i = .02	% Load. R_i = .03	% Load. R_i = .10
Phosphinic						
2% DVB	4.92	0.09	0.86	1.82	2.63	8.93
10% DVB	3.90	0.09	0.78	1.57	2.48	7.92
Sulfonic						
10% DVB	3.57	0.01	0.01	---	---	0.03
Carboxylic						
10% DVB	5.72	0.05	0.56	1.13	1.41	3.41
With 4M NaCl						
Phosphinic						
2% DVB	4.92	0.10	0.98	1.95	2.91	9.15
10% DVB	3.90	0.10	0.96	1.89	2.80	7.86
Sulfonic						
10% DVB	3.57	0.07	0.63	---	---	1.96
Carboxylic						
10% DVB	5.72	0.96	0.92	1.71	2.35	2.93

[a]Run number DW-01-266.

As can be concluded from the data in Table XXXIII, the phosphinic resins extract considerably more Au(III) than the sulfonic and carboxylic resins. The addition of sodium has no significant effect on the loadings of Au(III) by the phosphinic resin. The % redox of the phosphinic resin was not determined due to the low concentration of gold within the resin. The loadings of the sulfonic acid resin with Au(III) were lower in both cases investigated (with and without sodium) than the carboxylic acid resin. Based on these results, the

phosphinic acid resin has a better extraction capability with gold than the sulfonic and carboxylic resins combined.

Phosphinic Resins and Fe(III)

Along with the study of mercury and silver, another metal, with an apparently favorable reduction potential was tried, Fe(III) (E° = +0.770). The reduction potential of Fe(III) is only slightly less than that of silver (E° = +0.7996), and was predicted to have similar oxidation properties with the phosphinic resins. However, after contacting the resin with solutions of ferric chloride and ferric nitrate at a R_i = 2 for 24h, it was observed that the resin was not oxidized. Even with Cu(II) (E° = +0.340) after 24h the resin was 34% oxidized (Table XXIX, p. 48). In an attempt to understand why the redox process apparently did not work, an R_i study was performed with the phosphinic resin with ferric nitrate. For comparison, sulfonic, phosphonic and carboxylic resins were included in the study. Table XXXIV outlines the loadings of the ion-exchange resins with ferric nitrate at different R_i.

The loadings of Fe(III) in Table XXXIV do not resemble the loadings of the redox processes previously examined (Tables XXIII and XXV, pp. 41 and 43), but Fe(III), if reduced to Fe(II), would exhibit an ion-exchange loading such as the ones found with Zn(II) (Table XIV, p. 25). We thus concluded that Fe(III) does not oxidize the resin. This unexpected selectivity against the reduction of Fe(III) by the phosphinic acid resin could be used to an advantage in the separation of Cu(II) from Fe(III) in ores. During the process, Cu(II)

TABLE XXXIV

THE LOADINGS OF 10% DVB ION-EXCHANGE RESINS WITH FERRIC NITRATE AT DIFFERENT R_i[a]

Type	TAC mequiv/g	% Load.[b] R_i = 0.1	% Load. R_i = 0.5	% Load. R_i = 1.0	% Load. R_i = 1.5
Phosphinic	4.68	9	24	23	24
Phosphonic	5.66	2	--	12	12
Sulfonic	5.00	10	50	83	88
Carboxylic	5.43	7	--	22	23
With 4M $NaNO_3$					
Phosphinic	4.68	10	30	30	29
Phosphonic	5.66	2	--	14	11
Sulfonic	5.00	5	16	31	48
Carboxylic	5.43	7	--	23	27

[a]Run number DW-02-218.

[b]Loadings ±3%.

could be reduced to elemental copper by the resin without the loss of redox capacity to Fe(III). Since the Fe(III) is only ion-exchanged with the resin, an elution with acid could remove the Fe(III) and leave the copper within the resin for selective recovery.

The loadings of the sulfonic and carboxylic resins with Fe(III) were excellent in both cases examined (with and without sodium nitrate). The sulfonic resin at a R_i = 1 loaded more Fe(III) than any other metal examined in water or sodium nitrate. In addition, the weakly acidic carboxylic resin actually extracted as much Fe(III) as the phosphinic acid resin. The phosphonic acid, if the less acidic proton is discounted, also possesses similar loadings as the phosphinic and carboxylic resins. Therefore, it is concluded that the sulfonic

resin possesses the highest affinity for Fe(III) than all resins examined.

$FeCl_3$ as a Catalyst for Phosphorus Containing Ion-Exchange Resins

As part of our fundamental study of phosphinic ion-exchange resins, another Friedel-Crafts catalyst, $FeCl_3$ was used instead of $AlCl_3$. Upon the synthesis and analysis of the resin, it was discovered that the resin was not a phosphinic but a phosphonic resin (Table XXXV).

TABLE XXXV

THE PROPERTIES OF A PHOSPHONIC ACID ION-EXCHANGE RESIN SYNTHESIZED BY $FeCl_3$ CATALYSIS[a]

Type	Capacity mequiv/g	EPC mequiv/g	% Solids
Gel 2% DVB	4.23	2.23	53

[a]Run number DW-02-189B.

A zinc loading analysis of the $FeCl_3$ catalyzed resin was performed and compared to the other phosphonic resins (Table XXXVI).

As can be seen from the data in Table XXXVI, the loadings of the $FeCl_3$-phosphonic resins are significantly lower than the other phosphonic resins. These results led us to have an analysis for iron performed on the beads to determine if iron were present. The

TABLE XXXVI

THE COMPARISONS OF THE ZINC NITRATE LOADINGS OF THE $FeCl_3$ CATALIZED PHOSPHONIC RESINS TO PHOSPHONIC RESINS WITH A 4M $NaNO_3$ BACKGROUND[a]

Type	Cross-Link Level % DVB	Initial Capacity mequiv/g	% Load.[b] R_i = .1	% Load. R_i = 1	% Load. R_i = 1.5
Phosphonic[c]	2	7.04	3	21	27
Phosphonic[c]	10	5.66	3	16	22
Phosphonic $FeCl_3$-Cat.	2	4.23	2	11	18

[a]Run number DW-02-226.

[b]All loadings reported are ±3%.

[c]Run number DW-02-052.

analysis by Galbraith Laboratories showed that the beads contained 4.56% by weight iron [2.45mequiv/g Fe(III) or 1.63mequiv/g Fe(II)]. We therefore concluded, that the iron present in the bead must compete with zinc in the ion-exchange process, thus lowering the amount of zinc loaded.

Conclusion

Based on the ion-exchange data presented in this chapter, the phosphinic resin shows good selectivity towards divalent cations, e.g., Zn(II) and Sr(II), in large excesses of sodium. The resin shows a high affinity for trace quantities of a lanthanide, Eu(III) in a 4M sodium nitrate solution. The resins diffusion properties have been shown to be similar to those of the sulfonic resins if MR beads are

employed. In addition, the phosphinic resin has exhibited the capability to reduce certain metals to their zero valent state. The redox mechanism greatly enhances the recovery of those metals in water and alkali solutions. Conceivably, the resin could be used to separate metals with different reduction potentials, e.g., Zn(II) and Ag(I). Those metals which undergo an ion-exchange process could be removed by elution with acid leaving the reduced metal in its zero valent state within the resin. Furthermore, the resin could be made commercially since a similar process was employed in the synthesis of the once available phosphonic resins.

CHAPTER III

EXPERIMENTAL SECTION

Suspension Polymerization[21]

Aqueous phase preparation. Pharmagel (3.84g) was dissolved in water (400g) with heat and was added to a solution of 47.6g padmac, 25.3g boric acid and 865.8g of water adjusted to pH 10.3 with 50wt% NaOH. The pH was rechecked and the solution was divided into four equal portions of 343g each. The individual aqueous portions were added to 1L 3-neck round bottom flasks equipped with a condenser, thermometer and an overhead stirrer. The stir rate was adjusted to 250rpm for gel beads (185rpm for MR beads) and steady purge of nitrogen through the round bottom flask was begun and continued throughout the polymerization.

Organic phase preparation. Technical Grade DVB was utilized (55.4% DVB, 44.6% ethyl vinyl benzene); to obtain a 2wt% solution of DVB, a total of 3.6wt% of the technical grade DVB was added.

Gel beads. Table XXXVII outlines the composition of DVB/ styrene in the organic phase. After the monomers have been mixed well, 3.0g of benzoyl peroxide (BPO) was added. The organic phase was added to the 1L round bottom flask and the stir rate checked (250rpm). A cycle of 2min on and 1min off was repeated three times.

MR beads. Table XXXVIII outlines the composition of DVB/ styrene in the organic phase. After the monomers were mixed well,

TABLE XXXVII

THE WEIGHTS OF STYRENE AND DVB FOR THE SYNTHESIS OF GEL BEADS

Cross-Link Level %DVB	wt Styrene (g)	wt DVB (g)
2	286.28	20.72
5	270.20	26.80
10	243.39	53.61
15	216.58	80.42

TABLE XXXVIII

THE WEIGHTS OF STYRENE AND DVB FOR THE SYNTHESIS OF MR BEADS

Cross-Link Level %DVB	wt Styrene (g)	wt DVB (g)
2	143.14	5.36
5	135.10	13.40
10	121.70	26.80
15	108.29	40.21

1.50g BPO and 150g 4-methyl-2-pentanol (4M2P) were added. The organic phase was poured into the 1L round bottom flask and the stir rate checked (185rpm). A cycle of 2min on and 1min off was repeated three times.

Polymerization. The two phases were heated up to 80°C over 2h and held at 80°C for 10h.

Work up and washing of the beads.

Gel beads: After 10h at 80°C, the roundbottom flask was heated to 100°C and held at that temperature for 2h. The solution was allowed to cool, and the copolymer was washed with 500mL of pH 4 water/HCl four times and four times with 500mL of water (pH 7). Each cycle consisted of 15min of stirring. After the last water wash, the beads were removed and placed in a drying oven at 60°C until dry.

MR beads: After 10h at 80°C, the 4M2P was removed by azeotropic distillation with water. The beads were then washed with 500mL of pH 4 water/HCl four times and four times with 500mL of water (pH 7). Each cycle consisted of 15min of stirring. After the washing was completed, the beads were removed and air dried.

Synthesis of Phosphinic Acid Resins

The copolymer (10g) was added to a 250mL 3-neck round bottom flask equipped with a thermometer, condenser and overhead stir motor. Phosphorus trichloride (80mL) was added and the beads were allowed to swell for 1h. Aluminum chloride, 9.9g (0.77mole $AlCl_3$/mole styrene) was added, the round bottom flask heated to 73°C over 1h, held for 4h and cooled. The contents of the round bottom were hydrolyzed with a saturated NaCl/ice solution and conditioned.

