To the Graduate Council:

I am submitting herewith a dissertation written by Marc A. Strand entitled "Synthesis of New Solid-Supported Phosphorus Reagents and Application to Metal Ion Recovery." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

S. D. Alexandratos,
Major Professor

We have read this dissertation
and recommend its acceptance:

James Q Chambers

John F. Fellers

Jeffrey Kovac

Richard Peaper

Accepted for the Council:

Vice Provost and Dean
of The Graduate School

SYNTHESIS OF NEW SOLID-SUPPORTED PHOSPHORUS REAGENTS AND APPLICATION TO METAL ION RECOVERY

A Dissertation

Presented For The

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Marc A. Strand

March 1987

To my wife Becky, your love and support has made this possible, and to mom and dad for the vision to dream big.

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ABSTRACT

A new series of solid-supported phosphorus reagents has been developed. The first (Part I) is a bifunctional phosphorus ion exchange resin containing primary phosphinic acid and secondary phosphinic acid or secondary phosphine oxide ligands which have been covalently bound to polystyrene beads. These ion exchange resins have been evaluated for their Zn^{+2}, Cu^{+2}, and Rb^{+} extraction ability. In general, when compared with sulfonic acid and carboxylic acid ion exchange resins, the phosphinic acid resins show superior extraction ability and selectivity. Recent studies have shown that phosphinic acid resins operate by both a redox and ion exchange mechanism depending on the reduction potential of the metal.

Part II is a discussion of high stability solid-supported liquid complexing agents. The high stability is obtained by incorporating polymerizable double bonds into the phosphorus complexing agent. The polymerizable extractants are swollen into polymer supports (macroporous polystyrene beads and macroporous polypropylene membranes) with toluene and polymerized with AIBN to form interpenetrating polymer networks (IPN's).

Diundecenyl phosphoric acid (DUP) IPN's show increased stability over polymer absorbed extractants (PAE's) as long as the DUP concentration in the swelling

solution is 0.5M or greater. Copolymerization of DUP with acrylonitrile (AN) allows for IPN formation which can incorporate up to 85% of the DUP. This DUP/AN IPN can not be eluted from the solid-support with ethanol. Totally stable IPN's have been developed by incorporating styrene groups into the phosphorus complexing agent. These IPN's are 100% stable at 0.5M or higher or if copolymerized with styrene.

A high stability solid-supported liquid membrane has been synthesized by copolymerizing DUP with AN within a polypropylene membrane. Its permeability coefficient vs. time gives a slope of -0.007 (cm sec^{-1} day^{-1}) over 42 days while that for a di-2-ethylhexyl phosphoric acid solid-supported liquid membrane gave a slope of -0.031 under the same conditions which limits its lifetime to six days.

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PART II

INTRODUCTION

The work presented in this dissertation involves the use of organic and polymer chemistry to advance the field of ion separations. Ion separation is important in waste water treatment, hydrometallurgy, trace metal analysis and other metal recovery processes.[I-1-12,II-1,43,44*]

The ideal is to develop separation systems that can be operated for years without loss of capacity and to make them as ion specific as possible. This will enable the recovery process to be operated at a reasonable cost with little contamination of the environment and afford the isolation of pure metals or metal salts.

It is with this goal in mind that we have set out to develop selective ion exchange resins and stable liquid extraction and membrane processes. Selectivity is obtained by adjusting the chemical nature of the metal ion extractant,[I-53] whereas stability is gained through physical modifications to avoid problems of attrition, entrainment and solubility.[II-59] The currently available ion

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* The Roman Numeral refers to the section in which the reference can be found.

exchange resins are fairly stable with respect to attrition but lack selectivity. Liquid ion exchangers have been made that are selective but are subject to losses via entrainment (to be drawn into the aqueous phases) and solubility.[II-43] It is the combination of resin stability with liquid extraction selectivity that we have studied. Both ion exchange and liquid extraction are important techniques. Ion exchange is best for high concentration metals while liquid extraction is best suited for dilute and trace samples.[I-1-12,II-1] The dividing line between high and low concentration is generally considered to be in the range of 10^{-3} to 10^{-4}M.

The first part of this dissertation involves synthesis of a new class of ion exchange resins. Polystyrene beads have been functionalized using PCl_3 and $AlCl_3$ to give a bifunctional resin which contains primary phosphinic acid and secondary phosphine oxide or secondary phosphinic acid ligands. This new class of polymer resins shows enhanced ability to extract zinc and copper ions when compared to commercial sulfonic and carboxylic ion exchange resins.

The second part of this dissertation shows the development and use of polymerizable liquid ion exchangers. Liquid ion exchangers are used quite extensively by absorbing them into polymer supports to form supported liquid membranes and polymer absorbed

extractants.[II-59,90-101,113-115] In these forms, they are used in ion chromatography,[II-60-63] extraction chromatography, solid—liquid ion exchange,[II-59] and coupled ion transport.[II-90-101,113-115] These supported liquid ion exchangers possess the ability for improved metal ion separation due to their chemical nature. However as ion exchange reagents they are somewhat polar in their salt form and are therefore subject to attrition by aqueous phase solubility.[II-52-54] This is the major problem that we have addressed. By making polymerizable liquid ion exchange reagents it is possible to form interpenetrating polymer networks. Intermesh polymerization causes physical entanglements to form which entraps the extractant within the polymer network and thus greatly improves its usable lifetime.

PART I

BIFUNCTIONAL ION EXCHANGE RESINS

CHAPTER 1

INTRODUCTION TO PHOSPHORUS-BASED ION EXCHANGE RESINS

The synthesis of ion exchange resins has evolved from the use of natural materials through modifications of the natural materials such as the sulfonation of coal to the modern synthetic materials used today. Even now there is constant change in the use and requirements placed on ion exchange resins so the need for improvements is always there.

Ion exchange may be defined as the reversible exchange of ions between one phase (solid or liquid) and a second liquid phase in which no permanent change in structure is seen.[1] "Reversible" and "no permanent change" are the key points of this definition.

The use of ion exchange resins has spread far beyond the ion exchange role to catalysis, drying agents, and other forms of separation. However this discussion will deal only with their role in ion separation.

There are several books that review the field quite well and establish a good working background.[1-12]

The first critical observation to begin the concept of ion exchange was made by Thompson and Spence in 1845.[12-14] They observed that passing ammonium sulfate

through soil resulted in the formation of calcium sulfate. In the years following (1850-5) Way further developed the concept and found that ammonium, sodium, potassium, and magnesium cations would exchange with soil.[15] Way was also able to establish the equivalency of cation exchange and observed that some ions exchanged better than others.

Around the turn of the century Gans was able to use natural and synthetic silicates to soften industrial water by removing magnesium and calcium.[16] He was also able to regenerate the aluminosilicates with sodium hydroxide.

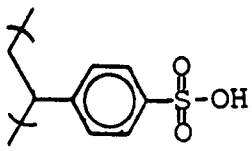
Synthetic ion exchangers were first developed by Adams and Holms.[17] They made cation exchangers from tannins and phenol-formaldehyde and anion exchange resins from aniline or 3-aminoaniline with formaldehyde. These early resins were unstable, especially in base, and would tend to break down.

The development of stable polymer supports (e.g. polystyrene) led to a significant improvement in resin performance.[1,18] Styrene (STY) is copolymerized with divinylbenzene (DVB) via a free radical suspension polymerization to give beads.[19] The physical properties of the beads can be altered by controlling the polymerization conditions. Crosslinked polystyrene is totally insoluble and highly resistant to degradation due to its carbon backbone. In addition the aromatic ring allows for ease of functionalization. Other polymers are used (phenolics,

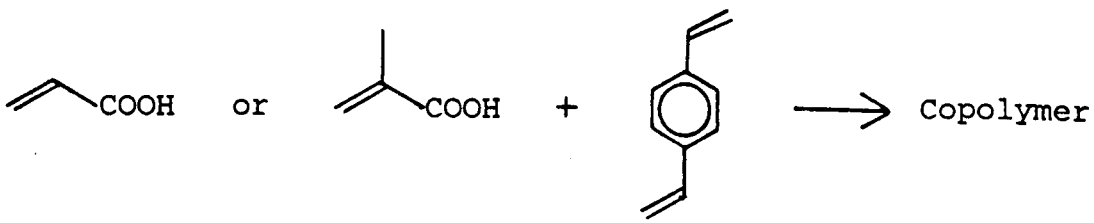
acrylics, etc.) but polystyrene remains the mainstay of industrial ion exchange and was the support used in our research.

There are four general types of ion exchange resins commercially available. There are two for cations (strong acid $-SO_3H$ and weak acid -COOH) and two for anions (strong base $-NMe_3OH$ and weak base $-NMe_2$).[12] Many other resins have been studied but, their commercial availability remains very limited. Our work has focused on cation exchange resins and so the remainder of this discussion will be focused there.

The functionalization of polystyrene to form the sulfonic acid resin (shown below) can be accomplished by several methods.[19-41]



The weak acid ion exchange resin can be synthesized as follows:[42]



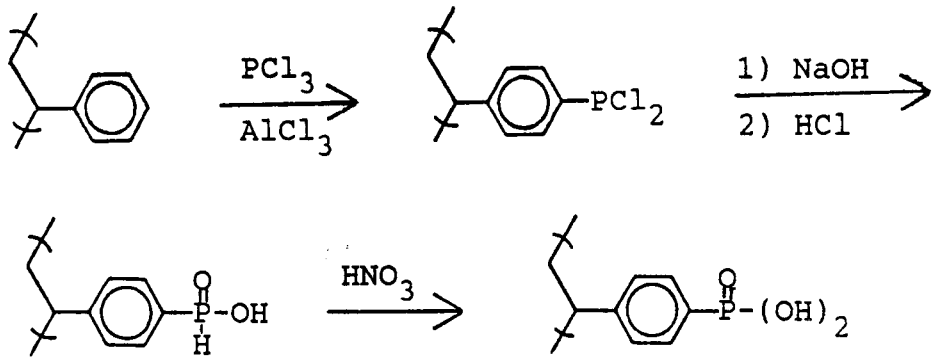
The strong acid resin can exchange very well with almost all cations in a wide pH range but lacks good

selectivity. The weak acid resin is more selective but needs to operate at a relatively high pH or its exchange capacity is very low. What is needed is an intermediate resin, one that will have a high capacity and good selectivity over a wide range of pH. Phosphorus acids can be synthesized to fill this gap due to their intermediate acidity.

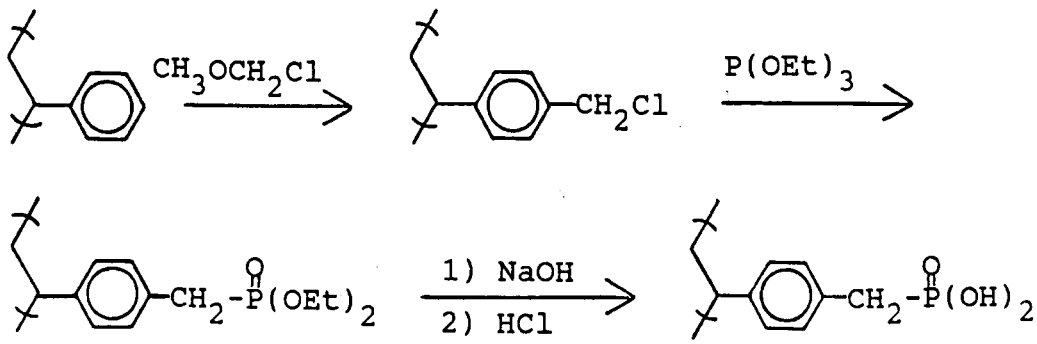
Commercially, Diamond Shamrock, under the name of Duolite resins, studied a few experimental phosphorus resins (Rohm and Haas is the current owner of the Duolite line).[43]

Resin Name	Phosphorus Group	Polymer Support
ES-60	-HPOOH	Styrene
ES-61	$-PO(OH)_2$	Styrene
ES-65	$-OPO(OH)_2$	Phenolic

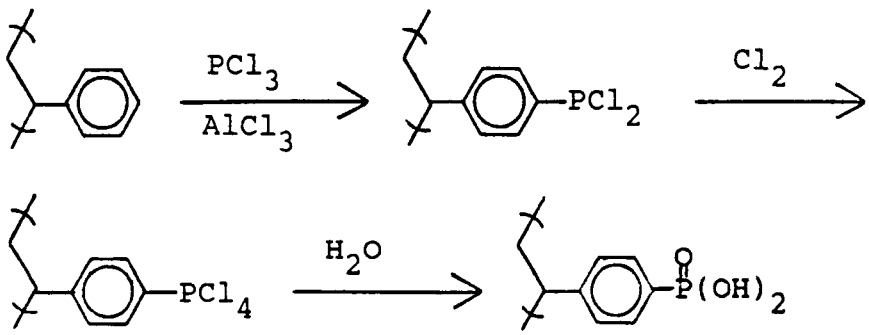
For the most part, high capacity phosphorus resins have been used only on an experimental basis. The following reaction schemes will demonstrate some of the routes to phosphorus—containing styrenic ion exchange resins:



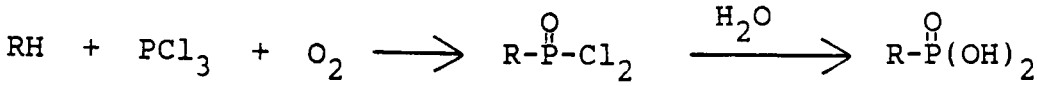
ref. 44-46



ref. 45,47

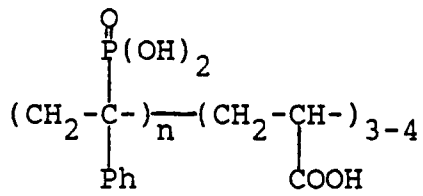


ref. 48



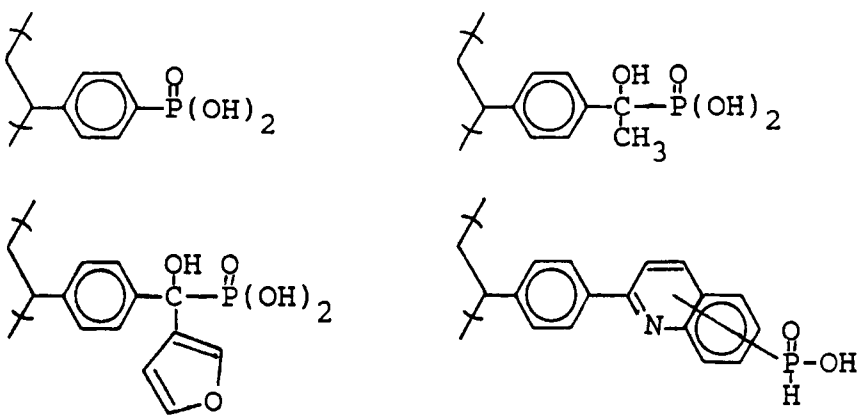
ref. 49

The above examples are general methods that have been employed. In recent years, several attempts have been made to alter the selectivity order of phosphorus resins. The copolymerization of alpha-styryl phosphonic acid with acrylic acid affords a copolymer with the phosphorus attached to the aliphatic portion of the polystyrene which alters its selectivity.