Synthesis of Sulfonic Acid Resins

The copolymer (10g) was placed in a 3-neck 250mL round bottom flask equipped with a thermometer, condenser and overhead stirrer. Dichloroethane (20.6g) was added to swell the beads (10min) and a

solution of 88.4g of 96% H_2SO_4 was added to the round bottom flask. The reaction mixture was allowed to stir for 15min at room temperature and heated to 130°C over 3h. The temperature was held for 15min and the system allowed to cool to 110°C, at which time, 56.4g of water was added at a rate to maintain the temperature between 110-120°C. The solution was siphoned out (55mL) and an additional water wash was added at a rate to maintain the temperature at 95-110°C. Three additional water washes were utilized at a rate to maintain the temperature of 50°C. Two additional water washes were performed at room temperature. The beads were then transferred to a column and eluted with water at a rate of 1L/h until neutral and conditioned.

Synthesis of Carboxylic Resins

Ten g of poly(vinyl benzyl chloride) beads were placed in a 3-neck 250mL round bottom flask equipped with a thermometer, condenser and overhead stirrer. Concentrated nitric acid (200mL) was added and the mixture was heated to 80°C over 1h and held for 23h. The mixture was then allowed to cool to room temperature and the contents transferred to a 4L beaker containing 3L of ice water. The beads were transferred to a column and eluted with water at a rate of 1L/h until neutral and conditioned.

Synthesis of Phosphonic Resins

Ten grams of phosphinic resin were added to a 250mL 3-neck round bottom flask equipped with a thermometer, condenser and overhead stirrer. Added were 200mL of an aqueous 20wt% H_2O_2

solution and the resin was allowed to stir 1h at room temperature. The round bottom flask was heated to 100°C over 4h, held for 1h and cooled. The resin was transferred to a column and eluted with 3L of water (1L/h) and conditioned.

Synthesis of Phosphonic Resins with $FeCl_3$

The copolymer (10g) was placed in a 250mL 3-neck round bottom flask equipped with a thermometer, condenser and overhead stirrer. Added were 80mL of PCl_3 and the beads were allowed to swell for 1h. Added were 31.19g of $FeCl_3$ (2mole $FeCl_3$/mole styrene), the round bottom heated to 73°C over 1h, held for 4h and cooled. The contents of the flask were hydrolyzed with a saturated NaCl/ice solution and conditioned.

Percent Solids Determination

The excess water was removed by suction filtration with a Buchner funnel equipped with a latex membrane to maintain the pressure at 720mm for 5min. The resin was transferred to a jar and shaken for several minutes. One to two g of the wet resin were transferred to a tared bottle and weighed to the nearest milligram. The bottle was placed in a drying oven for 16h at 110°C, removed, allowed to cool in a desiccator and reweighed. All weights to be reported for the remainder of this section will be in terms of gram dry resin.

Conditioning Ion-Exchange Resins

All resins discussed with the exception of the phosphinie oxide/ phosphinic acid resins were treated as follows: ten grams of resin

were placed in a column and eluted with 1L (1L/h) of the following solutions: water, 4wt% NaOH, water, 4wt% HCl and water.

TAC Measurements

One gram of resin was contacted with 200mL of a standard 0.1N NaOH/5wt% NaCl solution. After 12h, a 50mL aliquot was taken and titrated with a standard 0.2N acid solution.

CEC Measurement

Five grams of resin were placed in a column and rehydrated with 1L (1L/h) of the following solutions: water, 4wt% HCl and water. The resin was eluted with 1L of 4wt% $NaNO_3$ (1L/h), the liter collected and a 100mL aliquot taken and titrated with standard 0.1N NaOH.

PAC Measurement

The resin (0.5g) was added to a bottle and 20mL of a standard 0.2N iodine and potassium iodide. Two milliliters of pyridine were added, the bottle sealed and shaken for 22h on a wrist action shaker. Fifty milliliters of a standard 0.1N sodium thiosulfate solution were added and the bottle was shaken until all of the iodine was reduced. The contents of the bottle was back titrated with the standard iodine solution to a starch endpoint.

EPC Measurement[22]

An oven dried sample (0.02g) (110°C/16h) was digested in 10mL of a 1:1 perchloric/nitric acid solution with heat. The contents were quantitatively transferred to a 100mL volumetric flask and brought to

volume with water. The flask was shaken well and 5mL of solution was pipeted to a 50mL volumetric flask.

The amidol reagent was prepared as follows: 1.0g of amidol was dissolved in 60g of water followed by 20g of sodium sulfate. A solution of 2.7g H_2SO_4 (96%) and 20g of water was added and mixed well.

To the 50mL volumetric flask were added 3.5mL of 72% perchloric acid, 4.5mL of the amidol reagent and 3.5mL of a .071M ammonium molybdate (4.15g/50mL water) in that order. The volumetric flask was brought to volume with water and mixed well. After 30min, the absorption of the solution and a reagent blank was measured on a Spec 21 at 700nm. From the absorbance, the phosphorus content was determined with the aid of a graph from potassium dihydrogen phosphate standards.

Radiotracer Analysis

The resin, 0.5g, was placed in a 20mL tared bottled and weighed. The following calculations were performed to determine the concentration of the metal in solution:

1. (dry wt)(TAC) = mequiv acid sites present
2. (mequiv acid sites)(R_i) = mequiv of metal
3. (mequiv metal)/(Normality of stock solution) = mL of metal
4. 5.00mL-mL of metal = mL of water or 4M $NaNO_3$

To the bottle was pipeted the volume of water, stock metal solution and 20λ of tracer (Table XXXIX) in that order. A blank was prepared consisting of 4.00mL of water, 1.00mL stock solution and 20λ

TABLE XXXIX

GAMMA EMITTING TRACERS EMPLOYED FOR LOADING STUDIES OF THE ION-EXCHANGE RESINS

Tracer	$t_{1/2}$
$^{65}Zn(II)$	244.1d
$^{203}Hg(II)$	46.8d
$^{110}Ag(I)$	252.0d
$^{198}Au(III)$	64.8h
$^{152-154}Eu(III)$	13-8.5y
$^{59}Fe(III)$	44.6d
$^{42}K(I)$	12.4h
$^{85}Sr(II)$	64.8d

of tracer. The bottles were placed on a wrist action shaker for 17h, a 1mL aliquot removed and counted on a Tracor Northern TN-1314 Multi-Channel Analyzer. Two 1min counts per sample were performed and the pH of the sample was measured. The raw data were corrected for background and the following calculations were performed:

$$\text{mequiv } H^{+}/g = (5)\ 10^{-pH}/\text{dry wt}$$

$$\text{mequiv } M^{+n}\text{Absorbed/g} = (\text{Blank-Sample})(\text{mequiv } M^{+n})/(\text{Blank})(\text{dry wt})$$

$$\% M^{+n} \text{ Loading} = ((\text{mequiv } M^{+n}\text{Absorbed/g})/\text{TAC})(100\%)$$

$$\% M^{+n} \text{ Absorbed} = ((\text{Blank-Sample})/(\text{Blank}))(100\%)$$

MR Dilution Factor for Radiotracer Analysis

H_2O in Beads

$$\frac{\text{dry wt MR}}{\% \text{ Solids MR}} - \frac{\text{dry wt MR}}{\% \text{ Solids gel}} = \text{wt } H_2O \text{ in MR}$$

Correction Factor

Correction Factor = (5mL + wt H_2O in MR)/5mL

Corrected cpm

Corrected cpm = (cpm)(Correction factor)

Determination of Increase in TAC by Redox Mechanism

$AgNO_3$. The resin (4g) was placed in a 120mL bottle, 100mL of a standard $AgNO_3$ solution was added and the bottle shaken for 17h on a wrist action shaker. A 25.0mL aliquot was taken and a Volhard titration[23] was performed to measure the amount of silver extracted from solution. The resin was placed in a column, eluted with 1L of 4N HNO_3 over 2h and with water at a rate of 1L/h until neutral. The resin was removed and a TAC measurement was performed.

$Hg(NO_3)_2$. Four grams of resin were placed in a 120mL bottle, 100mL of a standard $Hg(NO_3)_2$ solution was added and the bottle shaken for 17h on a wrist action shaker. The bottle was removed and the beads placed in a column, eluted with 8N HNO_3 over 2h and with water at a rate of 1L/h until neutral. The resin was removed and a TAC measurement was performed.

H_2O_2. Four grams of resin were placed in a 120mL bottle, 100mL of a 20% H_2O_2 solution were added and the bottle shaken for a predetermined length of time on a wrist action shaker. The bottle was removed, the beads placed in a column, eluted with 3L of water (1L/h), conditioned and a TAC measurement performed.

$Cu(NO_3)_2$. Four grams of resin were placed in a 120mL bottle, 100mL of a $Cu(NO_3)_2$ solution were added and the bottle shaken for a predetermined length of time on a wrist action shaker. The bottle was removed, the beads placed in a column, eluted with 1L of 4N HNO_3 over 2h and with water at a rate of 1L/h until neutral. The resin was removed and a TAC measurement performed.

REFERENCES

REFERENCES

1. Thompson, H. S. J. Roy. Agr. Soc. Engl. 1850, 11, 68.

2. Kunin, R. "Ion-Exchange Resins," John Wiley: New York, 1958, 2nd ed. Chapter 1, 2.

3. Adams, B. A.; Holmes, E. L. J. Soc. Chem. Ind. 1935, 54, 1-6T.

4. Reichenberg, D. In "Ion Exchange"; Marinsky, J.A., Ed.; Marcel Dekker: New York, 1966; Vol. 1, Chapter 7.

5. Diamond, R. M.; Whitney, D. C. In "Ion Exchange"; Marinsky, J. A., Ed.; Marcel Dekker: New York, 1966, Vol. 1, Chapter 8.

6. Wheaton, R. M.; Hatch, M. J. In "Ion Exchange"; Marinsky, J. A., Ed.; Marcel Dekker: New York, 1969, Vol. 2, Chapter 6.

7. D'Alelio, G. F. U.S. Patent 2,366,007, 1945.

8. Wiley, R. H.; Allen, J. K. J. Phys. Chem. 1964, 68, 2830.

9. Lenz, R. W. "Organic Chemistry of Synthetic High Polymers"; John Wiley & Sons: New York, 1967, Chapter 11.

10. Kun, K. A.; Kunin, R. J. Poly. Sci., Part A-1 1968, 6, 2689.

11. Tennessee State Water Control Board, Private Communication.

12. Jones, R. "Physical and Mechanistic Organic Chemistry,"; Cambridge University Press: Cambridge, 1979, Chapter 5.

13. Serjeant, E. P.; Denpsey, B. "Ionization Constants of Organic Acids in Aqueous Solution"; Pergamon Press: New York, 1980.

14. Jaffe, H. H.; Freedman, L. D. J. Amer. Chem. Soc., 1953, 75, 2209.

15. Peppard, D. Adv. Inorg. Chem. Radiochem. 1966, 9, 1.

16. Shoun, R. R.; McDowell, W. J. "Actinide Extractants: Development, Comparison and Future"; Navratil, J. D., Schulz, W. W.; Eds.: American Chemical Society: Washington, D.C., 1980; ACS Symp. Ser. No. 117, Chapter 6.

17. Brown, J.; Silver, B. Chem. and Ind., 1961, 24.

18. Kosolapoff, G. J. Amer. Chem. Soc. 1947, 69, 2020.

19. Frank, A. W. J. Org. Chem. 1959, 24, 966.

20. Fox, R. B.; Venezky, D. L. J. Amer. Chem. Soc. 1953, 75, 3967.

21. Barrett, J. H.; U.S. Patent 3,843,566, 1974.

22. Arcus, C. L.; Matthews, R. J. J. Chem. Soc. 1956, Part IV, 4607.

23. Peters, D. G.; Hayes, J. M.; Hieftje, G. M. "Chemical Separations and Measurements"; W. B. Saunders Company: Philadelphia, 1974, Chapter 8.

PART II

SYNTHESIS OF HOMOGENEOUS EXTRACTANTS: INITIAL STUDIES

CHAPTER I

INTRODUCTION

In 1805, Bucholz discovered that an inorganic salt, uranyl nitrate, was very soluble in diethyl ether.[1] From such a humble beginning, liquid/liquid extraction has expanded to become one of the most useful tools in the laboratory and in industry.[2,3] In the last 30 years, significant advances have been made [2-6] and many new types of selective extractants are commercially available.[7]

Liquid/liquid extraction is a binary system. The organic phase, which contains the extractant, is placed in contact with the aqueous phase. The two phases are agitated and once extraction is complete, the phases are allowed to separate. The aqueous phase is then removed, a new aqueous phase introduced and the cycle repeated. The cycle continues until the extraction capabilities of the organic phase are exhausted. The extractant can be regenerated upon acidification with the recovery of the complexed metal.[4-6]

There are many types of liquid/liquid extractants, each one being unique in its extracting capabilities and utility.[4-6] Neutral extractants do not have an ion-exchange group, but have a polar head group, usually oxygen and extract metals by a coordination mechanism.[4-6] Acidic extractants exchange a proton from the organic phase for a metal in the aqueous phase.[4-6] Table I outlines the two general types of extractants and gives examples of each type found in the literature.

TABLE I

TYPES OF LIQUID EXTRACTANTS

Neutral Extractants	Ref.	Acidic Extractants	Ref.
Diethyl ether	1,3	Naphthalene sulfonic acid	3
Methyl isobutyl ketone	3	Di(2-ethylhexyl) phosphoric acid	3,7
Tributyl phosphate	3,5	Di(n-octyl) phosphinic acid	8
Trioctyl phosphine oxide	3,6	n-octyl phosphonic acid	9

Acidic Extractants

For acidic extractants, one of the most important aspects for ion-exchange is the apparent pK_a.[13] A very high pK_a shows a very strong proton affinity and as a result, would make a poor metal extractant at a low pH. Conversely, an extractant with a very low pK_a would have in general excellent extracting capabilities but poor selectivity.[13]

The acidic properties of an organic molecule are due to a combination of internal and environmental effects. The strength of the acid is determined by the relative stability of the conjugate base, which in turn is highly dependent upon the solvation of the corresponding anion.[14] Therefore, by branching the alkyl tail one might expect an increase in the apparent pK_a. Carboxylic acids demonstrate such a trend (Table II).

Dialkyl phosphoric acids are intermediate in acid strength between carboxylic and sulfonic acids. In addition, they have been shown to have excellent selectivity towards certain transition metals,[16] actinides,[4-6] and lanthanides.[4-6] As was found with carboxylic acids, the

TABLE II

IONIZATION CONSTANTS OF HINDERED ACIDS, IN 50% METHANOL-WATER AT 40°C[15]

Acid	Apparent pK_a
Acetic	5.55
Methyl neopentyl acetic	6.05
Methyl t-butyl acetic	6.25
Diisopropyl acetic	6.40
Triethyl acetic	6.44
Dimethyl t-butyl acetic	6.72

branching of the alkyl tail does increase the apparent pK_a.[17] Table III lists some of the dialkyl phosphoric acids that have been investigated.

TABLE III

ACIDITIES OF PHOSPHORIC ACID EXTRACTANTS IN 75% ETHANOL[17]

Acid	pK_a
Di(n-octyl)	3.30
Di(2-ethylhexyl)	3.49
Bis(2,2-dimethylhexyl)	3.55
Bis(diisobutyl methyl)	4.74

Alkyl phosphinic acids are slightly less acidic than phosphoric acids. They also display the trend in increasing pK_a values with the branching of the alkyl tail (Table IV). The increase in the pK_a has little effect on the extraction capabilities of the acid,[11] but does increase the selectivity towards certain metal cations.[4-6,11]

TABLE IV

PHOSPHINIC ACID ACIDITIES IN 75% ETHANOL[17]

Acid	pK_a
Di(n-hexyl)	5.27
Di(3,3-dimethyl butyl)	5.29
Di(isobutyl)	5.60
Di(sec-butyl)	5.75
Di(n-octyl) H(DOP)	5.30
Di(2-ethylhexyl) H(DEHP)	5.88

The pK_a of an acidic extractant is not the only consideration involved in the selection of a liquid/liquid extractant. The concentration of the acid at the solution interface is of great importance also. Vangrift and Horwitz[17] found by comparing H(DOP) and H(DEHP) that the minimum bulk concentration necessary to saturate the interface was less for the branched phosphinic acid than for the straight chain acid. If one also takes into consideration the fact that the pK_a of H(DEHP) is higher than H(DOP), one might speculate that the rate of extraction would be slower for the branched phosphinic acid. Evidence does exist that supports this idea: Peppard[11] found in a comparison of di(n-octyl) and di(2-ethylhexyl) phosphoric acids that the differences in the relative rate ratios was between 5 to 9 for the nonbranched vs. branched extractants.

As the relative rate of extraction decreases due to the branching of the alkyl tail, selectivity increases for some metal cations. Studies performed by Mason[23] using bis(t-butyl) phosphinic acid demonstrated that extractant's selectivity towards U(VI) with respect to Th(IV) and

all lanthanides (III). Mason also found that in general, the highly hindered extractants discriminate strongly in favor of U(VI) and Pa(V) relative to Th(IV) and the actinides (III). Along the same lines, it has been noted that bis(2,6-dimethyl-4-heptyl) phosphoric acid separates a mixture of Am(VI)/Cm(III)[24] and di(2,4,4-trimethylpentyl) phosphinic acid has a high selectivity for Co(III) in a Co(III)/Ni(II) mixture.[25]

Based on the information in the literature, branched phosphinic acids possess great potential in liquid/liquid extraction. However, only the butyl derivatives have been studied in any detail.[23] What is entirely missing is a systematic study of the branched dialkyl C_8 phosphinic acids and the corresponding impact on extraction properties. The C_8 acids are an extremely important class of extractants due to their superior organophilicity. We thus planned to synthesize the following extractants: di(n-octyl), di(2-ethylhexyl), di(2-octyl), di(3-octyl), di(2-methylheptyl), di(3-methylheptyl), di(4-methylheptyl), and di(4-methyl-4-heptyl) phosphinic acids. From this list, only the first two, H(DOP) and H(DEHP), were made and purified. This chapter will present the planned and attempted extractant syntheses. Also to be discussed will be the problems encountered during the synthesis and purification and recommendations will be made as to how the purification problem could be solved.

Outline of Syntheses of Phosphinic Acids

1. Di(n-octyl) phosphinic acid

$$CH_3(CH_2)_6CH_2Br + Mg \xrightarrow[3)\ H_2O]{2)\ POCl_3} (CH_3(CH_2)_6\ CH_2-)_2POOH \quad \text{(Ref. 26)}$$

2. Di(2-octyl) phosphinic acid

$$CH_3(CH_2)_5CHBrCH_3 + Mg \xrightarrow[3)\ H_2O]{2)\ POCl_3} (CH_3(CH_2)_5\underset{\displaystyle CH_3}{\underset{|}{CH}}-)_2POOH \quad \text{(Ref. 26)}$$

3. Di(2-ethylhexyl) phosphinic acid

$$CH_3(CH_2)_3\underset{\displaystyle CH_2CH_3}{\underset{|}{CHCH_2OH}} + SOCl_2 \rightarrow CH_3(CH_2)_3\overset{\displaystyle CH_2CH_3}{\overset{|}{CHCH_2Cl}} \quad \text{(I)} \quad \text{(Ref. 27)}$$

$$\text{(I)} + Mg \xrightarrow[3)\ H_2O]{2)\ POCl_3} (CH_3(CH_2)_3\ \underset{\displaystyle CH_2CH_3}{\underset{|}{CHCH_2-}})_2POOH \quad \text{(Ref. 26)}$$

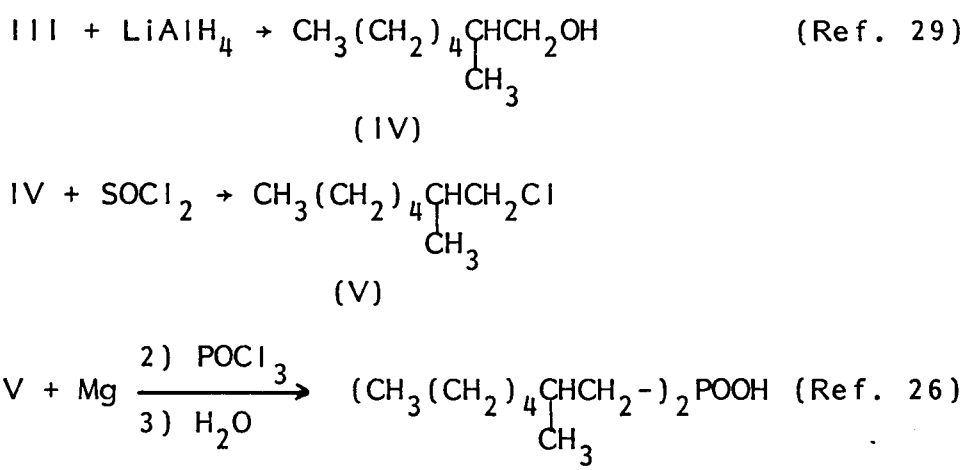
4. Di(3-octyl) phosphinic acid

$$CH_3(CH_2)_4\underset{\displaystyle OH}{\underset{|}{CHCH_2CH_3}} + SOCl_2 \rightarrow CH_3(CH_2)_4\underset{\displaystyle Cl}{\underset{|}{CHCH_2CH_3}} \quad \text{(II)} \quad \text{(Ref. 27)}$$