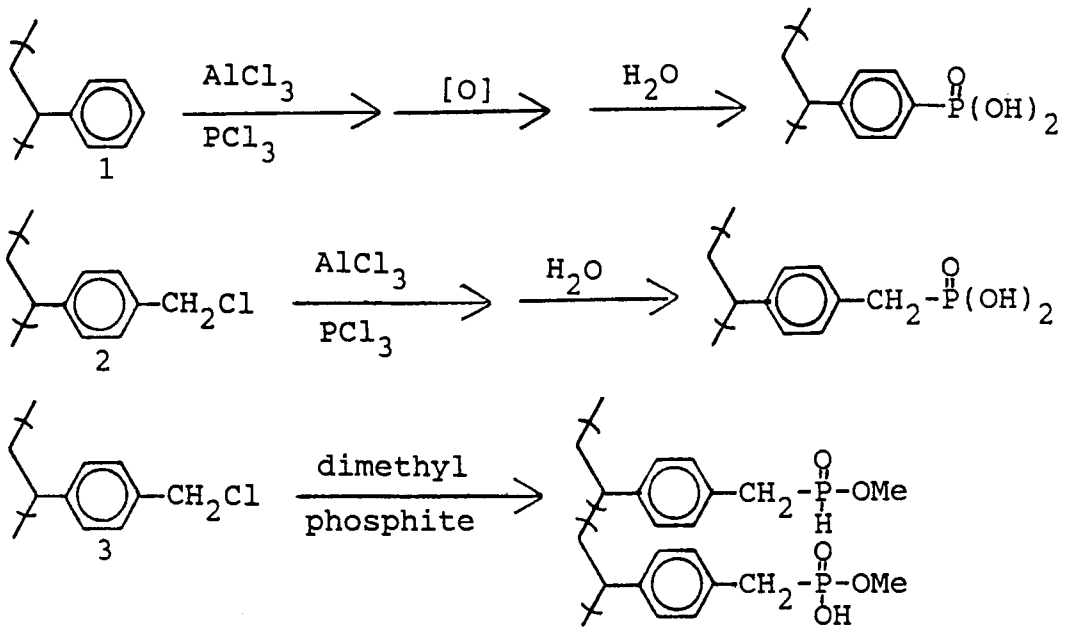
ref. 50

Marhol synthesised a series of phosphorus acid resins:



It was found that as the steric hindrance around the phosphorus acid changed so did its selectivity with respect to divalent and trivalent metals.[51]

Bogoczek and Surowiec developed and studied a series of phosphorus resins based on the functionalization of polystyrene, chloromethylated polystyrene and polyacrylic acid.[52]



The extraction ability of these resins and commercial ion exchange resins was determined for several cations. Cations were contacted with the ion exchange resins in a one to one ratio of milliequivalents of metal to milliequivalents of what were considered to be "available" ion exchange sites. Their determination of available ion exchange sites was based on how many sites would exchange with sodium hydroxide at a certain pH. An affinity factor was defined as the percent metal absorbed. Based on the differences in these affinity factors, the separating ability of the phosphorus acids was determined to be:

$$-\overset{O}{\overset{\|}{P}}(OH)_2 \rangle -CH_2-\overset{O}{\overset{\|}{P}}(OH)_2 \rangle -\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{P}}(OH)_2$$

The following table gives a comparison of phosphonic, sulfonic, and carboxylic acid ion exchange resin affinity factors:

Cation	Phosphonic*	Carboxylic	Sulfonic
Na^{+}	10.1	4.6	61.7
UO_2^{+2}	80.4	7.1	89.2
Zn^{+2}	22.0	5.6	75.8
Al^{+3}	52.0	11.5	75.3
Th^{+4}	69.8	7.1	100.0

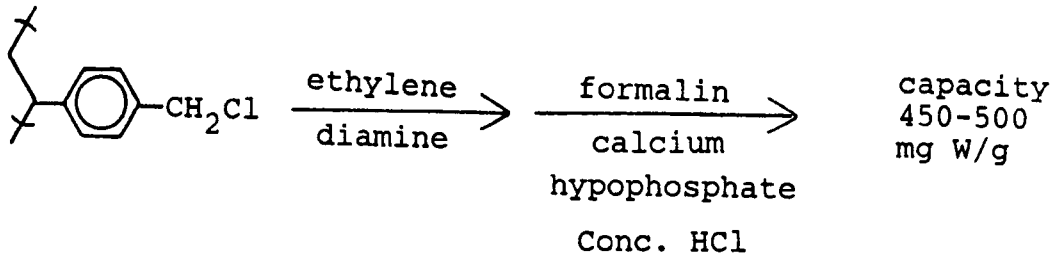
* See number 1 on the preceding page

The size of the affinity factor expresses the metal ion loading while the differences between the values indicates how well ions can be separated. For good separation, affinity factors should be widely spaced.

Some of the same resins that were used by Bogoczek and Surowiec were also studied by Hubicka and Hubicki.[53] The resins are those labeled 1 and 2 on page 11 It was found that the benzylic phosphonic acid was best for the extraction of ytterbium and lutetium. At low levels of metal ions, less than 0.01% of Lu and 0.001% of Yb remained in solution.

Biswas and Packirisamy used $AlCl_3$ and PCl_3 to functionalize furfural containing copolymers.[54] Copolymers were synthesised from furfural and N-vinylcarbazole or poly-N-vinylcarbazole with $AlCl_3$ as a catalyst for condensation polymerization. The structure was determined only by IR spectroscopy to identify the phosphorus group. A differentiation between furfural and carbazole bound phosphorus groups was not made.

In a recent British patent, a resin with a high capacity for tungsten was synthesised.[55] No specific structure was given; however, the synthetic scheme is shown below:



Phosphorus reagents show improved performance over other resins. However, there is still one additional factor which can improve performance. In 1958, Blake introduced the concept of synergistic extraction.[56] This involves the use of a complexing agent in addition to the ion exchange group to enhance metal recovery. In the recovery of uranium with di-2-ethylhexyl phosphoric acid, the addition of tributylphosphate extracts a higher level of metal than either could do alone. Several other examples can be found in the literature.[57-59]

The research presented in Part I of this dissertation is based on the use of phosphorus functionalization to obtain novel bifunctional resins having superior extraction ability. Phosphorus ion exchange resins are far superior in selectivity to commercial ion exchange resins. However the literature on phosphorus—based resins is sporadic at best. In light of what has been done in liquid—liquid extraction (see introduction to supported liquid extractants) it is clear that a phosphinic acid resin should possess superior separating ability.

CHAPTER 2

SYNTHESIS OF BIFUNCTIONAL PHOSPHORUS ION EXCHANGE RESINS

Choice of Polymer Support

An ion exchange resin is simply a solid support containing an ion exchangeable group. In principle most solid supports will work but there are several requirements for an effective support: 1) low cost, 2) chemical stability, 3) attrition resistance, 4) simple methods for attaching ion exchange groups, 5) good exchange kinetics, and 6) a usable form. In order for a support system to become commercially important it must meet all of these requirements.

Polystyrene was the support of choice for the following reasons: 1) styrene is an inexpensive and easily obtainable monomer, 2) polystyrene contains only carbon and hydrogen and is therefore chemically stable to most aqueous systems, 3) styrene can be copolymerized with divinyl benzene (DVB) to form attrition resistant beads, 4) the porosity of the beads can be adjusted which in turn will affect the kinetics, and 5) the aromatic ring on the polymer easily functionalized to give high capacity resins.

Copolymerization

Polystyrene beads that are crosslinked with divinyl benzene are made via suspension polymerization.[60] The monomer mixture is suspended in an aqueous phase containing padmac (polydiallyl dimethyl ammonium chloride, Calgon Corp), Pharmagel (a form of gelatin), and boric acid adjusted to pH 10.3 with 50% sodium hydroxide. The padmac and the pharmagel coat the monomer droplets and keep them from coalescing. The boric acid is a buffer and the pH of 10.3 is to keep the pharmagel from breaking down.

For the formation of "gel" beads (pores of 100Å or less), the monomer mixture contains 1% benzoyl peroxide (BPO, a free radical initiator) and 2-30% DVB with the remainder being styrene. The DVB used is a mixture of DVB (55.4%) and ethyl vinyl benzene (EVB, 44.6%) and thus the crosslink determination is based on 55.4% purity. The monomer mixture is added to the aqueous phase and stirring is begun.

The rate of stirring will determine the size of the organic droplets that will be formed. The stirring is cycled on and off to allow all of the organic phase to become suspended in uniform droplets.

The entire suspension is heated over two hours to 80 ^{o}C. Slow heating allows for a controlled breakdown of the BPO which in turn allows for reasonable polymerization rates. The temperature (80^{o}C) is maintained for 10 hours

at which point it is increased to 100 ^{o}C for two additional hours to ensure the total decomposition of BPO and the consumption of any pendent double bonds.

After cooling, the beads are washed with dilute acid to remove the padmac, pharmagel, and excess sodium hydroxide and then air dried. The beads may be heated to increase the drying rate if the temperature is kept below 60 ^{o}C. After drying, the beads are sized by seiving.

When gel beads are functionalized and used as ion exchange resins, their exchange kinetics are slow due to slow diffusion rates. This can be overcome by making macroporous (macroreticular, MR) beads.[61] MR beads are formed when a portion of the monomer mixture is replaced with a diluent. If the diluent concentration is too high the polymer will not be very strong. This diluent is a solvent for the monomer and a nonsolvent for the polymer. A good diluent must also not affect the monomer polymerization and be easily removed from the resultant polymer bead. Diluents are generally alcohols containing four to ten carbon atoms or hydrocarbons of seven or more carbons. For styrene/DVB copolymers 4-methyl-2-pentanol (4M2P) is used. The 4M2P is incorporated into the monomer droplets and causes phase separation of the growing polymer chains. As the polymer chain grows it will reach a certain length where it now prefers to self-solvate rather than be solvated by the 4M2P. At this point the polymer chain

will collapse upon itself. If the resulting MR bead is enlarged it resembles many tiny beads glued together to form one large sphere.[61,62]

The MRs have a very large surface area ($11m^2/g$ if 50% 4M2P is used).[63] The high surface area generally allows for increased kinetics. However, this bead form is more friable than is a gel bead. Therefore to maintain the same level of stability as a gel the amount of DVB must be increased. Increasing the crosslink level does, however, slow diffusion rates and lower the resin capacity. Therefore we have studied both MRs and gels with DVB levels of 2% to 15%.

The sizing of the beads is done using USA Standard Testing Sieves.

USA Standard Testing Sieves

mesh	inches	millimeters
16	0.0469	1.18
20	0.0331	0.850
40	0.0165	0.425
60	0.0098	0.256

For the most part the stir rate has been controlled so that the majority of the beads are between the 20 and 40 mesh size (referred to as a -20 +40 cut). This means that they are small enough to pass through the 20 mesh screen

but remain above the 40 mesh screen. For the studies in this work both -16 +20 and -20 +40 mesh cut beads have been used.

The effective crosslinking is quantitatively determined by a swelling ratio. This is done by contacting dried beads with excess toluene and taking the volume ratios.

%DVB	Swell Ratio
2% MR	3.9
5% MR	2.3
10% MR	1.7
15% MR	1.4

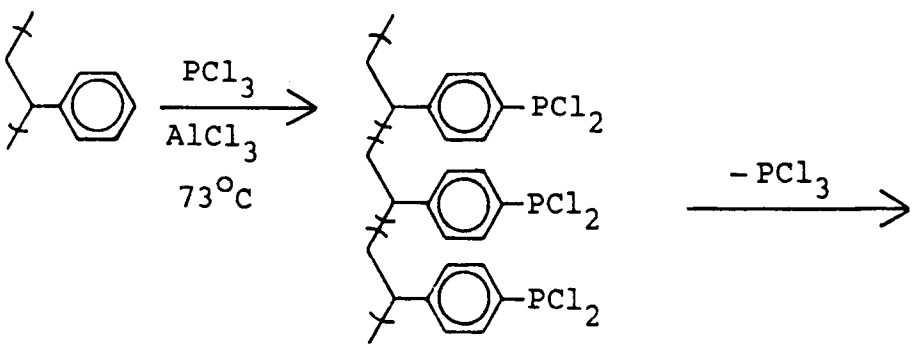
The swelling ratio was used to check the consistency in the crosslink level of the polymer beads.

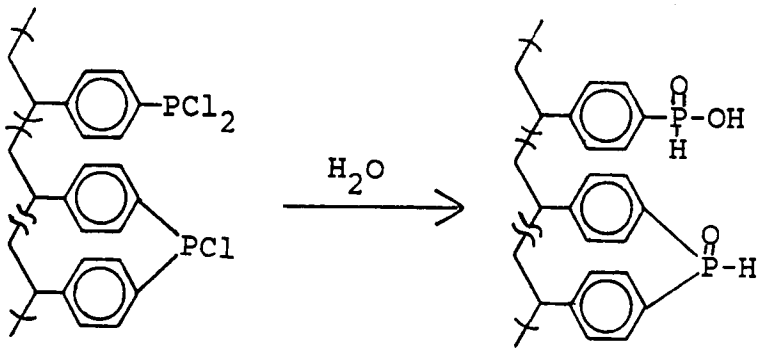
Functionalization of Polystyrene Beads

The functionalization of styrene/DVB copolymers with $AlCl_3/PCl_3$ has been known for quite some time (see Chapter 1). However in most of the cases mentioned the intermediate was further oxidized to obtain a phosphonic acid. The phosphonic acid was formed to give a higher capacity resin. The pKa of the second proton is small and does not necessarily exchange with all metal ions. If the intermediate is hydrolyzed a phosphinic acid results.

The functionalization is carried out by swelling a styrene/DVB copolymer in PCl_3. Enough PCl_3 is added to form a slurry. $AlCl_3$ is then added in a molar ratio based on the available styrene. A typical value is 0.77 mole $AlCl_3$/mole styrene. The mixture is heated to the reflux temperature of PCl_3 (73°C) over one hour and then maintained for four hours. The reaction turns yellow to deep brown upon addition of the $AlCl_3$. Also the beads tend to deswell as the reaction proceeds. The heat is then removed and the mixture allowed to cool to room temperature. The mixture is then poured into a half saturated NaCl solution with ice. The ice and salt cause the solution temperature to drop to approximately -8C° which helps to control the exotherm. The high ionic strength also slows the rate of H_2O diffusion into the beads and helps to avoid cracking and peeling. The beads revert back to colorless upon hydrolysis.

The reaction scheme is shown below:





The disproportionation step (secondary crosslinking) is consistent with the product analysis and the following literature precedents:

$$2\ Ph\text{-}PCl_2 \xrightarrow{\Delta} (Ph)_2\text{-}PCl + PCl_3$$

ref. 64

$$RH + PCl_3 \xrightarrow{AlCl_3} RPCl_2 + RPCl$$

ref. 65

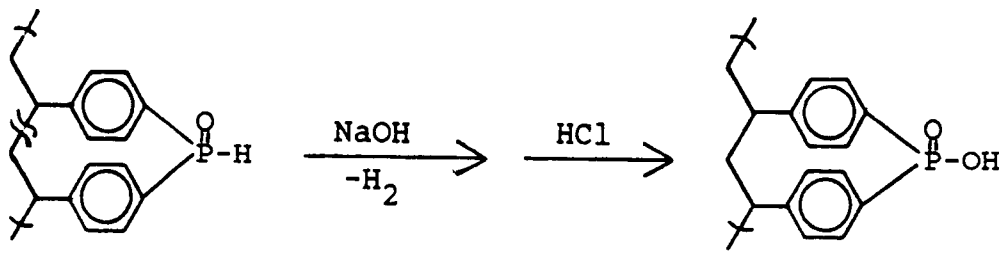
$$Ph\text{-}H + 3\ PCl_3 \xrightarrow{AlCl_3} \underset{59\%}{Ph_2\text{-}PCl} + \underset{40\%}{Ph\text{-}PCl_2}$$

ref. 66

The formation of the secondary crosslinking was further established by the functionalization of linear polystyrene

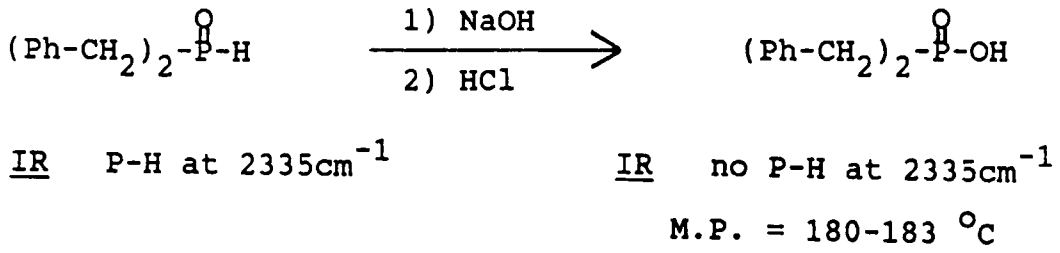
with $PCl_3/AlCl_3$ to yield an insoluble crosslinked polymer.[67]

Before a resin is used or analyzed, it is important to condition the resin to remove remaining reactants and by-products. The normal conditioning involves washing the beads with water, 1N sodium hydroxide, water, 1N hydrochloric acid, and water again. The base causes the neutralization of the phosphorus acid and causes an increase in the resin hydrophilicity which in turn causes the resin to swell. Swelling the resin allows for more efficient washing. It was observed that gas was evolved when the sodium hydroxide was passed through the resin. A glowing splint test confirmed that the gas was hydrogen. The hydrogen was hypothesized to be from the oxidation of the secondary phosphine oxide to a secondary phosphinic acid.



This hypothesis is consistent with the analysis reported in chapter three. We were also able to substantiate this idea by the synthesis of dibenzylphosphine oxide. When

this was contacted with sodium hydroxide, followed by an acid work up dibenzylphosphinic acid was isolated.



CHAPTER 3

ANALYSIS AND RESULTS

The chemical composition and nature of the resins have been determined by the combination of several elementary analytical techniques. Each technique will be discussed in light of its analytical procedure, theoretical understanding and the meaning of its results.

Percent Solids

The determination of the solids content of a resin gives information on water content of a wet bead. Most of the subsequent analyses need to be performed on hydrated beads. Therefore the percent solids allows for the conversion of wet weight to dry weight. Qualitatively the value of the percent solids indicates both crosslink and functionality levels. The percent solids is determined by drying a known sample of wet beads at 110C^{o}. The dry weight divided by the original wet weight gives the percent solids.

Phosphorus Elemental Analysis

A sample of dried beads is analyzed for total phosphorus content.[68] The sample is totally digested using a

nitric acid/perchloric acid mixture heated to boiling. The polymer backbone becomes CO_2 and water while the phosphorus becomes phosphoric acid. The sample is then diluted and treated with perchloric acid, amidol (a color developing agent, see experimental section), and ammonium molybdate. The resultant molybdate-phosphoric acid complex is blue in color. The quantitative determination was performed by absorbance measurements at 700nm. The absorbances were compared to a standard Beer's law plot in order to obtain the resin's phosphorus capacity.

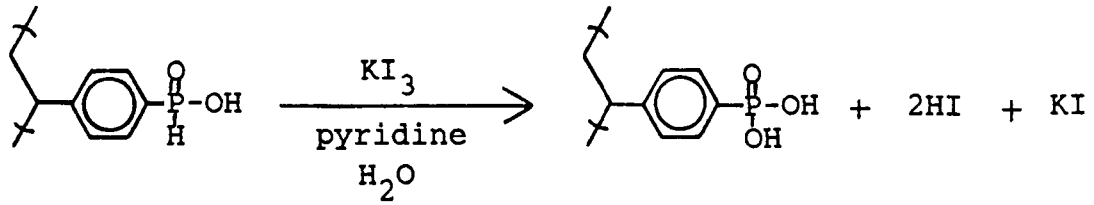
Titration of Acid Capacity

The total acid capacity of the resin can be determined by an aqueous base potentiometric titration. The only special consideration involves the base addition rate. Due to the solid state of the acid the kinetics of the acid/base reaction are slow due to slow diffusion rates. Therefore, the base was added at a rate of 1ml per hour over 24 to 48 hours. The results of this method were checked by equilibrating excess base with the beads for 12 hours followed by a titration of the excess base.[67]

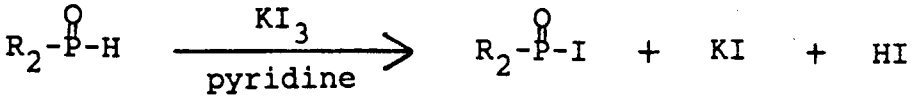
Iodine Titration Method

The iodine titration is the tool for determining the relative proportions of primary and secondary acid. The

primary acid contains an oxidizable P-H. The iodine reaction is as follows:[69]



Blake, Brown, and Coleman of Oak Ridge National Laboratory (ORNL) established the iodine method for the determination of dialkylphosphine oxide content in trialkylphosphine oxides. The reaction they proposed is shown below:[70]



The procedure set forth at ORNL was:

a) Place in a 50ml Erlenmeyer flask

approx. 1 g phosphine oxide

10 ml benzene

10 ml 0.1N I_2 in 2% KI

2 ml pyridine

b) Shake vigorously for 16 hours (Burell "wrist-action" shaker was used in this work).

c) Titrate excess iodine in mixed phases with standard sodium thiosulfate.

d) Titrate original iodine in the 10ml benzene - 10ml iodine - pyridine mixture.

e) Subtract titer (c) from titer (d).

f) Calculate percent dialkylphosphine oxide in the following manner:

$$\%P\text{-}H = \frac{ml_{titer} \times NNa_2S_2O_3 \times M.W.R_2POH/2x100}{\text{Sample weight (mg)}}$$

Several modifications to the above procedure have been made. Analysis was done on a sample of wet beads that corresponded to about 0.5g dry resin. The benzene was determined not to be important for most resins. In a low capacity (hydrophobic) resin the addition of benzene increased the accessibility of the resin. However, in a high capacity (hydrophilic) resin the benzene caused the reaction rate to slow. Benzene was only added to very low capacity resins if the back titration with $Na_2S_2O_3$ had difficulty removing the excess I_2 from the resin. The volume of 0.1N I_2 was determined so as to allow for a reasonable volume for the back titration.

The level of pyridine is important to maintain a good pH. If the pH is too low the reaction will not go to completion. If the pH is too high I_2 will be converted to HIO.[69] The results in table I were used to determine that 2ml of pyridine would be used.

The validity of the I_2 method was determined by the reproducibility of the results as well as a base titration of the oxidized beads. The phosphonic acid resin

TABLE I

pH EFFECT ON I_2 DETERMINATION[a]

Code Number	ml Pyridine	Blank	P-H Capacity	Capacity Corrected
MS-01-066	0	0.0	2.52	2.52
MS-01-066	2	0.0	2.91	2.91
MS-01-066	5	0.48	3.30	2.82
MS-01-066	10	0.93	3.72	2.79
MS-01-066	15	1.31	3.77	2.46

[a]units of mequiv/g

resulting from the I_2 titration has two distinct protons. The second proton gives a measure of the original primary acid capacity (mequiv/g).

MS-01-066

Before I_2		After I_2	
-PH(O)OH	= 2.77	$-PO(OH)_2$	= 2.70
=POOH	= 1.72	=POOH	= 1.79

The results of the I_2 method have been considered to be accurate at least to $\pm$ 0.2mequiv/g.

Results

The synthesis and analysis of all phosphinic acid resins is given in tables 2 and 3.

Theoretical Capacity

The theoretical capacity is based on the following assumptions:

1) The I_2 value gives the primary acid capacity.
2) DVB and EVB are inert.
3) Each styrene ring is substituted only once.
4) 100% reaction is obtained.

The calculation is based on mixing the theoretical capacities of a pure primary acid resin and a pure secondary acid resin. If the starting resin contains 2% DVB then

TABLE 2

SYNTHETIC CONDITIONS FOR

PHOSPHINIC ACID RESIN SYNTHESIS

Code Number	Copolymer[a]	Moles $AlCl_3$[b]	Reaction Temperature	Reaction Time
MS-01-014A	2%MR	0.77	73°C	4hr[c]
MS-01-014B	5%MR	0.77	73°C	4hr
MS-01-014C	10%MR	0.77	73°C	4hr
MS-01-014D	15%MR	0.77	73°C	4hr
MS-01-039	2%MR	0.77	25°C	6hr
MS-01-043A	2%MR	0.77	73°C	18hr
MS-01-043B	2%MR	0.77	0°C	6hr
MS-01-066	2%MR	0.77	73°C	4hr
MS-01-103A	2%gel	0.77	73°C	4hr
MS-01-103B	2%gel	1.20	73°C	4hr
MS-01-103C	2%gel	2.0	73°C	4hr
MS-01-103D	2%gel	1.20	19°C	6hr

[a]Given as % DVB in styrene/DVB copolymer

[b]Moles of $AlCl_3$/mole styrene

[c]At temperatures above 25°C add 1hr heat—up and 1hr cool—down to times

TABLE 3

ANALYSIS RESULTS OF PHOSPHINIC ACID

ION EXCHANGE RESINS

Code Number	%Solids	I_2[a]	-OH[b]	P[c]	Theoretical Capacity
MS-01-014A	26.5	2.31	4.41	4.61	4.48
MS-01-014B	29.1	2.54	4.13	4.59	4.41
MS-01-014C	32.2	2.45	3.95	4.29	4.13
MS-01-014D	31.8	2.48	3.90	3.83	3.88
MS-01-039	25.0	2.28	2.25	2.94	4.47
MS-01-043A	28.2	----	----	4.41	----
MS-01-043B	19.2	1.72	1.22	1.63	4.25
MS-01-066	24.7	2.52	4.49	4.54	4.56
MS-01-103A	49.7	3.02	4.76	4.78	4.75
MS-01-103B	34.8	2.83	5.44	5.42	4.68
MS-01-103C	41.7	2.28	5.81	5.62	4.47
MS-01-103D	34.5	1.99	2.15	2.43	4.36

[a]Results of iodine technique in mequiv/g

[b]Results of hydroxide titration in mequiv/g

[c]Results of phosphorus elemental in mequiv/g

there will be 3.61% DVB and EVB. This will leave 96.39% styrene. If we assume 100% reaction to the primary acid and 100g of starting copolymer then the final resin weight is as follows:

3.61g DVB/EVB -----> 3.61g

96.39g styrene x M.W. 1^{o} acid/M.W. styrene -----> 155.7g

This now means that the resin is 97.73% by weight primary acid. The capacity of pure styrene phosphinic acid is 5.95 meq/g so the theoretical capacity of a 2% DVB all primary acid resin is 5.81 (5.95 x 0.9773). The same treatment can be applied to the secondary acid. The only difference is that now the molecular weight is divided by two to account for the consumption of two styrene rings the formation of the secondary acid.

3.61g DVB/STY -----> 3.61g

96.39g styrene x M.W. 2^{o} acid/2M.W. styrene -----> 125.1g

The results of this treatment for several different starting copolymers is shown in table 4. The values shown in table 4 are corrected for the inert material and therefore a linear combination of these values will give the capacity of a mixed primary and secondary acid resin in which 100% of the styrene has been substituted. The

TABLE 4

THEORETICAL CAPACITY OF PURE PRIMARY AND SECONDARY ACID RESINS[a]

Copolymer		Resin	
%DVB	%DVB/EVB	1^{o}capacity	2^{o}capacity
2	3.61	5.81	3.60
5	9.03	5.60	3.43
10	18.05	5.24	3.16
15	27.08	4.84	2.88

[a]units = mequiv/g

theoretical capacities for several different ratios of primary and secondary acid are shown in table 5 for a 2% DVB resin.In order to calculate the theoretical capacity the primary or secondary acid capacity must be known. The iodine value is taken to be equal to the primary acid capacity. Therefore the weight fraction of primary acid is determined as follows:

$$\frac{I_2 \text{ mequiv/g}}{\text{Primary theoretical capacity}} = \text{Primary wt. fraction}$$

The secondary weight fraction is then the remainder. The theoretical capacity is then calculated by taking the sum of the weight fractions of both components multiplied by their respective capacities.

Resin Model

Based on the results presented in table 2, a model for the formation of the resin has been developed. Initially only primary $-PCl_2$ groups are formed on the resin. However, the $-PCl_2$ concentration will reach a maximum value at which point additional $-PCl_2$ groups will result in disproportionation and the formation of a secondary (=PCl) group. This limiting value is between 2.28 and 2.54 meq/g for MR resins and is 3.02 for gel resins (all at 0.77 mole $AlCl_3$). The effect of the

TABLE 5

CAPACITY OF MIXED PRIMARY AND SECONDARY ACID RESINS[a]

%primary	%secondary	capacity
100	0	5.81
80	20	5.37
60	40	4.93
50	50	4.70
40	60	4.48
20	80	4.09
0	100	3.60

[a]units = mequiv/g

crosslink level is very small as can be seen in the primary capacities of MS-01-014A-D. However, the effect of the level of $AlCl_3$ catalyst is very pronounced, as can be seen in MS-01-103A-C. The low temperature resins demonstrate that the primary group is attached first.

CHAPTER 4

METAL ION SEPARATION STUDIES

Metal ion separation studies were performed on the ion exchange resins to determine metal ion extraction ability. The metal ions studied were: Zn^{+2}, Cu^{+2}, and Rb^{+1}.

Initial Ratio

The initial ratio (R_i) is a term that we have developed. It refers to the initial ratio of milliequivalents (mequiv) of metal ions to mequiv of ion exchange sites. If 5mequiv of metal ions are contacted with 10mequiv of ion exchange sites then the $R_i = 0.5$.