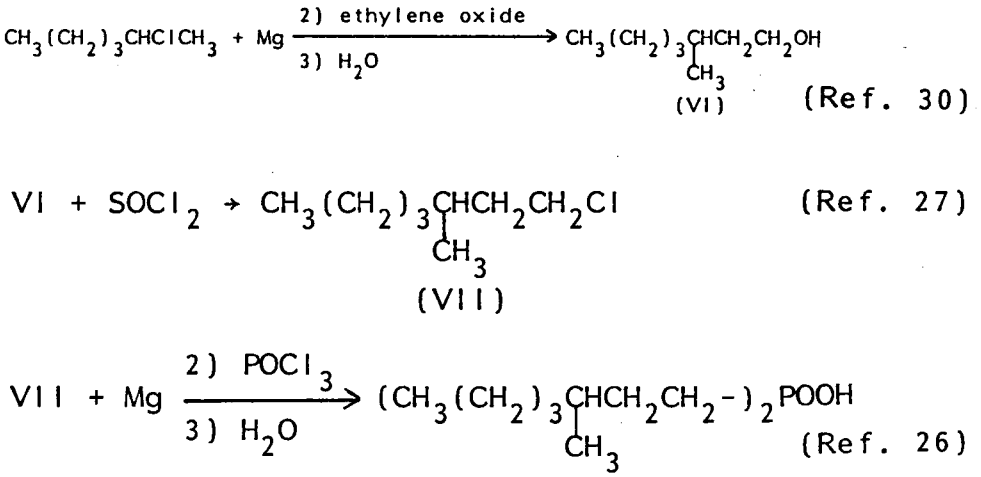
$$\text{II} + Mg \xrightarrow[3)\ H_2O]{2)\ POCl_3} (CH_3(CH_2)_4\underset{\displaystyle CH_2CH_3}{\underset{|}{CH}}-\ \ )_2POOH \quad \text{(Ref. 26)}$$

5. Di(2-methylheptyl) phosphinic acid

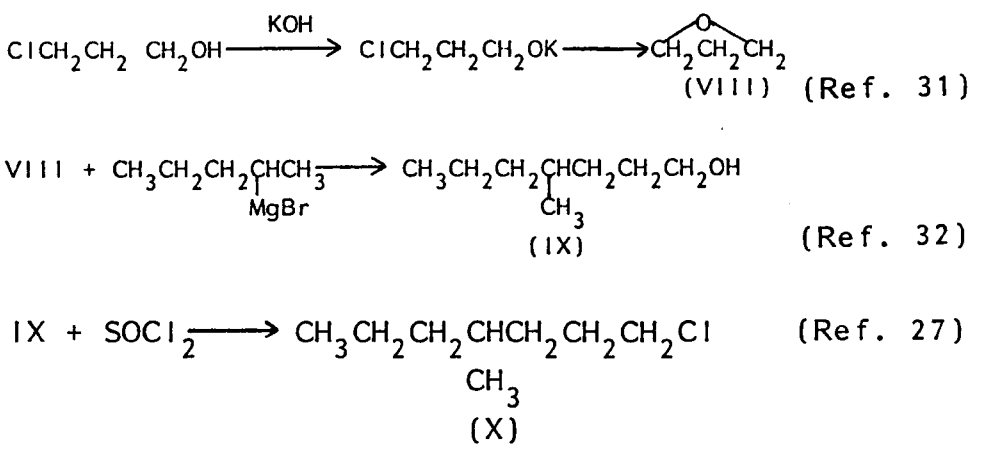
$$CH_3(CH_2)_4CHBrCH_3 + Mg \xrightarrow[3)\ H_2O]{2)\ CO_2} CH_3(CH_2)_4\overset{\displaystyle CH_3}{\overset{|}{CHCOOH}} \quad \text{(III)} \quad \text{(Ref. 28)}$$

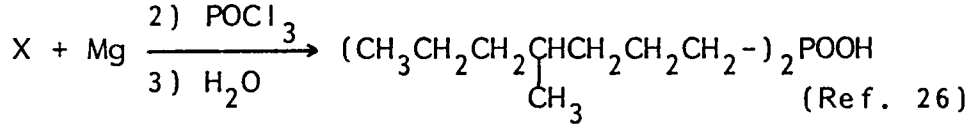


6. Di(3-methylheptyl) phosphinic acid



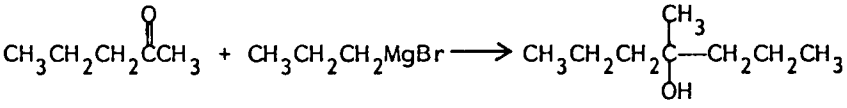
7. Di(4-methylheptyl) phosphinic acid



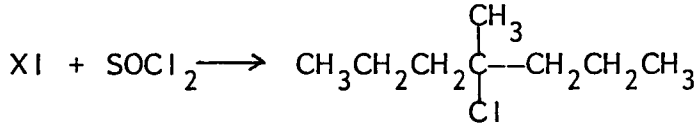


(Ref. 26)

8. Di(4-methyl-4-heptyl) phosphinic acid

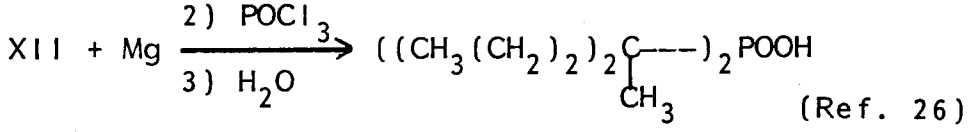


(XI) (Ref. 33)



(Ref. 27)

(XII)



(Ref. 26)

CHAPTER II

EXPERIMENTAL SECTION

H(DOP) Synthesis: Grignard Preparation

Magnesium, 16.05g (.66mole), was added to a flame dried 500mL 3-neck round bottom flask. Diethyl ether (240mL) was added and a solution of 115.88g (.6mole) of n-octyl bromide dissolved in 150mL of diethyl ether was added dropwise at a rate sufficient to maintain a gentle reflux (3h). The solution was heated until most of the magnesium had disappeared. The solution was allowed to cool and was transferred to a dropping funnel.

Synthesis of the Phosphinic Acid

The Grignard solution was added dropwise to a solution of 46g (.3mole) $POCl_3$ in 500mL of ether at a rate sufficient to maintain reflux (4h). The solution was allowed to stir overnight at room temperature. The hydrolysis and work up of the solution was conducted as follows: To a 1L dropping funnel was added 750mL of ice water which was added dropwise to the round bottom flask at such a rate as to maintain a gentle reflux. After the addition was complete, the contents of the round bottom flask were transferred to a 2L separatory funnel, the organic layer removed and the aqueous phase extracted twice with 500mL of diethyl ether. All organic phases were combined and condensed to a volume of 500mL. The organic phase was transferred to a 2L separatory funnel and treated twice with 250mL of 1N NaOH followed by several water washes. The remaining organic layer was discarded.

The aqueous phases were combined and reacidified with concentrated nitric acid. The crude solid was isolated by Buchner filtration and recrystallized in absolute ethanol twice to yield 26.19g of product (30% yield). A titration of the product showed it to be monoacidic with an equivalent weight of 289.4 (99.65% pure).

^{1}H NMR (CCl_4)_11.5 (s,1H,POOH), 1.2 (broad s,28H,-2$(CH_2)_7$-), .9 (s, 6H, 2CH_3-).

IR (neat) P = O 1090cm^{-1}, POH 950cm^{-1}.

H(DEHP) Synthesis

Synthesis of 2-Ethylhexyl Chloride. Thionyl chloride (146mL) was added dropwise to a solution of 238mL of 2-ethylhexanol in 150mL of pyridine at such a rate as to maintain the temperature at -10°C (2h). The solution was heated from -10°C to 104°C over a period of 6h and held at 104°C for 1.5h. The solution was cooled to room temperature, transferred to a 1L separatory funnel washed three times with 100mL 0.1N HCl and three times with 300mL of a saturated sodium bicarbonate solution. The organic layer was dried with sodium sulfate, filtered and distilled. B.P. 155°C, yield 81.84g (36%).

Synthesis of Grignard Reagent. Magnesium, 16.0g (.66mole), was added to a flame dried 500mL 3-neck round bottom flask. Diethyl ether (240mL) was added and a solution of 81.84g (.55mole) of 2-ethylhexyl chloride dissolved in 150mL of diethyl ether was added dropwise at a rate sufficient to maintain gentle reflux (3h). The solution was

heated until most of the magnesium had disappeared. The solution was allowed to cool and was transferred to a dropping funnel.

Synthesis of the Phosphinic Acid. The Grignard solution was added dropwise to a solution of 34.54g (.22mole) $POCl_3$ in 500mL of ether at a rate sufficient to maintain reflux (4h). The solution was allowed to stir overnight at room temperature. The hydrolysis and work up of the solution was conducted as follows: To a 1L dropping funnel was added 750mL of ice water which was added dropwise to the round bottom at such a rate as to maintain a gentle reflux. After the addition was complete, the contents of the round bottom flask were transferred to a 2L separatory funnel, the organic layer removed and the aqueous phase extracted twice with 500mL of diethyl ether. All organic phases were combined and condensed to 500mL. The organic phase was transferred to a 2L separatory funnel and treated four times with 250mL of 1N NaOH. The aqueous phase was discarded. The remaining organic layer was reacidified with 1N HCl and washed several times with 250mL additions of water until neutral. The organic layer was vacuum distilled at 2.5mm. The fraction obtained at 220°C (26.42g) was titrated and found to contain a very small amount of phosphonic acid but a large amount of product and the trialkyl phosphine oxide (eq. wt. 333.3).

To purify the product, a copper precipitation technique was employed.[34] The oil was dissolved in 125mL of toluene and treated with 63mL of a saturated sodium sulfate solution containing 2.79g of sodium hydroxide. The phases were mixed for 5min and the aqueous

phase removed and discarded. The organic phase was contacted with 75mL of 0.5M copper sulfate solution for 5min. The aqueous phase again was removed and discarded. The organic layer was condensed to 75mL and added to a rapidly stirring solution of 250mL of acetone. The precipitate was recovered by filtration and washed with excess acetone. The powder was dried overnight. To reacidify the extractant, the dry powder was added to a mixture of 62.3mL of toluene and 125mL of 4M sulfuric acid. The mixture was transferred to a 250mL separatory funnel, the aqueous phase removed and discarded. The organic phase was treated with two additional washings of acid and 5X125mL water. The toluene was removed at reduced pressure and the oil redissolved in ether and dried with sodium sulfate. The solution was filtered and the ether removed at reduced pressure. The product obtained, a clear oil, was titrated and found to be monoacidic with an equivalent weight of 296.3 (98% pure). Yield 15.33g (20% yield).

^{1}H NMR (CCl_4),δ12.3 (s,1H,POOH), 1.2 (m,12H,2-$(CH_2)_6$-), .9 (m,12H,4CH_3-).

IR (CCl_4), P = O 1245cm^{-1}, POH 1150cm^{-1}.

Di(2-Octyl) Phosphinic Acid Synthesis

Synthesis of 2-Chlorooctane. Thionyl chloride (146mL) was added dropwise to a solution of 238mL of 2-chlorooctane in 150mL of pyridine at such a rate as to maintain the temperature at -10°C (2h). The solution was heated from -10°C to 95°C over a period of 6h and held at 95°C for 1.5h. The solution was cooled to room temperature,

transferred to a 1L separatory funnel, washed three times with 100ml 0.1N HCl and three times with a saturated sodium bicarbonate solution. The organic layer was dried with magnesium sulfate, filtered and distilled. B.P. 155°C, yield 104.48g (47%).