Radio Tracer Technique

The use of radioisotopes to follow metal ion extraction is a very straightforward technique. A known quantity of hydrated resin is contacted with a metal ion solution at a constant ionic strength of 4N $NaNO_3$. To the solution a spike of radio tracer is added. The radio isotope is of the same element as that being studied. By determining the radioactivity before and after contact

with the resin the extent of metal ion extraction can be determined.

Zinc Extraction

The extraction of zinc was studied for several different resins at varying R_i's. Table 6 contains the results of zinc extraction with MS-01-014A (see table 2 for details on resin form).The pH range of the final solutions in table 6 was 0.65-0.99. A much wider R_i range was studied for MS-01-66 which is shown in table 7.

Tables 6 and 7 involve MR resins. Table 8 contains the zinc extraction of MS-01-103A-D which are all gel resins.

In addition to phosphinic acid resins, sulfonic and carboxylic resins have been studied. Tables 9 and 10 give the results of these resins.The results given in tables 6-10 demonstrate the effectiveness of phosphinic acid resins over sulfonic and carboxylic acid ion exchange resins.

The trends indicate that the cross-link level strongly determines the zinc extraction by sulfonic and carboxylic acid resins. However, cross-linking has no effect on phosphinic acid performance. The % loading at R_i = 1.0 for the sulfonic acid resin shows a considerable drop (from 41% to 18%) as the cross-link level increases (from 2% to 15%). The carboxylic acid ion exchange also

TABLE 6

ZINC R_i STUDY ON MS-01-014A

WITH 4M $NaNO_3$ BACKGROUND

R_i	% Absorbed	% Loading	% H^+ Removed
0.024	70.43	1.69	25.6
0.049	66.70	3.27	27.0
0.098	63.70	6.18	29.4
0.20	57.52	11.50	32.3
0.39	50.53	19.71	39.1
0.48	48.26	23.16	40.5
0.58	46.49	26.97	45.8
0.67	45.46	30.46	50.2
0.81	42.28	34.24	53.6
0.87	40.40	35.15	52.6

TABLE 7

ZINC R_i STUDY OF MS-01-066

WITH 4M $NaNO_3$ BACKGROUND

R_i	% Absorbed	% Loading	H^+ mequiv/g* Removed
0.084	68.43	5.73	1.18
0.89	46.19	40.85	----
1.15	44.19	51.22	1.55
1.36	25.39	34.52	3.61
4.07	14.67	59.73	6.49

* determined by pH measurement

TABLE 8

ZINC R_i STUDY OF MS-01-103A-D

WITH 4M $NaNO_3$ BACKGROUND

Resin	R_i	% Absorbed	% Loading	H^+ mequiv/g Removed
A	0.12	72.09	8.81	1.52
A	1.11	40.41	44.71	2.51
A	1.70	35.00	59.40	3.67
B	0.11	68.32	7.52	2.19
B	1.08	43.47	46.72	3.03
B	1.65	36.09	59.62	3.86
C	0.10	68.74	6.84	2.27
C	0.95	43.71	41.52	3.30
C	1.42	37.09	52.61	3.63
D	0.077	57.73	4.42	0.63
D	0.28	52.71	14.61	1.11
D	0.39	42.55	16.47	0.80
D	0.75	37.95	28.58	0.91
D	2.61	24.28	63.27	1.68
D	3.87	21.22	82.22	1.72

TABLE 9

ZINC LOADING AS A FUNCTION OF CROSS-LINK LEVEL FOR GEL SULFONIC ACID ION EXCHANGE RESINS WITH A 4M $NaNO_3$ BACKGROUND[71]

Cross-link Level % DVB	TAC[a] meequiv/g	% Load. R_i=0.1	% Load. R_i=1.0	% 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]TAC = total acid capacity

TABLE 10

ZINC LOADING AS FUNCTION OF CROSS-LINK LEVEL FOR MR CARBOXYLIC ACID ION EXCHANGE RESINS WITH 4M $NaNO_3$ BACKGROUND[71]

Cross-link Level % DVB	TAC mequiv/g	% Load. R_i=0.1	% Load. R_i=1.0	% 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)	5.00	1	4	5

shows strong dependence of extraction on cross-link level (see table 10). However the phosphinic acid ion exchange resin remains nearly constant at about 40% loading at R_i = 1. Table 11 gives the result of table 8 data calculated to R_i = 1.0. The calculation to obtain the values in table 10 were done using the closest known value to R_i = 1.0 and assuming linear behavior.

Macroporosity Factor

In general, it is observed that MR resins extract zinc slightly better than do gel resins. This is due to what we have termed the "macroporosity factor". MR resins contain extra water in their macropores. This water is free to mix with the aqueous phase and thus slightly reduces the concentration of metal ions. This causes the data to show more metal ion pickup than is actually happening. The outline of the reasoning and calculation of the macroporosity factor is given below:

1) The % solids of a gel resin is greater than an MR resin.
2) The difference is due to water in the macropores.
3) Water contained in the gel micropores does not dilute the system.
4) The total aqueous volume is equal to the added aqueous phase plus the water in the macropores.

TABLE 11

ZINC EXTRACTION DATA OF MS-01-103

CALCULATED AT R_i = 1.0

Resin	Cross-link Level % DVB	% Loading
A	2	42.0
B	5	44.9
C	10	42.7
D	15	37.0

5) 1mL H_2O = 1g

6) Assume equal weights of a gel and MR resin and work backwards to obtain the excess water.

$$\frac{\text{dry weight MR}}{\text{\% solids MR/100}} - \frac{\text{dry weight gel}}{\text{\% solids gel/100}} = H_2O \text{ in macropores}$$

7) $$\text{Correction factor} = \frac{5\text{mL} + g H_2O \text{ in macropores}}{5\text{mL}}$$

8) Corrected count = (count)(correction factor)

The dilution of the system causes the radiotracer count to be low. The macroporosity factor increases the count and thus brings the MR and gel results into agreement (see table 12).

Copper Extraction

The extraction of copper (II) is summarized in table 13. In copper extraction, as in zinc extraction, the cross-link level of a sulfonic acid resin has a far greater effect on the metal extraction than does the cross-link level of a phosphinic acid.

Table 14 contains the results of a copper/zinc competitive study. The comparison of copper with zinc shows that the phosphinic acid does not possess the ability to separate these two ions. One interesting item

TABLE 12

EFFECT OF THE MACROPOROSITY FACTOR ON

ZINC EXTRACTION

Resin	Type	R_i	% Loading	Corrected % Loading
MS-01-066	MR	1.0	44.54	38.51
MS-01-103A	gel	1.0	40.28	

TABLE 13

COPPER (II) EXTRACTION WITH SULFONIC AND PHOSPHINIC ACID RESINS WITH 4M $NaNO_3$ BACKGROUND

Resin	Type	% Load. R_i = 0.1	% Load. R_i = 1.0
MS-01-066	2% MR -POOH[a]	----	37.5
MS-01-103A	2% gel -POOH	----	27.1
MS-01-103C	10% gel -POOH	----	23.3
DR-01-068A	2% gel $-SO_3H$[b]	54.9	28.5
DR-01-068B	5% gel $-SO_3H$	71.2	36.7
DR-01-068C	10% gel $-SO_3H$	68.3	19.6
DR-01-068D	15% gel $-SO_3H$	90.3	18.4

[a]Phosphinic acid resin

[b]Sulfonic acid resin

TABLE 14

COPPER/ZINC COMPETITIVE STUDY USING MS-01-066

WITH 4M $NaNO_3$ BACKGROUND

Zn^{+2} R_i	Cu^{+2} R_i	Zn^{+2} % Absorbed	Cu^{+2} % Absorbed
0.096	-----	63.6	----
0.955	-----	40.8	----
-----	0.097	----	74.7
-----	1.447	----	30.9
0.097	0.097	57.1	74.6
0.965	0.965	33.0	33.7
0.72	0.72	50.6[a]	57.8[a]

[a]MS-01-066 in its sodium salt form

is the final entry of table 14 where the resin is converted to its sodium salt form before the metal ion extraction experiment. In this case there are no protons to compete for the exchange sites and the resin is able to pick up more metal ions. This same type of behavior would be expected if the aqueous phase was buffered.

Rubidium Extraction

The results of the rubidium (I) extraction study are summarized in table 15. The sulfonic acid resins show by far the greatest uptake of rubidium. This is consistent with its high ion exchange ability but low selectivity.

Conclusion

In general, phosphinic acid resins will extract divalent metals as well as sulfonic acid resins. However, they tend to extract monovalent ions only as well as carboxylic ion exchange resins. This indicates that the phosphinic acid resins possess high capacity as do the sulfonic acid resins and good selectivity as do the carboxylic resins.

TABLE 15

RUBIDIUM EXTRACTION WITH PHOSPHINIC, SULFONIC, AND CARBOXYLIC ACID ION EXCHANGE RESINS WITH 4M $NaNO_3$ BACKGROUND

Resin Type[a]	% Absorbed $R_i = 0.1$	% Absorbed $R_i = 1.0$	% Absorbed $R_i = 1.0$[b]
2% gel -POOH	6.61	7.18	7.69
10% gel -POOH	0.93	0.42	0.0
10% gel $-SO_3H$	15.55	12.22	11.26
10% gel -COOH	2.67	3.24	3.11

[a]Resins synthesized by David L. Wilson

[b]Rb^+ $R_i = 1.0$ and $Zn^{+2} = 1.0$

CHAPTER 5

CONTINUING STUDIES

The work presented up to this point was completed in early 1984. A considerable amount of research on these ion exchange resins has been completed since that time and is still continuing.[72-74]

Reaction Parameters

The parameters for the formation of the bifunctional phosphorus—based resins have been thoroughly investigated.[72] The parameters of interest have been: 1) reaction time, 2) reaction temperature, and 3) the nature of the catalyst. The time and temperature studies have been consistent with the model presented in chapter 3. This model involves the formation of primary groups first followed by disproportionation to give secondary groups.

A study of Friedel-Crafts catalysts gave the following reactivity order:

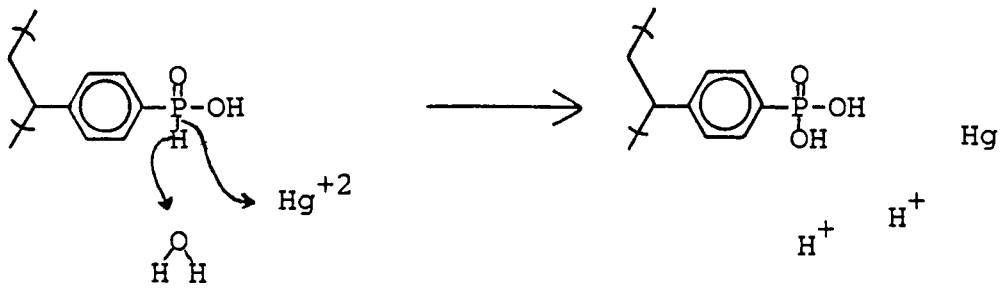
$$AlCl_3 > FeCl_3 > SnCl_4 > ZnCl_2$$

The above result indicates that $AlCl_3$ was the best choice for a catalyst. $FeCl_3$ causes the formation of phosphonic

acid ($-PO(OH)_2$) to take place directly during the synthesis (-OH = 2.8, P = 1.6). $ZnCl_2$ has a very small catalytic effect while $SnCl_4$ gives the same result as a reaction done with no catalyst.

Dual Mechanism (Ion Exchange/Redox)

A major development was the discovery of a dual mechanism in the phosphinic acid resins.[73] The dual mechanism involves the ion exchange process discussed earlier with the addition of a redox process for certain metal ions. Metals which have a proper oxidation potential to be reduced by the resin include gold, silver, and mercury. The redox process is illustrated below for mercury (II).



The resin operates by the redox mechanism until all of the primary acid sites have been oxidized. At this point the ion exchange mechanism takes over.

Ongoing work in the area of resin redox properties has led to the development of a regeneration method. The regeneration involves the use of trichlorosilane/

dimethylaniline to reduce the resultant phosphonic acid back to its original phosphinic acid form. Currently the kinetics of the redox reaction are being studied.

Metal Ion Extraction Studies

Several metals in addition to those mentioned earlier have been studied by radiotracer techniques. Several ions that are important to the nuclear processing industry have been extracted in trace quantities with phosphinic acid resins. The ions studied include: UO_2^{+2}, Th^{+4}, Eu^{+3}, and Am^{+3}.[74] Currently a study of transition metal extraction with various ion exchange resins is in progress.

CHAPTER 6

EXPERIMENTAL SECTION

All reagents were purchased commercially and used without further purification unless otherwise noted.

Copolymer Synthesis

Styrene/DVB copolymer beads are synthesized by suspension polymerization.[61] In a typical preparation, gelatin (0.96g), poly(diallyldimethylammonium chloride) (11.90g, Calgon Corp.), and boric acid (6.33g) are dissolved in 316.5mL of H_2O. The pH is adjusted to 10.3 with 50% NaOH. The aqueous phase is poured into a 1-L round-bottom flask equipped with a condenser, dry nitrogen purge, a thermometer to which is attached a Therm-O-Watch temperature-control device (Instruments for Research and Industry, Cheltenham, PA), and an Eberbach Con-Torque stirrer with double-paddle stir shaft. The monomer mix is then added (286.7g of styrene (Aldrich), 10.3g of technical DVB (Dow Chemical Co.; analyzed to be 55.4% m- and p-DVB) for 2% cross-linking, and 3.00g of benzoyl peroxide); the stir speed is set at 250 rpm. The suspension is heated over a 2-h period to 80^{o}C and this temperature held for 10h. Complete polymerization is ensured by heating

the system at 100°C for 2 h. After cooling,the beads are then washed 4 times with water and dried. MR beads are synthesized by replacing half the monomer mix with 4-methyl-2-pentanol (Aldrich) and adjusting the stir rate to 200 rpm. A 6-h steam distillation to remove the alcohol replaces the 2-h finish-off employed with gel synthesis.

Polymer-Supported Phosphorus Acid Resin

Copolymer beads (10g, 0.10 mol, -20 +40 mesh) are placed with 130 mL of PCl_3 (Aldrich) into a 250-mL round-bottom flask equipped with an overhead stirrer, a condenser, and a thermometer. The copolymer is allowed to swell with the PCl_3 for 1 h. The $AlCl_3$ catalyst (Aldrich) is added at the levels indicated and the system taken to the desired temperature over a 1-h period. The temperature is held for 4-h and then taken to room temperature. The beads are isolated from the PCl_3 solution and hydrolysis is effected at 0°C with 500 mL of 1 N NaOH of H_2O half-saturated with NaCl. The resin is washed with H_2O until neutral, placed in a glass frit funnel, and conditioned with 1 L of H_2O, 1 N NaOH, H_2O, 1 N HCl, and H_2O, each with 1-h elution times. The NaOH elution must be omitted if the phosphine oxide groups are to be maintained. The resin is then suction dried at 720 mmHg/5 min. A weighed sample is dried at 110°C/16 h in

order to determine the amount of water absorbed by the resin.