Preparation of Grignard Reagent. Magnesium, 17.13g (.71mole), was added to a flame dried 500mL 3-neck round bottom flask. Diethyl ether (200mL) was added and a solution of 104g (.7mole) 2-chlorooctane dissolved in 100mL of ether was added dropwise at a rate sufficient to maintain gentle reflux (3h). The solution was heated until most of the magnesium had disappeared. The solution was allowed to cool and was transferred to a dropping funnel.

Synthesis of the Phosphinic Acid. In an attempt to aid in the separation of the phosphonic acid, a new procedure was utilized.[23] The Grignard solution was added dropwise to a solution of 24.4mL (.28mole) PCl_3 in 300ml of ether at a rate sufficient to maintain reflux (3h). The solution was cooled and 200mL of a saturated NaCl solution was added dropwise to the round bottom flask at such a rate as to maintain a gentle reflux. After the addition was complete, the contents of the round bottom flask were transferred to a 2L separatory funnel, the organic layer removed and vacuum distilled at .15mm. Three fractions were obtained and fraction #2 (65g, 175°C) contained the desired product, the dialkyl phosphine oxide. The fraction also contained some monoalkyl phosphinic acid impurities.

IR (CCl_4), P-H 2400cm^{-1}, P = O 1200cm^{-1}, POH 980cm^{-1}.

The dialkyl phosphine oxide was oxidized at room temperature to the phosphinic acid with 100mL of 30% H_2O_2. The contents were transferred to a 500mL separatory funnel, the organic layer removed and the aqueous phase extracted three times with 100mL of toluene. The organic phases were combined and dried with magnesium sulfate. The solution was filtered, the solvent removed by distillation and the oil titrated. The product was found to be monoacidic, but had a high equivalent weight (369.0).

The oil was dissolved in 335mL of toluene and treated with 170mL of a saturated sodium sulfate solution containing 7g of sodium hydroxide. The phases were mixed for 5min and the aqueous phase removed and discarded. The organic phase was contacted with 390mL 0.5N copper sulfate solution for 5min. The aqueous phase was again removed and discarded. The organic layer was condensed to 150mL and added to a rapidly stirring solution of 500mL acetone. A precipitate was not obtained, instead an oil/gel was found. The oil/gel was isolated by centrifuging and the excess acetone was removed by air drying. The residue was reacidified by adding it to a mixture of 200mL of toluene and 150mL of sulfuric acid in a 500mL separatory funnel. The aqueous phase was removed and discarded and the organic layer was treated with two additional washings of acid and 5X125mL of water. The organic layer was then dried with sodium sulfate, filtered and the toluene removed at reduced pressure. The product obtained an oil, was titrated and found to be monoacidic but with no improvement in the purity (eq. wt. 369.0). The entire process was repeated several times with no improvement in the purity.

The problem associated with the purification of the product was the formation of the gel instead of a precipitate. The gel proved very difficult to isolate and purify. Other precipitating solvents were tried: Methanol, 2-propanol, tert-pentanol, and methyl isobutyl ketone. All of these solvents gave a gel similar to the one obtained with acetone.

Chromatography was tried as well on the copper/extractant complex with silica gel and alumina. Silica gel with petroleum ether as the solvent had no retention time and gave very poor results. On the other hand, the copper/extractant complex did adsorb onto alumina, but could not be removed by any common organic solvents. The complex was removed by the placing of the packing material in a 1L separatory funnel and the extractions of the packing material with a mixture of 4M sulfuric acid and toluene. The organic layer was washed with water until neutral and dried over magnesium sulfate. The solution was filtered, the toluene removed by distillation and the oil titrated. The product was found to be monoacidic but with only a slightly improved equivalent weight of 327.0.

Sequential caustic scrubbings were also tried, including several washes with water in an attempt to isolate the sodium salt of the acid. The reacidification of the aqueous phase and isolation of the oil did not improve the purity of the product.

Recommendations for the Purification of the Remaining Phosphinic Acids

Based on the results obtained from the chromatographic elution of the copper/extractant complex with alumina, we believe that the

product can be purified with HPLC equipped with an alumina type column. Since the copper complex is blue, a UV-visible detector could be utilized to separate the phosphinic acid from the phosphine oxide. By exploring the parameters of the separation with HPLC, the possibility of a scale up to a preparative LC would be highly probable.

Conclusion

The syntheses of all the extractants listed are possible requiring only a fundamental knowledge of organic chemistry. The purification of the remaining extractants will be much more difficult if the copper/extractant complex can not be isolated in powder form. If the powder form can not be obtained, then a form of liquid chromatography will be required.

REFERENCES

REFERENCES

1. Bucholz, C. J. Chem. Ber. 1805, 4(17), 134.
2. Morrison, G. Anal. Chem. 1962, 34, 64.
3. Morrison, G. Anal. Chem. 1964, 36, 93.
4. Peppard, D. Adv. Inorg. Chem. Radiochem. 1966, 9, 1.
5. Peppard, D. Ann. Rev. Nuc. Sci. 1971, 21, 365.
6. Peppard, D. Proc. Sci. Tech. of Rare Earths 1963, 1, 89.
7. Cyanamid Promotional Literature 1980.
8. Tedesco, P.; Rumi, V. J. Inorg. Nuc. Chem. 1980, 42, 269.
9. Akiba, K.; Wada, M.; Kanno, T. J. Inorg. Nuc. Chem. 1980, 42, 261.
10. Kandil, A.; Farah, K. J. Inorg. Nuc. Chem. 1980, 42, 277.
11. Peppard, D.; Mason, G.; Lewey, S. J. Inorg. Nuc. Chem. 1965, 27, 2065.
12. Peppard, D.; Mason, G.; Andrejasish, C. J. Inorg. Nuc. Chem. 1966, 28, 2347.
13. Freiser, H.; Morrison, G. Ann. Rev. Nuc. Sci. 1959, 9, 221.
14. Jones, R. Physical and Mechanistic Organic Chemistry, Cambridge University Press: Cambridge, 1979, Chapter 5.
15. Hammond, G.; Hogle, D. J. Amer. Chem. Soc. 1955, 77, 338.
16. Islam, F.; Biswas, R. J. Inorg. Nuc. Chem. 1980, 42, 421.
17. Vandegrift, G.; Horwitz, E. J. Inorg. Nuc. Chem. 1980, 42, 119.
18. Katzin, L.; Mason, G.; Peppard, D. Spectrochimica Acta 1978, 34A, 57.
19. Peppard, D.; Mason, G.; Andrejasich, C. J. Inorg. Nuc. Chem. 1965, 27, 697.
20. Crofts, P.; Kosolapoff, G. J. Amer. Chem. Soc. 1953, 75, 3379.

21. Kosolapoff, G.; Struck, R. J. Chem. Soc. 1957, 3729.

22. White, J. J. Amer. Chem. Soc. 1950, 72, 1859.

23. Mason, G.; Lewey, S. J. Inorg. Nuc. Chem. 1974, 36, 911.

24. Mason, G.; Bollmeier, A.; Peppard, D. J. Inorg. Nuc. Chem. 1970, 32, 1011.

25. Cyanamide Canada Inc. European Patent Application Number 0 046 933.

26. Kosolapoff, G. J. Amer. Chem. Soc. 1942, 64, 2982.

27. Whitmore, F.; Karnatz, F.; Popkin, A. J. Amer. Chem. Soc. 1938, 60, 2540.

28. Gilman, B.; Parker, F. J. Amer. Chem. Soc. 1924, 46, 2816.

29. Schlesinger, H.; Brown, J. H. J. Amer. Chem. Soc. 1940, 62, 3429.

30. Huston, R.; Aget, A. J. Org. Chem. 1941, 6, 123.

31. Derick, C.; Bissel, D. J. Amer. Chem. Soc. 1916, 38, 2478.

32. Searles, S. J. Amer. Chem. Soc. 1951, 73, 124.

33. Kharasch, M. Grignard Reactions of Nonmetallic Substances, Prentice-Hall: New York, 1954, Chapter 6.

34. McDowell, W.; Perdue, P.; Case, G. J. Inorg. Nuc. Chem. 1976, 38, 2127.

PART III

POLYMER ABSORBED EXTRACTANTS

CHAPTER I

INTRODUCTION

The technique of liquid/liquid extraction for the removal of metals from aqueous systems is a very common and useful tool in the laboratory and in industry. In addition, advances in recent years of new and highly selective chelating extractants have made this technique for metal extraction attractive from an environmental and economic standpoint.[1] However, the problems associated with liquid/liquid extraction, mainly the entrainment of the extractant and solvent in the aqueous phase, have resulted in the investigation of other options for metal recovery.[7]

One alternative is to use polymer supported ion-exchange resins. Unfortunately, the choice of commercially available resins is rather limited and what is available lacks the selectivity often found with liquid/liquid extractants.[2-7]

Another alternative, which is actually a combination of the two previous systems, is to entrap the liquid extractant in a cross-linked polymer matrix to give a liquid/solid extractant. The major advantage is the ability to place the ion-exchange material in a column and elute with the metal-containing aqueous solution. The ideal polymer absorbed extractant (PAE) would meet the following requirements:[7]

1. Good selectivity
2. Good metal ion mobility between the aqueous and resin phase
3. Reasonable ion-exchange capacity

4. Low extractant loss from the polymer matrix

5. A matrix with good chemical and physical stability

Selectivity is dependent on the type of extractant entrapped in the polymer matrix. The extractant must be a liquid or retained in the liquid state by the addition of a solvent.[7] Mobility, capacity, and stability requirements are more difficult to meet and require modifications of the polymer matrix to optimize the performance of the resin, as will be discussed below.

For this particular study, the extractant chosen was commercially available di(2-ethylhexyl) phosphoric acid (DEHP). This extractant was chosen for two reasons: (1) It is an acidic extractant subject to different retention properties within the polymer matrix in acid, base and water, and (2) it has been reported in the literature to have a very high affinity for certain transition metals.[8] The base polymer support chosen was a styrene/divinylbenzene (SDVB) copolymer in bead form (.42-.84mm diameter). The technique for the impregnation of the extractant in the SDVB matrix was the wet impregnation method.[7] This technique involves dissolving the extractant (DEHP) in a diluent (toluene) and contacting the polymer (SDVB) with an excess of solution until equilibrium is attained. For this particular study, 1M DEHP was utilized as the swelling solution. The excess solution was removed by Büchner filtration at reduced pressure. A systematic study was employed to define the problems associated with PAEs and to modify the polymer matrix in such a way as to meet the aforementioned requirements.

CHAPTER II

RESULTS AND DISCUSSION

PAE Hydrophobicity

In the initial phase of our investigation of PAEs, our first concern was the degree of hydrophobicity on the part of the impregnated copolymer. Unfunctionalized SDVB beads aggregate when contacted with water. Impregnated gel SDVB beads also display aggregation, which can result in a substantial decrease in the total resin bed surface area. This decrease in the surface area can greatly slow the kinetics of the process and decrease the overall efficiency of the extraction. Previous publications have discussed this problem at length and various solutions proposed.[7,9] For example, pretreating the PAEs with aqueous metal salts and reacidifying does help to hydrate the surface.[7] Small,[9] however, in his work with PAEs impregnated with tributyl phosphate (TBP), found that surface sulfonating the gel (gel-ss) before impregnation greatly aided the hydration of the surface of the PAE. Unfortunately, Small did not publish the exact procedure for surface sulfonation. We, therefore, embarked on a systematic study of the sulfonation of SDVB gel beads as a function of time, temperature, reaction conditions and cross-linking. From this study, we developed a procedure which gave sulfonation to .01mequiv/g (see experimental section for details). This low sulfonation of the surface of the copolymer gel did not affect the swelling ability of the gel (Table I) and did greatly enhance the surface hydration of the PAE gels.

TABLE I

SWELLING RATIO IN TOLUENE OF SDVB BEADS AS A FUNCTION OF CROSS-LINK LEVEL

Type	Cross-Link Level %DVB	Swelling Ratio
Gel	2	3.45
gel-ss	2	3.50
gel	5	2.50
gel	10	1.50
gel	15	1.50
MR	2	3.92
MR	3	3.00
MR	5	2.30
MR	10	1.68
MR	15	1.40

Also investigated were macroreticular (MR) copolymer beads. The principal advantage of MR over gel beads is the greater surface area (100-300m^2/g) due to the presence of pores within the bead (100-1000 Å) (see Part I). Preliminary experiments with MR-PAE showed very little aggregation when contacted with aqueous solution and allowed them to be used without any surface modifications.

PAE Cross-Link Level

The cross-link level of the PAEs are very important. It must be low enough to allow for sufficient swelling of the beads, but must be high enough to prevent the beads from becoming a jelly. Table I outlines the swelling ratio as a function of the cross-link level and bead type (gel, MR).

The 2% cross-linked gel and the 5% cross-linked MR beads were utilized in this study so comparisons could be made to the resins reported in the literature (Table II).

PAE Capacities

Table II lists the overall average capacities obtained for the PAE by the wet impregnation method in comparison to other resins reported in the literature. Also listed are the grams of the swelling solution absorbed by the beads as a function of bead type. The capacities were measured spectrometrically (see experimental section) and are reported in terms of milliequivalents of acid sites per gram of dry beads (mequiv/g).

There is clearly no difference in the uptake of solution and capacity of the gel and gel-ss PAE; however, the MR-PAE does have a much higher capacity by virtue of the amount of solution it absorbed.

TABLE II

AVERAGE PAE CAPACITY AND SWELLING SOLUTION UPTAKE WITH A 1M DEHP SWELLING SOLUTION

Type	Cross-Link Level %DVB	Uptake of Swelling Solution(g)/g beads[a]	Capacity[b] mequiv/g
XAD-2[6]	2	---	1.28
Levextrel 0C1026[6]	8	---	0.77
gel-ss	2	0.625	0.62
gel	2	0.605	0.61
MR	5	2.242	1.46

[a]Resin number DW-01-094 B,E,H.

[b]Capacity ±.05 mequiv/g.

Retention of Capacity

One of the most important aspects of a PAE is the retention of the extractant within the polymer matrix. It has been observed that the extractant does leach out of the gel-PAE polymer matrix with time: a 20% capacity loss after 3 weeks is typical. MR-PAEs, on the other hand, do not have this leaching problem and maintain their capacity after long periods of time.

To define what conditions are responsible for the extractant retention, an elution study of PAE beads was undertaken with solutions of different pH and ionic strength. The experiment was conducted by placing 5g of PAE in a column and eluting with various solutions at a rate of 1L/h. After each liter, a sample (.05g) was taken and analyzed for extractant content. To understand the role that the solvent plays in the retention of the extractant, PAE which had been oven-dried at 60°C were included in the study as well. Table III outlines the results of the elution study.

From the data in Table III, one can draw several conclusions:

1. At a neutral pH, both general types of PAE (toluene removed and present) had similar retention properties. In all other cases, the toluene removed PAEs were better at retaining the extractant.
2. PAEs utilized at a high pH show excessive loss of the extractant.
3. MR-PAEs have the best overall performance for capacity retention.

TABLE III

THE PERCENT RETENTION OF THE ORIGINAL CAPACITY OF PAE ELUTED WITH AQUEOUS SOLUTIONS[a]

Type	Capacity mequiv/g	Water		4wt% HCl		4wt%NaOH		4wt% $NaNO_3$		4wt% $NaNO_3$ .1N NaOH	
		1L	5L	1L	5L	1L	5L	1L	5L	1L	5L
Toluene Present[b]											
gel	0.63	97	89	84	84	10	--	81	65	2	--
gel-ss	0.60	93	98	81	80	22	26	77	59	13	--
MR	1.46	100	86	100	100	88	83	100	100	71	33
Toluene Removed[c]											
gel	0.62	98	91	100	100	87	82	100	88	74	73
gel-ss	0.61	82	83	100	98	77	68	87	82	81	80
MR	1.46	100	90	100	100	78	70	100	86	81	20

[a]All capacities are ±.05mequiv/g, % Retention ±5%.

[b]Run number DW-01-102.

[c]Run number DW-01-122.

Ion-Exchange: Definition of Terms

The experiments were carried out with the aid of a radioactive isotope of zinc (^{65}Zn). Every sample tested for a given series of experiments contained the same amount of radiotracer. After a specific period of time, depending on the experiment, 1mL of aqueous solution was removed and counted. All results for each series of experiments were based on an aqueous blank count which contained an identical concentration of solution and tracer, but without PAE being present.

The initial ratio (R_i) is the ratio of the mequiv of metal present initially to the mequiv of acid sites present.

The percent loading is the percent of acid sites occupied on the ion-exchange material for a given R_i. Examples:

At a R_i of .1, the maximum percent loading attainable is 10%.

At a R_i of 1, the maximum percent loading attainable is 100%.

Ion-Exchange Capabilities of DEHP

DEHP is a well-known extractant for the removal of divalent cations, especially transition metals.[1,11-14] The selectivity of DEHP for some of the first row transition metals has been determined to be Zn(II) > Cu(II) > Mn(II) ∿ Fe(II) > Co(II) > Ni(II).[11-14] However, in most organic solvents, DEHP exists as a dimer.[15] For the extraction of a monovalent ion such as sodium from solution, one dimer pair is required, but for the extraction of divalent cations such as zinc, four DEHP units or two dimers are required.[11-14] The zinc/DEHP complex is tetrahedral in structure, but can exist as a polymeric complex with DEHP as the bridging ligand. The degree of polymerization depends

on both the metal concentration and temperature.[11-14]. The separation of any ions, e.g., Zn(II) and Na(I), can be accomplished through direct complexation or indirect exchange.

We have investigated the loading behavior of DEHP as a function of DEHP concentration (Table IV), the initial ratio of zinc (Table V) and volume of organic phase (Table VI). In order to maintain a constant ionic strength in the aqueous phase, all extractions reported were performed in a 4M sodium nitrate background.

Based on the data in Tables IV through VI, two conclusions can be drawn: (1) For a given organic volume, the extent of DEHP loading of zinc remains fairly constant, and (2) at different R_i the DEHP extracts different amounts of zinc.

Metal Ion Mobility-Kinetics of PAE

Given the elution results of the toluene removed PAE (Table III), the question arose as to whether the better retention properties were a function of the lack of solvent or accessibility. If the problem was accessibility, the better retention properties of the toluene removed PAE could be offset by very slow rates of metal ion extraction. To test the question of accessibility, a kinetic study was performed at $R_i = 1$ with a 4M $NaNO_3$ background. Table VII outlines the kinetic data for the time required for the maximum absorption of zinc.

Four observations were made:

1. The times required for the extraction of the maximum amount of zinc for both types of PAE (toluene present and removed) were not

TABLE IV

THE LOADING BEHAVIOR OF DEHP/TOLUENE AS A FUNCTION OF DEHP CONCENTRATION[a] FOR THE EXTRACTION OF ZINC AT $R_i = 1$[b]

Capacity of Solution[c] mequiv/g	% Zn Loading (±3%)
0.41	16
0.54	16
1.27	15
3.10 (NEAT)	22

[a]5mL of total organic phase volume.

[b]Run number DW-01-154.

[c]Capacity ±.05 mequiv/g.

TABLE V

THE LOADING OF 1ML OF 1M DEHP[a] WITH DIFFERENT INITIAL RATIOS OF ZINC AND A 4M $NaNO_3$ BACKGROUND[b]

R_i	% Zn Loading[c]	R_i	% Zn Loading
0.1	8	1.0	23
0.3	16	1.1	23
0.5	19	1.3	26
0.7	21	1.5	25
0.9	23		

[a]Capacity 1M DEHP 1.11mequiv/g.

[b]Run number DW-01-180.

[c]Loading ±3%.

TABLE VI

THE LOADING BEHAVIOR OF 1M DEHP AS A FUNCTION OF THE ORGANIC PHASE VOLUME FOR THE EXTRACTION OF ZINC AT A $R_i = 1$[a]

Volume of 1M DEHP[b] mL	% Zn Loading (±3%)
1	22
2	19
3	16
4	16
5	16

[a]Run number DW-01-178.

[b]Capacity 1.11mequiv/g.

TABLE VII

KINETIC DATA FOR PAE: TIME VS. MAXIMUM PERCENT Zn ABSORBED IN A 4M $NaNO_3$ BACKGROUND[a]

Type	Capabity[b] mequiv/g	%Abs.[b] 1min	%Abs. 5min	%Abs. 10min	%Abs. 30min
Toluene Present					
gel-ss	0.59	20	26	28	26
MR	1.49	24	26	27	23
Toluene Removed					
gel-ss	0.59	40	43	48	50
MR	1.49	12	17	38	34

[a]Run number DW-01-143.

[b]Percent absorbed ±3%; Capacity .05mequiv/g.

significantly different. We conclude that extractant accessibility to the solution is not a problem for the toluene removed PAE.

2. There is no difference in the time required for the gel and MR-PAE to obtain maximum absorption. For ion-exchange resins, the time required for a MR to obtain equilibrium is much less than that of a comparable gel.[16] For example, a 10% cross-linked phosphinic gel ion-exchange resin takes between 1-2h for equilibrium to be attained with zinc. The corresponding 10% crosslinked MR phosphinic bead takes 5min.[16]

3. As had been noted in the literature,[17] PAE impregnated with DEHP extracts more zinc than does DEHP in solution.

4. The amount of zinc extracted for the toluene removed PAEs did decrease over time after the attainment of a maximum value (Table VIII).