NaOH Titration Analysis

A suction-dried (hydrated) resin sample corresponding to 0.5-g dry weight is placed with 50 mL of H_2O into a beaker and titrated with 0.1 N NaOH. Additions of 1.0 mL are made hourly (45 min is usually required for full exchange per addition) with the neutralization followed by a Corning Model 130 pH meter.

Phosphorus Elemental Analysis[65]

Oven-dried and powdered resin (20 mg) is digested by heating with 5 mL of HNO_3/(5 mL of 72% $HClO_4$) to a clear and colorless solution. The solution is cooled and diluted to 100 mL with H_2O. To a 10-mL aliquot is added 3.5 mL of 72% $HClO_4$, 4.5 mL of fresh amidol reagent (1g of recrystallized amidol (Aldrich), 2.7 mL of H_2SO_4, 10g of Na_2SO_3, and 90 mL of H_2O), and 3.5 mL of ammonium molybdate solution (4.14g in 50 mL of H_2O). The solution is diluted to 50 mL and allowed to develop for 30 min. Its absorbance is then measured at 700nm on a Bausch and Lomb Spectronic 21 and the %P determined from a Beer's law plot using a series of KH_2PO_4 standards. Excellent reproducibility is found as long as complete digestion is

obtained and all glassware is rinsed completely free of phosphate detergents.

Iodine Oxidation Analysis[66]

A suction-dried (hydrated) resin sample corresponding to 0.5-g dry weight is placed with 20 mL of 0.2 N KI_3 and 2 mL of pyridine into a 100-mL bottle. The bottle is shaken vigorously for 22 h. Excess KI_3 is titrated with standard $Na_2S_2O_3$ and the P-H capacity calculated.

Zinc Analysis

Each series of vials for a given resin contained a given zinc concentration in 5 mL of solution and a quantity of resin containing 1 mequiv of acid sites (usually about 0.5g). An amount of zinc stock solution (2 N $NaNO_3$) was used to yield initial milliequivalent ratios (R_i) of zinc ions to resin protons in the region 0.02-1.5; the remainder of the 5-mL solution consisted of 4 N $NaNO_3$. Each 5-mL solution contained 0.025 microcuries of ^{65}Zn initially and the solutions were counted after a 17-h equilibration period. Counting was done in a NaI-TlI well-type scintillation counter. A multichannel analyzer with a region-integrating feature allowed only the 1.1-MeV ^{65}Zn peak to be counted, thus reducing background count rate and increasing counting accuracy. One-milliliter samples were counted twice, each for 1 min, and the cpm's

averaged for all calculations. The solution pH was measured with a Brinkmann pH meter.

Copper and Rubidium Analysis

The analysis with ^{64}Cu and ^{86}Rb extraction was carried out in the same manner as the zinc analysis.

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PART II

SYNTHESIS OF HIGH STABILITY SUPPORTED COMPLEXING AGENTS FOR THE RECOVERY OF METAL IONS

CHAPTER 1

INTRODUCTION TO SUPPORTED LIQUID EXTRACTANTS

Solvent Extraction

Transport of material from one phase to another is the most basic procedure to obtain separation of mixed components. Examples of this are distillation, precipitation, and solvent extraction. Solvent extraction however may permit a simpler and cleaner separation (vide infra).[1]

Solvent extraction or liquid—liquid extraction has been known for some time. In 1842 Peligot was able to extract uranyl nitrate into diethyl ether.[2] In 1892 Rothe[3] and Hanroit[4] reported the extraction of iron from hydrochloric acid by diethyl ether. This method was then used to separate iron from many other metals.[5]

Liquid—liquid extraction was not widely used until the development of metal ion extraction via chelate complex formation. In 1925 "dithizone" was introduced by Fischer as a precipitant for some metals.[6] In 1934 he reported the extraction of metal dithizonates.[7] Other extractants developed in the 1930s were cupferron[8] and dimethylglyoxime[9] while 1-nitronaphthol[10] and 8-hydroxyquinoline[11] were developed in the early 1940s

A period of extremely fast advance began in the 1940s

during World War II. Atomic energy research necessitated the separation and purification of almost all of the elements. Since that time an extremely large amount of literature has been published in the area of liquid-liquid extraction.[1]

The use of liquid-liquid extraction seems almost endless and has been reviewed several times in books and articles.[12-42] The use of liquid-liquid extraction offers some very attractive advantages: 1) a wide range of liquid extractants are available, 2) good selectivity can be obtained, 3) fast reaction kinetics, and 4) very simple equipment needs.

Examples of liquid—liquid extraction can be found from both industrially applied methods and academic research. The Handbook of Solvent Extraction outlines many industrial hydrometallurgical processes.[43] One of the most significant was the development of copper—specific extractants (LIX reagents, hydroxyoximes, Henckel Corp.) which are now used in copper mining. The first commercial operation used LIX64N which is a mixture of an aliphatic hydroxyoxime and hydroxybenzophenone to remove copper from mine leachings in a pH range of 2.0 - 2.3. Other examples include the use of di-2-ethylhexyl phosphoric acid (DEHP) to extract vanadium, DEHP and/or versatic acid to extract cadmium and zinc, and the use of tributylphosphate, quaternary ammonium salts, tertiary

carboxylic acids, and DEHP to separate rare earth metals.

Tri-n-octylphosphine oxide and methyl trialkyl ammonium chloride have been used to extract americium and europium from concentrated chloride solutions.[44]

Argonne National Laboratory has had an extensive program in solvent extraction. Some of the extractants that they have developed and/or studied are listed below:

$(RO)_2PO(OH)$

R = p-tolyl, o-tolyl, beta-naphthyl, p-phenylphenylene, 3-phenylpropyl, p-isopropyl-phenyl, 2-phenylethyl, cyclohexyl. butoxyethyl.

ref. 45

$RPO(OH)_2$

R = cyclohexyl

ref. 46

(RO)RPO(OH)

R = phenyl/cyclohexyl, diphenyl, dicyclohexyl

ref. 46

$R_2PO(OH)$

R = cyclohexyl/hydrogen, dicyclohexyl, cyclohexyl/phenyl, phenyl/hydrogen, diphenyl

ref. 46

Di-n-octyl phosphinic acid

ref. 47

2-octylphenyl phosphinic acid

ref. 48

The almost infinite variations of extractants were all developed with the idea of increasing the selectivity for a particular metal or group of metals.

El-Naggar, Maghrawy and Ramadan have recently used DEHP with neutral extractants to extract protactinium (V).[49] The neutral extractants used were trioctylphosphine oxide (TOPO), triphenylphosphine oxide (TPPO), and tributyl phosphate. All of the neutral extractants caused synergistic enhancement of Pa(V) extraction. The one exception was that, at low concentrations, TBP caused a decrease in extraction (antagonism).[49]

Rickelton, Flett and West have studied the separation of cobalt and nickel under continuous countercurrent conditions.[50] The study involved the comparison of phosphinic, phosphonic, and phosphoric acid extractants. The following table of results shows the effective separation ability of the three acids:

Extractant	Co/Ni Separation Factor
$(RO)_2POOH$	14
R = 2-ethylhexyl	
(RO)RPOOH	280
R = 2-ethylhexyl	
R_2POOH	7000
R = 2,4,4-trimethylpentyl	

Schulz and Navratil have prepared a discussion on extractants containing more than one active site.[51] These include extractants with two or more acidic groups, two or more coordinating groups or any combination. The advantages of this type of extractant is obvious in light of synergistic enhancement (see Part 1, chapter 1).[51]

The development of solvent extraction has been able to solve many separation problems. However the technique is hampered by one major problem. The problem is the loss of extractant via entrainment and solubility in the aqueous phase.[43] This limits the use of the technique for both economic and environmental reasons. The solubility of the sodium salt of di-2-ethylhexyl phosphoric acid is about 50ppm at room temperature.[52] If the aqueous phase contains NaOH the solubility can exceed 70 g/l. At high salt concentrations the solubility can be decreased. In general the carboxylic acid extractants are more soluble

than the phosphorus acids and the neutral extractants such as the LIX reagents are less soluble. Some reported extractant losses are: 1) 900ppm for naphthenic acid in nickel extraction,[53] 2) 30ppm for DEHP in rare earth metal extraction,[54] and 3) 4-15ppm for LIX64 in copper extraction.[55-58] These values include losses by both solubility and entrainment. The loss of extractants requires that the extractant be replaced in the extraction process as well as it being removed from the waste water. The removal of lost extractant from the waste water is an important consideration. Extractants in waste water end up in the environment where they concentrate in biological systems.[52] The toxicity levels for some extractants are below 1ppm .

Supported Liquid Extractants

Small found that the problem of entrainment could be overcome by supporting a liquid extractant on a solid support.[59] Small called these composites "gels" and the separation technique gel—liquid extraction. The gel is now referred to as a polymer absorbed extractant (PAE) to avoid confusion with gel copolymers. Small formed his PAE by using a styrene bead that was crosslinked with 2% divinylbenzene as his solid support. Surface sulfonation of the bead to 0.001% of the total bead volume was done. This surface sulfonation lowered the hydrophobicity of the

bead surface and allowed for better bead contact with the aqueous phase during extractions. The copolymer bead was then contacted with a solution of tri-n-butyl phosphate in perchloroethylene. The perchloroethylene is needed to cause swelling of the bead and obtain uptake of the extractant. Using this PAE in a packed column Small was able to separate uranyl nitrate from iron and thorium.

The formation of a PAE allows for the use of liquid extractants as if they were ion exchange resins, but now with the advantages of liquid-liquid extraction (i.e. the best of both worlds).

Ion exchange chromatography involves passing mixtures of ions through packed columns of ion exchange resins to obtain separations.[60-63] If a PAE is used instead of the ion exchange resin it is possible to obtain enhanced separation ability due to the increased selectivity of the liquid extractants over classical ion exchange resins. This type of separation is called extraction chromatography.[64-70] Ghersini in a discussion on extraction chromatography mentions that DEHP on silica gel or Teflon has the ability to separate a solution of Tl, Ga, In, Al, and Ba, Sr, Ca.[64]

Teste and DelleSite were able to separate several mixtures of similar ions by extraction chromatography. The first set was Co^{+2}, Ni^{+2}, and Fe^{+3}, the second was uranium and thorium, and finally americium and plutonium.

They used Teflon and polyethylene as their supports with tri-n-octylamine, DEHP, and aliquot 336 (a commercial extractant from Henckel) as their extractants.[65]

The examples above show the utility of extraction chromatography. PAEs have the tendency to lose both solvent and extractant due to aqueous phase solubility which is keeping this technique from becoming an accepted industrial or analytical technique.[59] In addition Small noted that under certain conditions the organic phase would drain out of the polymer support.[59] Small commented that the experimental conditions could be adjusted so that solubility losses could be tolerated. However on a large scale industrial process these losses would pose difficulties for the reasons mentioned earlier.

Liquid Membranes (LM)

Liquid membrane separations involve the transport of a substrate from one liquid phase through a second liquid phase into a third. The second liquid phase is immiscible with the other two (e.g. water/chloroform/water).

In order to make this a practical industrial technique a high surface to volume ratio is needed. Several papers have been published regarding the use of emulsion membranes in carrier mediated transport[71-80] and diffusionally controlled separations.[81-82] The emulsion forms the barrier between the two miscible phases and

mediates transport. Both normal liquid membranes (e.g. water/chloroform/water in a U-tube) and emulsion liquid membranes are studied. The normal membrane is a simpler laboratory technique to study.

Melzner et.al. used LIX reagents (hydroxyoximes, Henckel Corp.) in emulsion liquid membranes to effect the separation of copper from zinc, cadmium, cobalt, and nickel.[80] Mikucki and Osseo-Asare have used LIX64N in an emulsion membrane to extract copper.[83] Span 80 (sorbitol monooleate) was used as the surfactant. It was observed that the extraction of copper increased with increasing surfactant levels due to a higher emulsion stability. However a maximum value was seen followed by a decrease in extraction rate at very high levels of surfactant. The decrease was related to increased surface tension and emulsion viscosity. Under a similar system Gu, Wason and Li have studied the mass transfer of cobalt, nickel and copper in a DEHP emulsion liquid membrane.[84]

Crown ethers are frequent carriers in liquid membranes for a wide range of cations.[71-76] Izatt and co-workers have extensively studied the use of macrocycles for metal ion separations.[71,72,85-89] The systems used involved both static (water/chloroform/water) liquid membranes and emulsion liquid membranes. Macrocycles have been found that have the ability to separate mercury and potassium ions, mercury and cadmium ions, and thallium

from other monovalent ions. The macrocycles used included crown ethers, cryptands, and crown ethers where sulfur and/or nitrogen have been substituted for oxygens.

Tertiary amines are typically used for the transport of anions such as $UO_2(SO_4)_3^{-4}$.[78]

Li has set up several systems that separate organic molecules by selective permeation through a liquid membrane.[81,82] An example is the removal of phenol from waste water.[81] A solution of sodium hydroxide is emulsified with sorbitan monooleate and then put in contact with the waste water containing the phenol. The phenol permeates through the membrane to the sodium hydroxide solution inside the membrane. Upon contact with sodium hydroxide the phenol is converted to sodium phenolate and can no longer travel through the hydrophobic membrane and is thus trapped within the emulsion.

Liquid membranes are effective in carrying out separations but are difficult to use. The same entrainment problems seen in liquid-liquid extraction are found with emulsion liquid membranes. In the emulsion membranes there is the additional problem of membrane stability which renders them totally impractical, even if entrainment were not a problem. The emulsion liquid membranes do have the advantage that extraction and stripping take place in the same system and therefore less extractant is required.

Supported Liquid Membranes(SLM)

Entrainment losses can be avoided by supporting the extractant on a solid support (the membrane equivalent of a PAE).[90] In laboratory experiments flat sheet solid supports are used. Additionally systems have been developed to use hollow fibers which enables a high surface to volume ratio for good kinetics.

Bloch introduced the idea of supported liquid membranes in a discussion on solvent membranes.[91] The idea was that if a liquid membrane layer could be made very thin the transport kinetics would increase substantially. Bloch's first attempt at a SLM was to support a solution of tributyl phosphate on filter paper.

Danesi and Horwitz have studied the transport of europium through a DEHP/dodecane liquid membrane supported on polypropylene.[90] They determined that the rate of transport was dependent only on the rate of transport within the membrane and the aqueous film on the membrane surface. They have also looked at the transport of actinides and lanthanides.[92] The LIX reagents have also been applied to supported liquid membranes for the separation of copper.[93,94]

Kreevoy and co-workers have studied LIX65N SLMs for copper transport.[95] The feed side containing copper was a pH 4 acetate buffer solution and the strip side was 2M

sulfuric acid. It was found that the loading of copper onto the membrane was an equilibrium process, but that the stripping process was somewhat slower than expected from equilibrium considerations.