TABLE VIII

ZINC ABSORPTION AS A FUNCTION OF TIME FOR TOLUENE REMOVED PAE IN A 4M $NaNO_3$ BACKGROUND[a]

Type	Capacity[b] mequiv/g	%Abs.[b] 10min	%Abs. 1h	%Abs. 3h	%Abs. 5h	%Abs. 17h	%Abs. 48h
gel-ss	0.59	48	50	47	33	27	29
MR	1.49	38	33	34	33	33	32

[a]Run number DW-01-143.

[b]Percent absorbed ±3%; Capacity ±.05mequiv/g.

The decrease in the zinc loading of the toluene removed PAE is caused by the loss of extractant to the solution over a period of time. The extractant loss was observed by the increasing opaqueness of the aqueous solution, but was never quantified by a phosphorus elemental analysis. However the loss of extractant to the solution is an equilibrium process with equilibrium being attained between 5 and 17h for the toluene removed gel-PAE and 1h for the toluene removed MR-PAE. Toluene present gel and MR-PAEs retained their extractant and no difference was noted between long and short contact times (Table IX).

TABLE IX

ZINC ABSORPTION AS A FUNCTION OF TIME FOR TOLUENE PRESENT PAE IN A 4M $NaNO_3$ BACKGROUND[a]

Type	Capacity[b] mequiv/g	%Abs.[b] 10min	%Abs. 17h	%Abs. 48h
gel-ss	0.59	28	27	29
MR	1.49	28	29	32

[a]Run number DW-01-143.

[b]Percent absorbed ±3%; Capacity ±.05mequiv/g.

Ion-Exchange Capabilities: The Loading of PAE with Zinc

The ion-exchange capabilities of the PAEs (toluene present and removed) were investigated with different ratios of zinc in a 4M $NaNO_3$ background. Based on the results in Table VIII indicating a strong time dependency for the extraction of zinc by the toluene removed PAE, all extractions were performed at 17h (Table X).

TABLE X

THE LOADINGS OF THE PAEs WITH DIFFERENT INITIAL RATIOS OF ZINC WITH 4M $NaNO_3$ BACKGROUND[a]

Type	Capacity[b] mequiv/g	% Load.[b] R_i = .1	% Load. R_i = .3	% Load. R_i = .5	% Load. R_i = .7	% Load. R_i = 1	% Load. R_i = 1.3	% Load. R_i = 1.5
Toluene Present[c]								
gel-ss	0.594	8	17	22	28	29	32	27
MR	1.498	8	16	19	22	28	26	26
Toluene Removed[c]								
gel-ss	0.594	8	14	17	19	27	--	--
MR	1.498	9	20	29	32	37	44	--
1M DEHP (1mL)[d]		8	16	19	21	23	26	25

[a]Extraction performed at 17h.

[b]Loadings reported are ±3%; Capacity ±.05mequiv/g.

[c]Run number DW-01-186.

[d]Run number DW-01-178.

At 17h, the loading capabilities of both gel-PAEs are similar. However, the MR-PAEs are slightly different, with the toluene removed MR-PAE extracting slightly more zinc (10% more, R_i = 1). In all cases investigated, the PAEs removed more zinc than 1M DEHP.

Modification of the Polymer Support: Study of the Microenvironmental Effect[18]

To better understand the role of the SDVB polymer matrix in the absorption and retention of the extractant, modifications of the matrix were made by copolymerizing different monomers with SDVB (M-SDVB). The monomers chosen for the copolymerization possess groups of varying degrees of polarity and hydrogen bonding capabilities. Concentrations of the new monomer (5 and 10wt%) were chosen as not to affect the overall swelling properties of the beads in toluene. Gel beads were chosen since, being lower in capacity, any enhancement of the capacity would be easily recognized. In addition, based on the retention properties previously discussed, toluene removed gel-PAEs were chosen. Table XI outlines the types, concentration and capacities of the resulting PAEs.

Based on the results in Table XI, it was concluded that the introduction of different types of monomers to the polymer matrix did not significantly increase the amount of DEHP absorbed by the beads. Since higher concentrations of the monomer would result in a change in the swelling ratio in toluene, no higher concentrations were investigated.

TABLE XI

MODIFIED SDVB POLYMER SUPPORTS WITH ADDITIONAL MONOMERS[a]

Monomer[b]	Concentration of Monomer (wt%)	Capacity[c] mequiv/g
Styrene (Sty)	--	0.47
Vinyl benzyl chloride (VBC)	5	0.47
VBC	10	0.52
Acrylic acid (AA)	5	0.50
AA	10	0.44
Methyl methacrylate (MMA)	5	0.48
MMA	10	0.47
Acrylonitrile (AN)	5	0.41
AN	10	0.41

[a]Run number DW-01-199.

[b]All resins contain 5wt% DVB.

[c]Capacity ±.05mequiv/g.

To test the retention properties of the M-SDVB PAE, an elution study was performed with water and a 4wt% $NaNO_3$/.1N NaOH solution. As before, the PAEs were eluted at a rate of 1L/h for a total of 5L. Samples of similar size were taken after each liter and analyzed. The results are outlined in Table XII.

The results obtained in Table XII were quite surprising. The addition of a nitrile, carbonyl or a chloride had virtually no effect on the retention properties of the PAEs. The exception was the acrylic acid-containing polymer matrix. The retention properties of both 5 and 10% AA-SDVB matrix were excellent even under the most adverse conditions investigated. Based on these results, one can conclude that the life expectancy of a AA-SDVB PAE would be much greater than that of a pure SDVB-PAE.

TABLE XII

THE PERCENT RETENTION OF THE ORIGINAL CAPACITY OF M-SDVB PAE ELUTED WITH AQUEOUS SOLUTIONS[a]

Type	Capacity[b] mequiv/g	Water[c] 1L	Water[c] 5L	4wt% $NaNO_3$/.1N NaOH 1L	4wt% $NaNO_3$/.1N NaOH 5L
Sty	0.47	94	86	83	58
VBC(5)	0.52	100	80	83	76
VBC(10)	0.52	100	86	87	72
MMA(5)	0.48	91	81	81	86
MMA(10)	0.47	97	80	79	69
AN(5)	0.41	100	87	86	64
AN(10)	0.41	97	87	84	50
AA(5)	0.50	99	99	99	99
AA(10)	0.44	100	100	100	100

[a]Run number DW-01-199.

[b]Capacity ±.05mequiv/g.

[c]Percent retention ±5%.

The next question addressed was the extracting capabilities of the M-SDVB PAE with zinc. The results obtained (Table XIII), with the exception of the AA-SDVB PAE, are very similar to those found with the toluene removed gel-PAE (Table X). The AA-SDVB PAE, however, picked up substantially smaller amounts of zinc. A model study was performed with a 10% caprylic acid/1M DEHP solution and similar results were obtained: the presence of a carboxylic acid decreases the amount of zinc extracted by DEHP (Table XIII).

Although the 10% AA-SDVB PAE had better retention properties than the other M-SDVB PAE investigated, their absorption of zinc makes them impractical for zinc extraction. However, if the retention

TABLE XIII

THE LOADING CAPABILITIES OF M-SDVB PAE WITH ZINC AT DIFFERENT INITIAL RATIOS[a] WITH A 4M $NaNO_3$ BACKGROUND

Type	Capacity[b] mequiv/g	% Load.[c] R_i = .1	% Load. R_i = 1	% Load. R_i = 1.5
Sty	0.47	9	39	42
VBC(5)	0.52	9	32	36
VBC(10)	0.52	9	36	34
MMA(5)	0.48	9	35	31
MMA(10)	0.47	9	40	46
AN(5)	0.41	9	33	36
AN(10)	0.41	9	35	40
AA(5)	0.50	7	21	19
AA(10)	0.44	0.2	2	0.1
1M DEHP	1.11	8	22	25
10% Caprylic Acid/ 1M DEHP	1.01	-	11	-

[a]Run number DW-01-199.

[b]Capacity ±.05mequiv/g.

[c]Loadings reported were measured at 3h, ±3%.

of the extractant is of greater importance than the removal of zinc, the 5% AA-SDVB would be an excellent choice.

Additional Extractant Used: Di(2-ethylhexyl) Phosphinic Acid

To further understand the loss of extractant from the polymer matrix, an extractant with a higher pK_a (Table XIV) di(2-ethylhexyl) phosphinic acid H(DEHP) was impregnated into a 5% MR bead. The solvent was removed and the PAE was analyzed by elution with water and a 4wt% $NaNO_3$/.1N NaOH solution. The results are outlined in Table XIV.

TABLE XIV

THE PERCENT RETENTION OF THE ORIGINAL CAPACITY OF A 5% MR-PAE IMPREGNATED WITH H(DEHP) ELUTED WITH AQUEOUS SOLUTIONS[a]

PAE Extractant	pK_a of Extractant[15]	Initial[b] Capacity mequiv/g	Water[c] 1L	Water[c] 5L	42t% $NaNO_3$/.1N NaOH 1L	42t% $NaNO_3$/.1N NaOH 5L
DEHP[d]	3.49	1.46	100	90	81	20
H(DEHP)	5.91	1.69	96	97	26	10

[a]Run number DW-01-139.

[b]Capacity ±.05mequiv/g.

[c]% Retention ±5%.

[d]Run number DW-01-122.

The retention of H(DEHP) in the bead is slightly better in water, but much worse in the $NaNO_3$/NaOH solution. Thus a higher pK_a of the extractant does not increase the retention properties of the extractant within the polymer matrix.

In addition to examining the retention properties of the extractant, the ion-exchange properties of the extractant and the PAE were measured with zinc. Table XV outlines these results.

DEHP has a higher affinity for zinc than does H(DEHP) (Table XV). As found with DEHP, H(DEHP) in the resin phase extracts more zinc than in solution.

TABLE XV

EXTRACTION CAPABILITIES OF ZINC WITH A H(DEHP)-PAE AT A R_i = 1 WITH A 4M $NaNO_3$ BACKGROUND[a]

Type	% Zn Loading[b]
MR-PAE DEHP[c]	33
MR-PAE H(DEHP)	17
1M DEHP (1mL)[d]	24
1M H(DEHP) (1mL)	9

[a]Run number DW-01-139.

[b]Loadings were measured at 17h (±3%).

[c]Run number DW-01-122.

[d]Run Number DW-01-180.

CHAPTER III

RECOMMENDATIONS AND CONCLUSION

Recommendations

Based on the retention properties of the AA-SDVB PAEs (Table XII), an additional experiment is required to define the type of interaction that is occurring with the extractant. Since the MMA-SDVB PAE had similar retention properties as the SDVB-PAE (Table XII), it is postulated that the better retention properties of the AA-SDVB PAE are due primarily to the acidic hydrogen via hydrogen bonding with the extractant. To determine if such a strong hydrogen bonding group is required, the study of a M-SDVB polymer incorporating a hydroxyl group in the backbone is needed. To accomplish this copolymerization, the following two experiments are proposed: (1) The copolymerization of SDVB with vinyl acetate followed by hydrolysis to the alcohol with base, and (2) the copolymerization of SDVB with VBC followed by hydrolysis to the benzyl alcohol. The extent of the hydrolysis of both M-SDVB can be measured as follows: (1) The vinyl acetate hydrolysis can be followed by IR via the decrease in the carbonyl stretch at 1750-1735cm^{-1}, and (2) the VBC hydrolysis can be followed by the loss of chlorine via a sodium fusion analysis.

Conclusion

From the convenience of ion-exchange resins to the selectivity of liquid/liquid extractants, PAEs offer the best of both worlds. Based on the overall results, the toluene removed MR-PAE had the highest

capacity and the best retention properties of the PAEs examined. The 5% AA-SDVB PAE, although not extracting as much zinc, did have excellent retention properties. The capacity problem of metal extractions can be circumvented on a larger scale by increasing the resin bed volume.

CHAPTER IV

EXPERIMENTAL SECTION

Suspension Beads

See experimental section of Part I.

Bulk Polymerized Beads

All M^a-SDVB copolymer beads were made by the following procedure:

5% M-SDVB: To a 20mL tared bottle having a plastic lined cap was added 8.51g of reagent grade styrene, .89g of technical grade DVB (55.4% DVB, 46.6% ethyl benzene) and .5g of M. The contents were mixed well and .1g of benzoyl peroxide (BPO) was added and dissolved.

10% M-SDVB: To a 20mL tared bottle having a plastic lined cap was added 8.01g of reagent grade styrene, .89g of technical grade DVB and 1g of M. The contents were mixed well and .1g of BPO was added and dissolved. (a) M = VBC, MMA, AA, AN, Sty.

Polymerization procedure: The sealed bottles were placed in an oil bath and heated up to 80°C over 2h. The temperature was then maintained for 10h.

Particle size: After copolymerization, the polymer mass was converted to particle form by grinding the polymer in a micromill. The particles were then sieved and only the -20+40 mesh cut was collected.

Wet Impregnation Procedure

Copolymer (2.5g) was added to a 25mL bottle having a plastic lined cap and to which was added 20mL of a 1.0M DEHP/toluene solution. The beads were allowed to swell with occasional shaking for 48h. Table XVI outlines the capacity of the PAEs as a function of swell time.

TABLE XVI

CAPACITY OF PAE AS A FUNCTION OF SWELL TIME IN 1M DEHP SOLUTION[a]

Type	Swell Time	Capacity[b] mequiv/g
gel-ss	48h[c]	0.61
gel-ss	168h	0.60
gel-ss	336h	0.60

[a]Run number DW-01-120.

[b]Capacity ±.05mequiv/g.

[c]Run number DW-122A.

After 48h, the excess swelling solution was removed by suction filtration with a coarse fritted funnel equipped with a natural rubber membrane to maintain the pressure of 720mm for 5min.

Solvent Removal Procedure

Wet PAE in a 20mL bottle was placed in a drying oven at 60°C for 16h. Other techniques for toluene removal are outlined in Table XVII.

TABLE XVII

DRYING OF PAE--THE REMOVAL OF TOLUENE[a]

Technique for Drying	Capacity[b] gel-ss mequiv/g	Capacity gel mequiv/g	Capacity MR mequiv/g
110°C 16h	0.62	0.70	1.46
60°C 16h	0.61	0.64	1.51
40°C 16h	0.53	0.56	1.34
10mm/40°C 48h	0.70	0.72	1.52
10mm/20°C 48h	0.56	0.58	1.43
Air Dry 6psi/20°C 72h	0.53	0.56	1.37

[a]Run number DW-01-102 ABC.

[b]All capacities ±.05mequiv/g.

Retention Properties of PAE after Elution with Base

The retention properties after the elution with base were measured by two methods:

1. 3g of PAEs were placed in a column and eluted with 500mL of 1N NaOH, 4N HCl and water, in that order, at a rate of 1L/h. After each elution, a sample (.05g) was taken and analyzed.

2. MR-PAEs, after elution with 5L of .1N NaOH over 5h (1L/h), were eluted with 1L of water (1L/h) and a sample was taken and analyzed. The results are outlined in Table XVIII.

Phosphorus Elemental Analysis

See experimental section of Part I.

TABLE XVIII

THE RETENTION PROPERTIES OF PAE AFTER ELUTION WITH BASE

Type	Initial[a] Capacity mequiv/g	0.5L 1N NaOH[b] % Retention	0.5L 4N HCl after NaOH % Retention	0.5L Water after NaOH/HCl % Retention	1L of Water after 5L .1N NaOH % Retention
Toluene Present					
MR[c]	1.22	--	--	--	0.0
gel-ss[d]	0.65	30	30	30	--
MR[d]	1.46	92	99	100	--
Toluene Removed					
MR[e]	1.03	--	--	--	10

[a]Capacity ±.05mequiv/g.

[b]% Retention ±5%.

[c]Run number DW-01-102.

[d]Run number DW-01-141.

[e]Run number DW-01-122.

Zinc Analysis

See experimental section of Part I.

Surface Sulfonation Procedure

The copolymer (20g) was placed in contact with 150mL of concentrated sulfuric acid at 105°C for 10min. The beads were removed by suction filtration and washed with water until neutral. The beads were dried at 110°C for 16h and analyzed by titration with .01N NaOH. Average capacity obtained .01mequiv/g.

Sulfonation Study of SDVB Gels

Procedure for Obtaining Fully Functionalized Sulfonic Resins. The SDVB copolymer (10g) is placed in a 3-neck 250mL round bottom equipped with a thermometer, condenser and overhead stirrer. Dichloroethane (EDC), 20.6g, is added to swell the beads (10min) and a solution of 88.4g of 96% H_2SO_4 and 1.79g of water is added to the round bottom. The reaction mixture is allowed to stir for 15 min at room temperature and is heated to 130°C over 3h. The temperature is held for 15min and allowed to cool to 110°C, at which time, 56.4g of water is added at such a rate to maintain the temperature between 110-120°C. The solution is siphoned out (55mL) and an additional water wash is added at a rate to maintain the temperature at 95-110°C. Three additional water washes are utilized at a rate to maintain a temperature of 50°C. Two additional water washes are performed at room temperature. The beads are transferred to a column and eluted with water until neutral (1L/h). For a list of the capacities obtained with this procedure see Part I.

Temperature Study. To understand the role of temperature in the sulfonation of SDVB gels, all reaction conditions except temperature were kept constant. Table XIX outlines the results thus obtained.

Swell Time Study. To see if the low temperature capacity could be increased, a swell time and reaction time study was carried out at 25°C. The copolymer was allowed to swell for various times in EDC

TABLE XIX

EFFECT OF TEMPERATURE ON THE CAPACITY OF SULFONIC ION-EXCHANGE RESINS

Run Number DW-01-	Cross-Link Level %DVB	Temperature °C	Capacity mequiv/g
31D	2	130	5.00
31B	15	130	3.11
43C	2	60	5.09
43D	15	60	3.13
45C	2	45	3.97
45D	15	45	0.36
45A	2	35	3.18
45B	15	35	0.24
48A	2	25	0.00
48B	15	25	0.00

before the addition of the H_2SO_4/water solution. Table XX outlines the results found with the swell time experiment.

TABLE XX

EFFECT OF SWELL TIME IN DICHLOROETHANE ON THE DEGREE OF SULFONATION AT 25°C

Run Number DW-01-048	Cross-Link Level %DVB	Swell Time in EDC	Reaction Time	Capacity mequiv/g
A	2	10min	4h	0.00
B	15	10min	4h	0.00
C	2	12h	4h	0.00
D	15	12h	4h	0.00
E	2	24h	12h	4.29
F	15	24h	12h	0.22

Based on these results, it was concluded that at high temperatures (e.g., 60°C), a fully functionalized resin can be made independent of swell time. At lower temperatures (e.g., 25°C), a long swell time is needed along with a long reaction time to obtain a reasonable degree of sulfonation.

Measurement of Capacity of Sulfonic Resins

Acid capacity was measured by cation exchange with 4wt% $NaNO_3$. See experimental section of Part I for details.

REFERENCES

REFERENCES

1. Peppard, D. Adv. Inorg. Chem. Radiochem. 1966, 9, 1.

2. Peppard, D. Ann. Rev. Nuc. Sci. 1971, 21, 365.

3. Kunin, R. "Ion-Exchange Resins," John Wiley: New York, 1958, 2nd ed., Chapter 1, 2.

4. Reichenberg, D. In "Ion Exchange"; Marinsky, J. A., Ed.; Marcel Dekker: New York, 1966, Vol. 1, Chapter 7.

5. Diamond, R. M.; Whitney, D. C. In "Ion Exchange"; Marinsky, J. A., Ed.; Marcel Dekker: New York, 1966, Vol. 1, Chapter 8.

6. Wheaton, R. M.; Hatch, M. J. In "Ion Exchange"; Marinsky, J. A., Ed.; Marcel Dekker: New York, 1969, Vol. 2, Chapter 6.

7. Warshawsky, A. In "Ion-Exchange and Solvent Extraction"; Marinsky, J. A., Ed.; Marcel Dekker: New York, 1981, Vol. 8, Chapter 3.

8. Peppard, D. Proc. Sci. Tech. of Rare Earths 1963, 1, 89.

9. Small, H. J. Inorg. Nucl. Chem. 1961, 18, 232.

10. Flett, D. Chem and Ind. 1977, 641.

11. Barnes, J.; Setchfield, J.; Williams, G. J. Inorg. Nuc. Chem. 1976, 38, 1065.

12. Grimm, R.; Kolarik, Z. J. Inorg. Nuc. Chem. 1974, 36, 189.

13. Grimm, R.; Kolarik, Z. J. Inorg. Nuc. Chem. 1976, 38, 1493.

14. Islam, F.; Biswas, R. J. Inorg. Nuc. Chem. 1980, 42, 421.

15. Kosolapoff, G.; Powell, J. J. Chem. Soc. 1950, 3535.

16. Wilson, D. This Thesis, Chapter 1.

17. Warshawsky, A. Trans. Instit, Min. Metal. 1974, 83, C101.

18. Healy, T; Peppard, D.; Mason, G. J. Inorg. Nuc. Chem. 1962, 24, 1429.

19. Vandegrift, G.; Horwitz, E. J. Inorg. Nuc. Chem. 1980, 42, 119.

VITA

David Leon Wilson II was born in Chattanooga, Tennessee, on September 10, 1958. He attended elementary schools in Huntingburg, Indiana, Ludlow, Kentucky, Danville, Kentucky, Bellville, Illinois, and graduated from Harriman High School, Harriman, Tennessee, in June 1976. The following September he entered The University of Tennessee, Knoxville, and in June 1981 he received a Bachelor of Arts degree in Chemistry. In the Fall of 1981, he accepted a teaching assistantship at The University of Tennessee, Knoxville, and began study towards a Master's degree. This degree was awarded in August 1985.

The author has accepted an offer for a teaching assistantship leading to a Doctorate of Philosophy in Chemistry at Oklahoma State University, Stillwater, and will be attending August 1985.