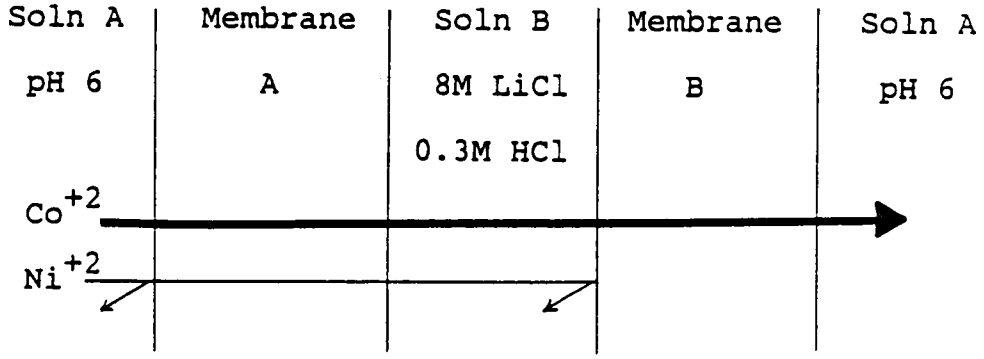
Baker and co-workers were able to "chemically pump" copper ions against a concentration gradient.[96] The transport took place across a LIX64N SLM on Celgard 2400. It was found that, if the pH of the strip side was two pH units less than the feed side, copper could be pumped against a 4000 fold concentration gradient. This system was able to extract copper 1000 times faster than iron (III).

Babcock and co-workers have developed methods for the separation of uranium from vanadium and uranium from molybdenum.[97] The SLM system used incorporated a solution of Alamine 336 (tertiary amine, Henckel Corp.) in Aromatic 150 (high boiling aromatic solvent, Exxon Inc.) supported on Celgard 2400 (Celanese). Uranium was separated from vanadium as uranyl sulfate when a 500 mv potential was placed across the membrane. If the feed side contained 1M chloride ions molybdenum was transported preferentially over uranium.

Danesi and Horwitz have used other phosphorus reagents in SLMs. Two examples are the use of n-octyl(phenyl)-N,N,-diisobutyl carbamoylphosphine oxide (CMPO) to obtain facilitated transport [98] and the use of

Cyanex 272 to separate cobalt and nickel.[99]

In order to improve further the separation of cobalt and nickel Danesi used SLMs in series.[100] A diagram of the system is given below:



Membrane A = Cyanex 272 on Celgard 2500

Membrane B = Tridodecylammonium chloride on Celgard 2500

The effect of putting membranes in series can be seen by the analysis of cobalt/nickel separations.

%Ni present at 99% Co Recovery	Membrane
2.1	Single A
1.1	Single B
0.07	A and B

Another adaptation of membranes in series by Danesi and Cianetti involved the separation of americium and europium.[101,102] Separation was obtained using a neutral

extractant SLM in series with an acid extractant SLM.

The supported liquid membrane is a major improvement in membrane separations, but is still bothered by the same problems that were associated with the PAEs. The loss of extractant due to solubility in the aqueous phase is now more detrimental because of the lower extractant level.

Interpenetrating Polymer Networks

What is needed in both the PAE and SLM is a method in which to keep the liquid extractant within the support. The formation of an interpenetrating polymer network (IPN) has the ability to permanently entangle two independent polymer networks. The formation of an IPN with a polymerizable extractant could greatly decrease extractant losses if not totally eliminate them.

Interpenetrating polymer networks are formed when an existing polymer network is swollen with the monomer of a second network which is then polymerized within the first.[103-107] The resulting system contains two polymer networks that are chemically independent but are physically interlocked.[108]

In 1960, Millar presented results of IPN formation with styrene/2%DVB with two and three interpenetrating networks.[109] He found that the physical entanglements resulted in an effective increase in the observed crosslink level. A styrene/2%DVB network which is

intermesh polymerized with another styrene/2%DVB network has an effective crosslink level of 3.6%. If a third network is intermesh polymerized, the effective crosslinking goes to 7.0%.

Dow Chemical, in 1962, proposed the formation of an IPN by polymerizing acrylic acid within a sulfonic acid ion exchange resin to form a composite ion exchange resin.[110]. A similar system was made by Rosek-Galina and Trochimczuk.[111] The IPN consisted of a styrene divinyl benzene network copolymerized in a polyethylene film. The styrene was then sulfonated with chlorosulfonic acid to give an exchange capacity of 2.01 meq/g which corresponds to 30 wt% styrene in the starting IPN.

Theory of Membrane Transport

Membrane ion transport kinetics have been determined to be diffusionally controlled and are therefore subject to a Nernst-Planck treatment.[112] The Nernst-Planck equations give the following result for permeant flux in an ion exchange medium for coupled transport:

$$J_i = -D_i(\text{grad } C_i + C_i \text{grad } \ln f_i + z_i C_i \, F/RT \text{ grad } \phi)$$

J = flux

D = diffusion coefficient

C = Concentration

f = activity coefficient

z = valence

F = Faradays constant

R = gas constant

T = temperature

ϕ = electric potential

The flux is equal to the diffusion coefficient multiplied by the adjusted ion concentration. If the permeating ion is in very low concentration, typically less than or equal to 0.001M the activity is nearly one and the second concentration term becomes zero. The third concentration term considers the effective electric potential seen by the ion. In coupled transport the two ions that are being transported will have different D values and most likely different concentrations. This means that at the initiation of transport the net fluxes of each ion will not be the same. This results in formation of an electric potential. This has the effect of slowing the faster ion and speeding up the slower ion.

Therefore over extended periods of time the net electric potential will be zero. Under these conditions ions will obey the simpler Fick's law equation.

$$J_i = -D_i \text{ grad } C_i$$

If this is the case it is obvious that both ions can not obey the Nernst-Planck equations at the same time. The over all diffusion coefficient obtained from the Nernst-Planck equations is:

$$D = \frac{(C_1 + C_2)D_1D_2}{C_1D_1 + C_2D_2}$$

$$D = D_1 \text{ if } C_1 << C_2$$
$$D = D_2 \text{ if } C_2 << C_1$$

Therefore the diffusion rate is controlled by the minority component and Fick's law applies only to the minor component.

The general conditions required for Ficks law to hold for membrane transport are: 1) dilute solution, 2) fast reaction kinetics (i.e. steady state loading and stripping),and 3) linear concentration gradients.[113] If these hold then Fick's law for membranes becomes:

$$J = PC$$

Where P is the permeability coefficient. If the experimental parameters of aqueous phase feed volume (V) and membrane area (Q, corrected for porosity) are incorporated, the equation becomes:

$$J = dC/dt \quad V/Q$$

Integration gives:

$$\ln C/C_o = -PTQ/V$$

This is the form of the equation most used to analyze membrane performance. The permeability coefficient is a time independent parameter containing the chemical and diffusional parameters of a given ion permeating a given membrane under specific conditions. If conditions are experimentally constant then changes in the permeability coefficient will be an indication of membrane performance and stability.

Danesi has further extrapolated this to hollow fiber liquid membranes.[114] The model is based on the same assumptions and considerations of normal membranes with the addition of the new geometric considerations. The validity of the theory was demonstrated using DEHP

supported on Celgard hollow fibers for copper transport.

Elhassadi and Do have looked at the effects of the carrier and the diluent concentration on SLM ion transport.[115,116] The system studied was DEHP supported on a Celgard 2500 membrane. Based on the transport of uranium a transport mechanism was proposed which involved the solubility of the metal ion complex within the membrane and the viscosity of the membrane. It was observed that, as the DEHP concentration increased, so did the uranium transport rate. However a maximum value was obtained at 50% DEHP at which point additional DEHP caused a decrease in transport rate due to increased viscosity.

The work presented in part II of this dissertation involves the use of IPN formation with polymerizable extractants to make stable PAEs and SLMs. The extractants are chemically similar to the phosphorus based liquid extractants with the addition of polymerizable double bonds. These extractants have been homopolymerized and copolymerized into polystyrene and polypropylene. In most cases the resulting IPN system was more stable than its nonpolymerized counterpart. The stabilization was accomplished without loss of extraction ability or selectivity.

CHAPTER 2

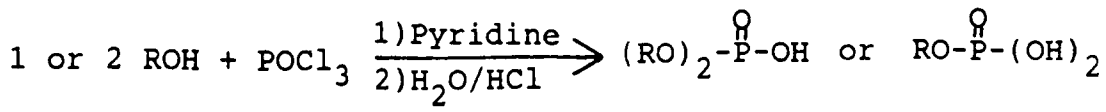
INITIAL SYNTHETIC APPROACHES TO POLYMERIZABLE EXTRACTANTS

The work presented in this chapter consists of experiments which developed the idea of incorporating polymerizable double bonds into a phosphorus—based extractant.

Choice of Synthetic Target Molecule

The choice of a target molecule was based on the following considerations: 1) the synthesis must be simple to allow for eventual large scale industrial synthesis, 2) the extractant needs to be phosphorus-based to allow both high capacity and good selectivity, and 3) the polymerizable group should form low degree of polymerization ($\overline{DP}$) polymers to maintain good extractant mobility. Based on these considerations several different syntheses were attempted based on the addition of one or two olefinic molecules to $POCl_3$.

The addition of an alcohol to $POCl_3$ under Schotten-Bauman conditions is a very straight forward reaction. This reaction will lead to the formation of a monoacid or diacid as shown below:

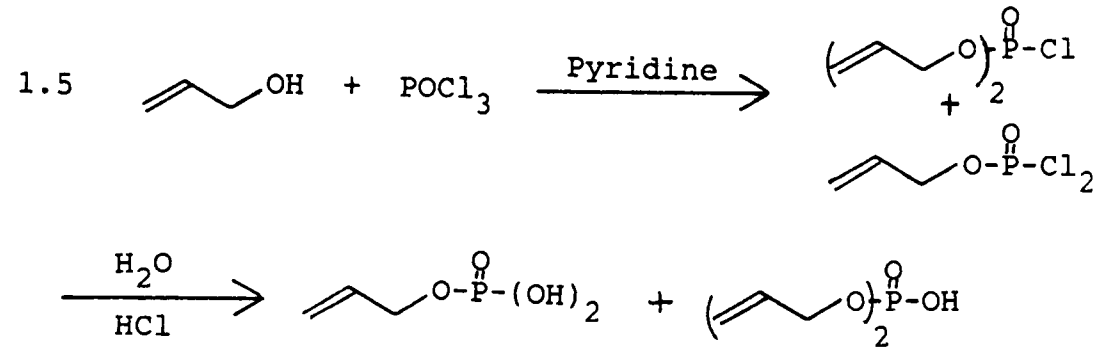


Both the monoacid and diacid could be used as metal ion extractants.

The olefinic alcohol selected was allyl alcohol. If the allylic group could be attached to the phosphorus an IPN could be formed by polymerizing the allylic double bond with a free radical initiator. Allylic double bonds tend to polymerize to form low molecular weight oligomers. The formation of oligomers should allow for IPN formation while maintaining good local extractant mobility.

Allyl and Diallyl Phosphoric Acid

The first synthetic attempt was of a mixture of allyl and diallyl phosphoric acid.



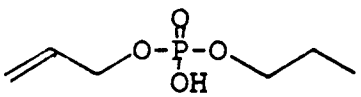
$POCl_3$ (1 equiv) and pyridine (3 equiv) were placed in a round bottom flask with diethyl ether. To this mixture, 1.5 equiv of allyl alcohol was added over two hours. The reaction was then quenched by the addition of a 1M HCl/4M NaCl solution. The HCl was present to aid in

the removal of the pyridine and the NaCl was present to maintain a high ionic strength to avoid product loss to the aqueous phase. Removal of the organic solvent yielded about 0.5g of acidic product. The product was mostly the diacid (78%).

Several additional synthetic attempts were made with a 1:1 ratio of $POCl_3$ to allyl alcohol. In each case the isolated product was mostly monoacid and yields were very low. It was thought that having two polymerizable groups would cause the network to be too highly crosslinked. It was therefore proposed that a mixed ester containing one aliphatic and one allylic group could be made and isolated in reasonable yields.

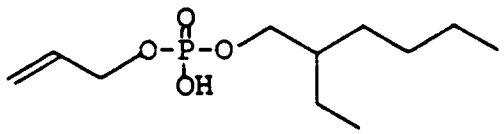
Aliphatic, Allylic Mixed Esters

The first synthetic attempt to form a mixed ester was that of allylpropyl phosphoric acid.



Allyl alcohol in diethyl ether was added to a mixture of $POCl_3$ and pyridine in diethyl ether. The ratio of allyl alcohol to $POCl_3$ was 1:1. This addition was followed by a second addition of 1-propanol in diethyl ether. The isolable product did not contain any allylic groups as determined by IR and NMR.

The problem was assumed to be one of product solubility in the aqueous phase. In order to decrease the hydrophilicity of the product it was determined that 2-ethylhexanol should be the second alcohol added. The synthesis was carried out in the same manner as the allylpropyl synthesis. The desired product is shown below:



A much higher yield of material was now isolable (78% based on AEHP). However the IR showed only a trace of the allylic group and the titration showed a mixture of mono and diacid.

Table 1 shows the results and analysis for attempts at an allyl-aliphatic diester using the procedure discussed. An analysis of the results of table 1 reveals that the allyl group was only incorporated in the product when it was the only alcohol added or it was added in excess of 1:1. Based on this observation it was suspected that the following side reaction was destroying the first equivalent of allyl alcohol.

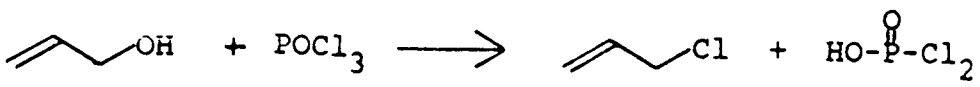


TABLE 1

ALLYL-ALIPHATIC PHOSPHORIC ACIDS

Code number	$POCl_3$/Pyr[a]/AA[b]	Second Addition	Allyl ID[c] IR	NMR
MS-01-184	1 / 3 / 1.5		+	
MS-01-192	1 / 3 / 1		+	
MS-01-196A	1 / 1 / 1		+	+
MS-01-204	1 / 2 / 1	1[d]	-	-
MS-01-212A	1 / 2 / 1	1[d]	-	
MS-01-212b	1 / 2 / 1	1[e]	-	
MS-01-224	1 / 2 / 1	1[e]	-	
MS-01-250A	1 / 5 / 1	1[e]	-	-
MS-01-250B	1 / 5 / 2	1[e]	+	+
MS-01-264B	1 / 5 / 1	1[e]	-	-

[a]Pyridine

[b]Allyl Alcohol

[c]Identification

[d]1-Propanol

[e]2-Ethyl-1-hexanol

A reverse order of addition may eliminate this side reaction since 2-ethylhexanol is less reactive than allyl alcohol.

The initial results of the reverse order of addition showed that AEHP was made. (see experimental section for details). The IR spectra showed peaks at 3080 cm^{-1} and 1635 cm^{-1} which are indicative of the C-H stretch of a double bond. The results of the reverse order of addition syntheses of AEHP are given in table 2. The NMR data given in table 2 was based on the integration of the five down field allylic hydrogens vs. the 17 up field aliphatic hydrogens (see figure 1 for NMR). These results indicate that some of the allyl alcohol may still be getting chlorinated instead of adding to the phosphorus oxychloride. An additional problem can be seen in MS-02-005. The ratio of mono to diacid decreases if the sample is reworked. The rework involves acid scrubbing to remove any cations that may have exchanged with the AEHP. This instability necessitated a change in the synthetic target. This new synthetic target is discussed in chapter 3.

In spite of difficulties with the final product, some significant observations were made. One problem that was confronted was how to remove the excess water and acid from the product. For normal organic systems magnesium sulfate and sodium bicarbonate would be used. However

TABLE 2

AEHP SYNTHESIS VIA REVERSE ADDITION

Code Number	Titration Data[a] 1st	2nd	NMR Ratio[b] exp	theory
MS-02-005	3.83	0.86	0.097	0.294
MS-02-005[c]	3.53	1.32		
MS-02-024	2.91	--	0.262	0.294
MS-02-024[c]	3.37			
MS-02-065I	3.22	0.61	0.256	0.294
MS-02-065II	4.41	1.11	0.230	0.294

[a]Units of mequiv/g

[b]Allyl/Aliphatic hydrogen ratio

[c]Sample after rework

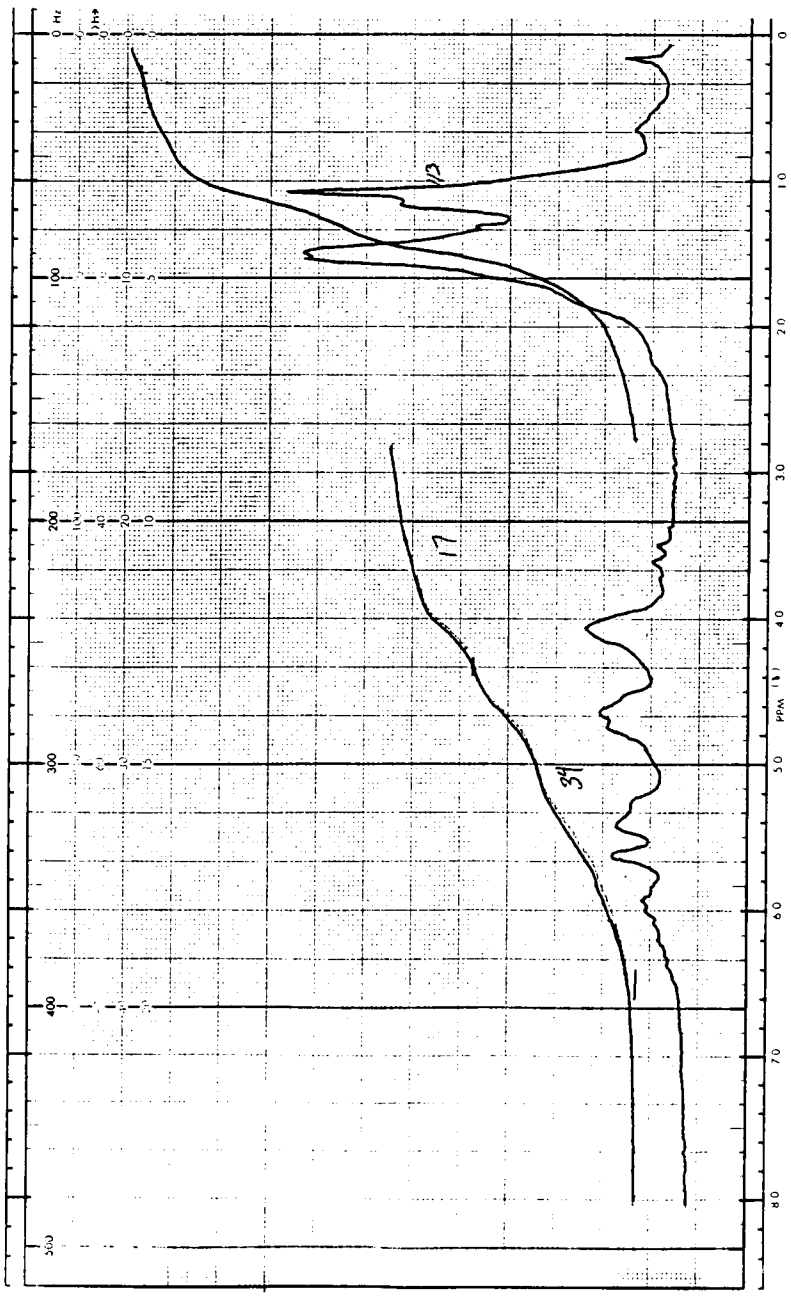


FIGURE 1

AEHP NMR, MS-02-024

both of these agents cause ion exchange to take place. As an alternative absolute ethanol was added and removed by rotary evaporation. This caused the water and excess hydrochloric acid to be azeotroped.

In addition some preliminary polymerization experiments were performed. Based on the NMR ratios of the allyl vs. aliphatic hydrogens only about 27% of the allylic groups were consumed. The polymerization was done at 80^{o}C for 10 h in toluene with 1% BPO as the initiator. The idea of two allylic double bonds on the same phosphorus group causing the formation of a restrictively tight network seems unfounded, due to the low level of polymerization.

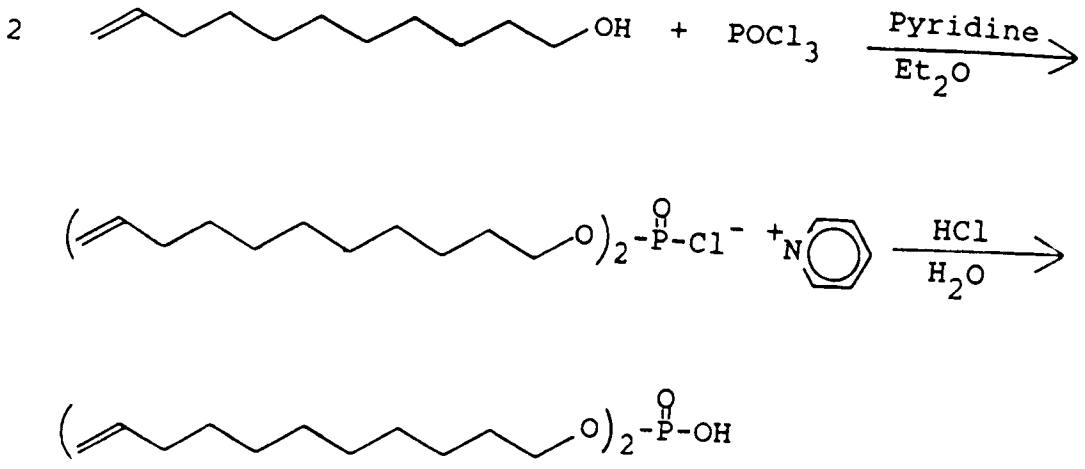
CHAPTER 3

DIUNDECENYL PHOSPHORIC ACID

The hydrolysis problems with the allyl phosphoric acids can be attributed to the reactivity of the allyl group. This was overcome by removing the double bond from the ester linkage. 10-Undecen-1-ol is commercially available and was used to obtain polymerizable phosphoric acids. Also, based on the preliminary polymerization results mentioned in chapter 2, it was determined that having two double bonds on the extractant would increase the chances of forming a network upon polymerization.

Synthesis of Diundecenyl Phosphoric Acid

The synthesis of diundecenyl phosphoric acid is outlined below.



Undecenyl alcohol (2.1 equiv) is added to a mixture of $POCl_3$/pyridine (1:5 molar ratio) in diethyl ether. The diethyl ethyl allows for a relatively dilute system (0.25M, based on $POCl_3$). This, in combination with a slow addition rate helps to maximize the yield of diaddition product. The excess of pyridine helps to complex the third chlorine on the $POCl_3$ and limits triaddition product.[117] The reaction is left at room temperature for an additional 16 hours to before the reaction is terminated. Termination is carried out by the addition of 1M HCl. This causes hydrolysis of the final chlorine and also takes care of the excess pyridine. The crude DUP product mixture is further washed with HCl to remove any remaining pyridine. No special precautions need to be made to avoid loss of DUP to the aqueous phase as long as it is in its acid form.

Copper Purification of DUP

Purification of the crude DUP is carried out by precipitating it as a $(DUP)_2Cu$ salt.[118] The copper (II) salt is formed by first converting the DUP to its sodium salt with sodium hydroxide. The organic salt solution is washed with saturated sodium sulfate to remove the excess base. The DUP sodium salt is then contacted with copper sulfate solution and ion exchange takes place to form the $(DUP)_2Cu$ salt. The excess organic solvent is removed and

the $(DUP)_2Cu$ salt is precipitated in cold acetone. The precipitate is then further washed with cold acetone. This precipitation technique allows for the separation of acidic products from neutral products and starting material. However it does not separate mono and diacid products. The synthetic conditions given earlier were chosen with these concepts in mind.

Analysis of DUP

The analysis of DUP included IR, phosphorus elemental analysis, and sodium ethoxide titrations. The IR analysis was used for qualitative identification of the product (see figure 2). The titration and phosphorus elemental analysis are complementary techniques and were used to determine the product purity. The results of several DUP syntheses are given in table 3. The majority of the products listed in table 3 are between 85% and 95% pure with the remainder of the product being diacid.

Polymer—Supported DUP

The DUP was used without further purification to form polymer—supported extractants. There are two types of systems that are of interest. The first is termed a polymer absorbed extractant (PAE see chapter 1). The second is based on interpenetrating polymer network formation (IPN see chapter 1). Both systems have been

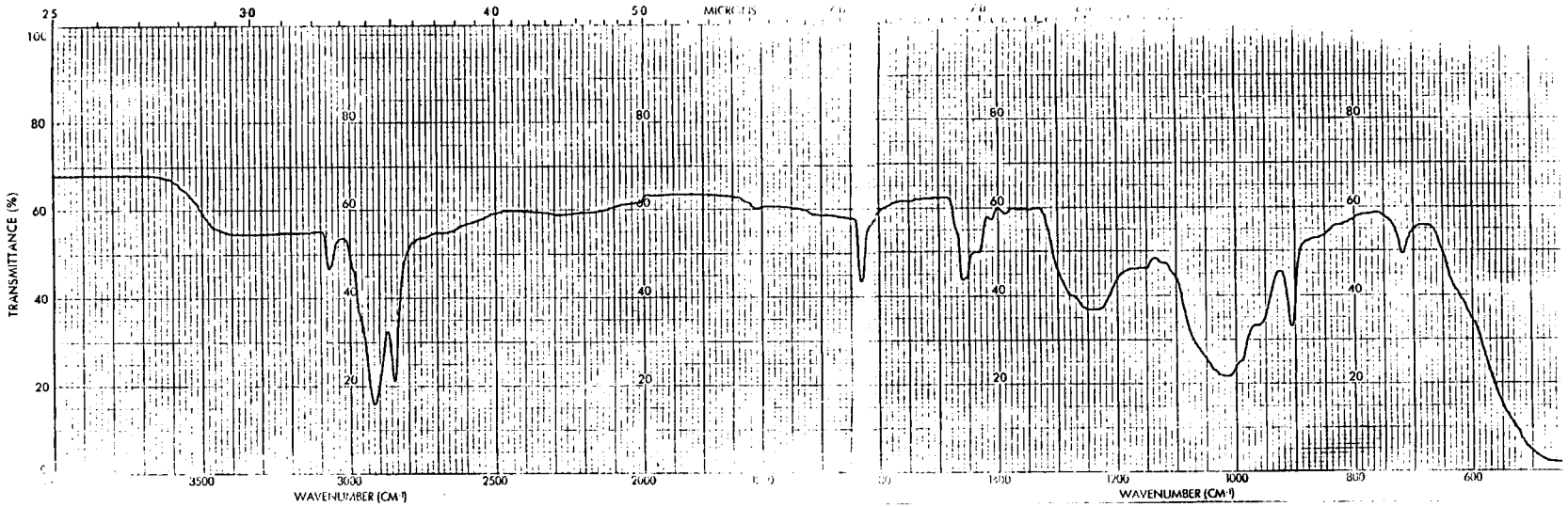


FIGURE 2

DUP IR, MS-02-071

TABLE 3

ANALYSIS OF DUP[a]

Code Number	P[b]	NaOEt[c]	Theoretical
MS-02-071	2.52	2.40/0.0	2.48
MS-02-095	2.50	2.73/0.20	2.48
MS-02-138	2.65	2.52/0.11	2.48
MS-02-156		2.44/0.15	2.48
MS-02-217	2.68	2.51/0.23	2.48
MS-03-066		2.63/0.20	2.48
MS-03-115		2.73/0.42	2.48
MS-03-133		2.89/0.24	2.48

[a]Units of mequiv/g

[b]Phosphorus elemental analysis

[c]Sodium ethoxide titration, first break/second break

made by contacting DUP in toluene solutions with macroporous polystyrene beads (see chapter 9). A PAE is converted to an IPN if the DUP is polymerized. The polymerization is done by incorporating 2%(w/v) AIBN (azo-bis-isobutyronitrile, a free radical initiator) into the swelling solution and heating the PAE at 60°C for 96 hours. The polymerization conditions were determined to be those required to consume all of the AIBN.

Elution Studies

The goal of this research is to stabilize the DUP within the polymer support via IPN formation. In order to determine stability differences between PAE and IPN systems several elution techniques were developed in order to quantify any differences between a PAE and an IPN. The absolute elution rate should be relatively fast in order to facilitate laboratory experiments of a reasonable length.

The first set of elution studies is shown in table 4. A phosphorus elemental analysis on a small sample of each resin gives the DUP remaining after each successive wash.

Continuous washing was tried with various aqueous solutions. After passing 10 liters of a 0.1N HNO_3/0.1N $NaNO_3$ solution through a PAE and an IPN, no detectable changes were seen in either. Several pure water continuous elutions were done. The best case was when a 1M

TABLE 4

ELUTION OF MS-02-091 A AND B[a]

Wash Solution[b]	P Capacity[c] A (PAE)	B (IPN)
Initial sample	1.44	1.74
H_2O	1.29	2.13
0.1N NaOH/0.5N $NaNO_3$	1.51	1.98
H_2O	1.29	1.67
1N NaOH	0.73	1.21
H_2O	0.56	1.75
95% EtOH	0.19	0.54
95% EtOH	0.15	0.28
Toluene	0.12	0.28
95% EtOH	0.13	0.20

[a]Swelling solution of 1M DUP/Toluene/2% AIBN, polymerization at 60°C for 72hr.

[b]Volume = one liter

[c]Capacity in mequiv/g

TABLE 5

ELUTION OF MS-02-095 A AND B[a]

Wash Solution[b]	P Capacity[c] A (PAE)	B (IPN)
Initial sample	1.10	1.15
H_2O	1.36	1.14
0.1N NaOH/0.5 $NaNO_3$	1.07	1.04
H_2O	0.87	0.62
1N NaOH	0.86	0.63
H_2O	0.69	0.61
H_2O/EtOH[d] (75/25)	0.14	0.23
" " (50/50)	0.11	0.20
" " (25/75)	0.07	0.14
95% EtOH	0.06	0.17

[a]Swelling solution 1M DUP/Toluene/2% AIBN, polymerization 60°C for 72hr

[b]Solution volume = one liter

[c]Units of mequiv/g

[d]EtOH = 95%

DUP/PAE was continuously extracted for five days with room temperature water. In this process a drop from 1.52 mequiv/g to 1.06 mequiv/g was seen. These aqueous conditions resemble end use conditions but are simply not efficient enough for continued experiments.

The ethanol washes seem to work very well at eluting the DUP from both the PAE and the IPN. What is needed is a determination of what ratio of water to ethanol would optimize the difference in elution rates. To this end an ethanol strength study was conducted. Figure 3 is the plot of an ethanol strength study using a 1M DUP/PAE and a 1M DUP/IPN. Based on the results given in figure 3 it was determined that a 1:1 ratio of 95% EtOH/H_2O would be sufficient to obtain reasonable elution results.

The next question to be considered is what concentration of DUP is required in the swelling solution so that upon polymerization entanglements will form. We called this the critical entanglement concentration (CEC). Four different concentrations of DUP have been studied (see table 6). Each resin was washed at a rate of 500 ml/hr with the aqueous ethanol solution. After each washing a small portion of each was removed and dried for phosphorus elemental analysis. The phosphorus capacity is equal to the DUP remaining in the resin. Plots of the phosphorus capacity vs. the number of EtOH/H_2O washes are given in figures 4-7.

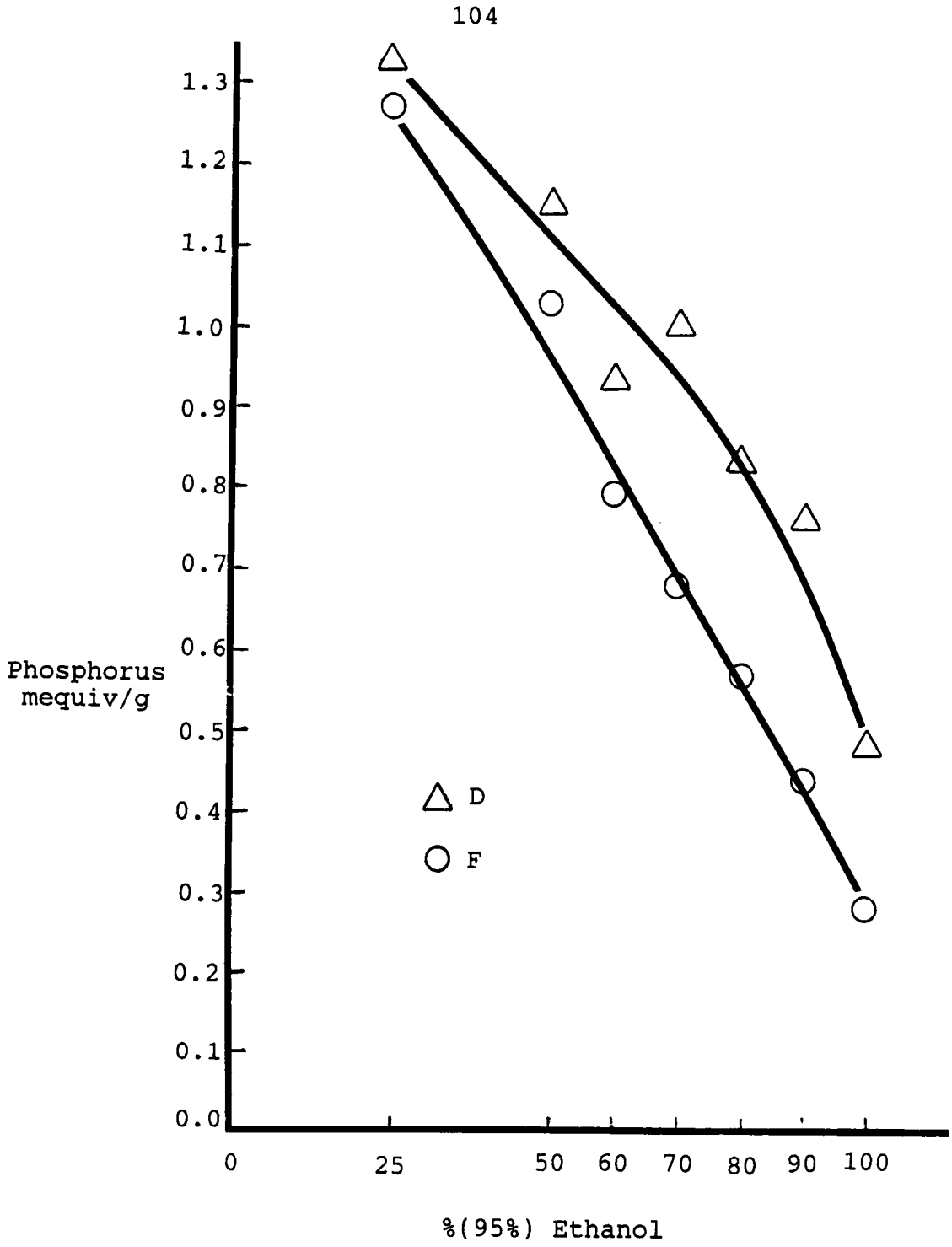


FIGURE 3

ETHANOL STRENGTH STUDY OF MS-O2-123D AND F

TABLE 6

IPN AND PAE FORMATION FOR THE DETERMINATION OF A CEC

Code Number	Swelling Solution[a]	Resin Type[b]
MS-02-144B	1.00M DUP/2% AIBN	IPN
MS-02-144C	1.00M DUP	PAE
MS-02-151C	1.50M DUP/2% AIBN	IPN
MS-02-151D	1.50M DUP	PAE
MS-02-151E	0.50M DUP/2% AIBN	IPN
MS-02-151F	0.50M DUP	PAE
MS-020151G	0.25M DUP/2% AIBN	IPN
MS-02-151H	0.25M DUP	PAE

[a]In toluene

[b]Polymer support = 5% MR polystyrene beads

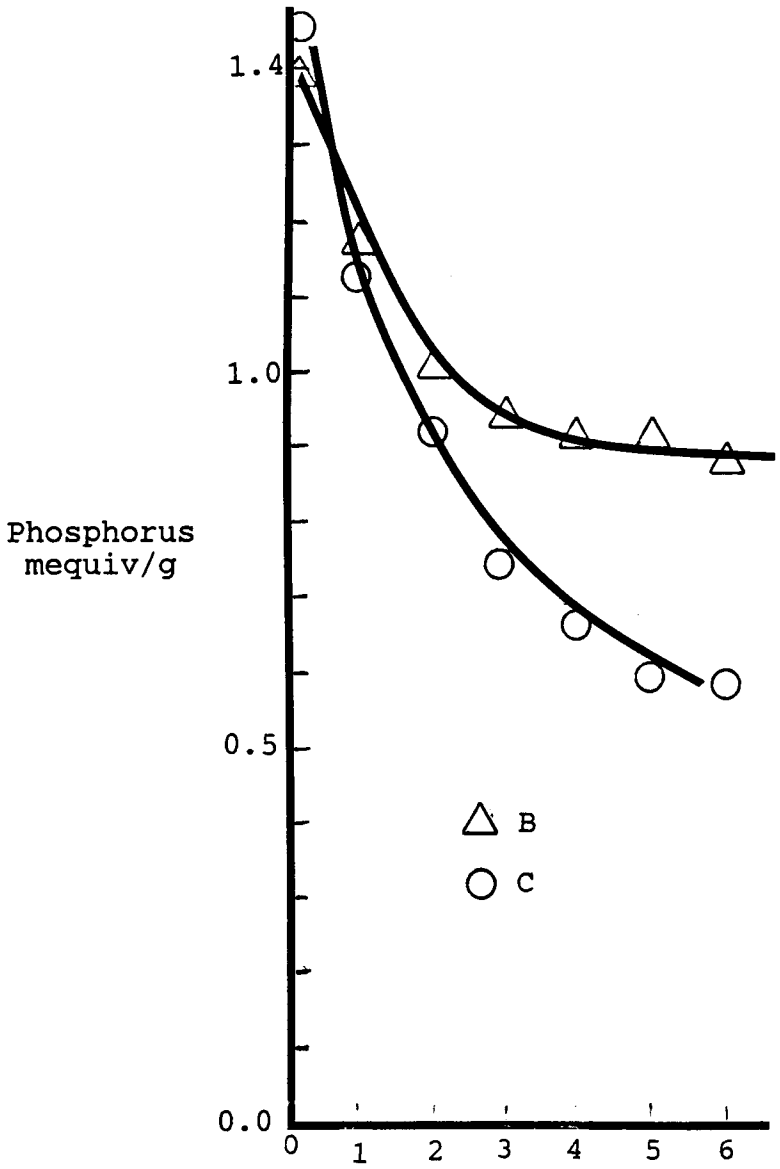


FIGURE 4

50% ETHANOL ELUTION STUDY OF MS-02-144B AND C

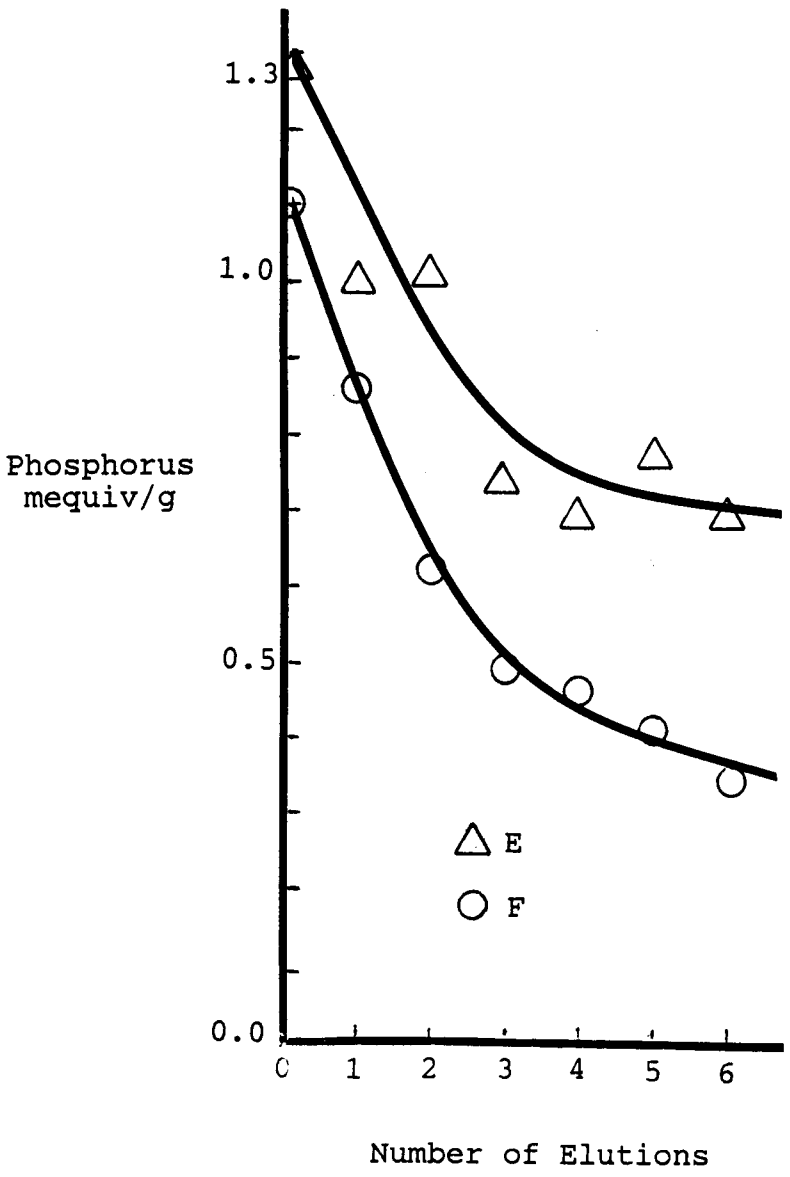


FIGURE 5

50% ETHANOL ELUTION STUDY OF MS-02-151E AND F

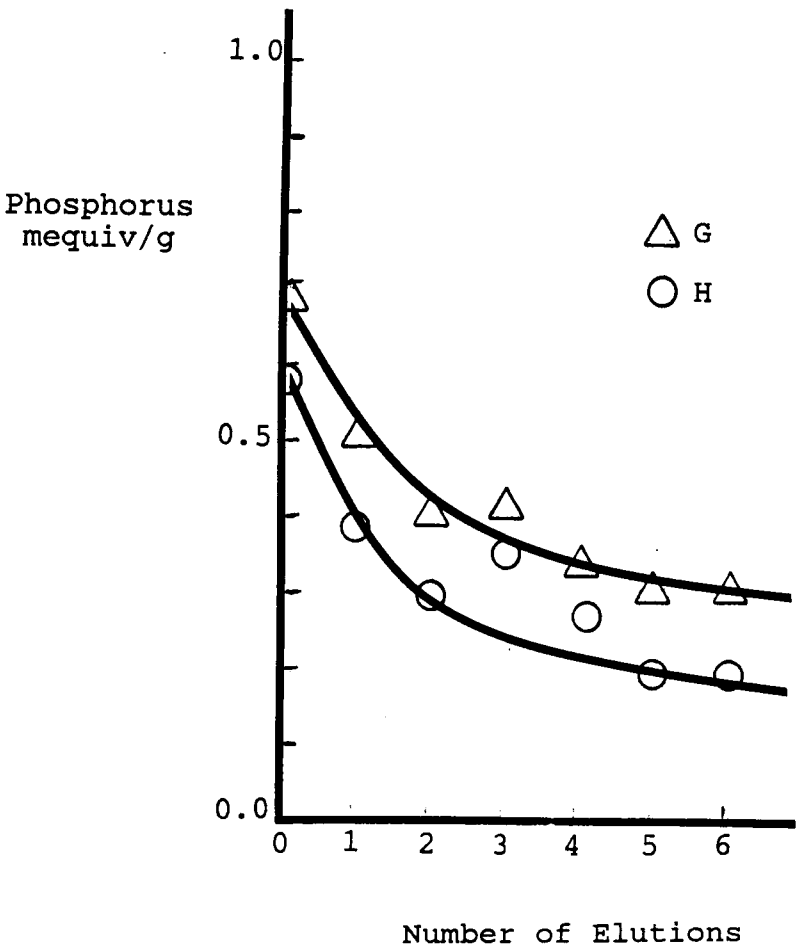


FIGURE 6

50% ETHANOL ELUTION STUDY OF MS-02-151G AND H

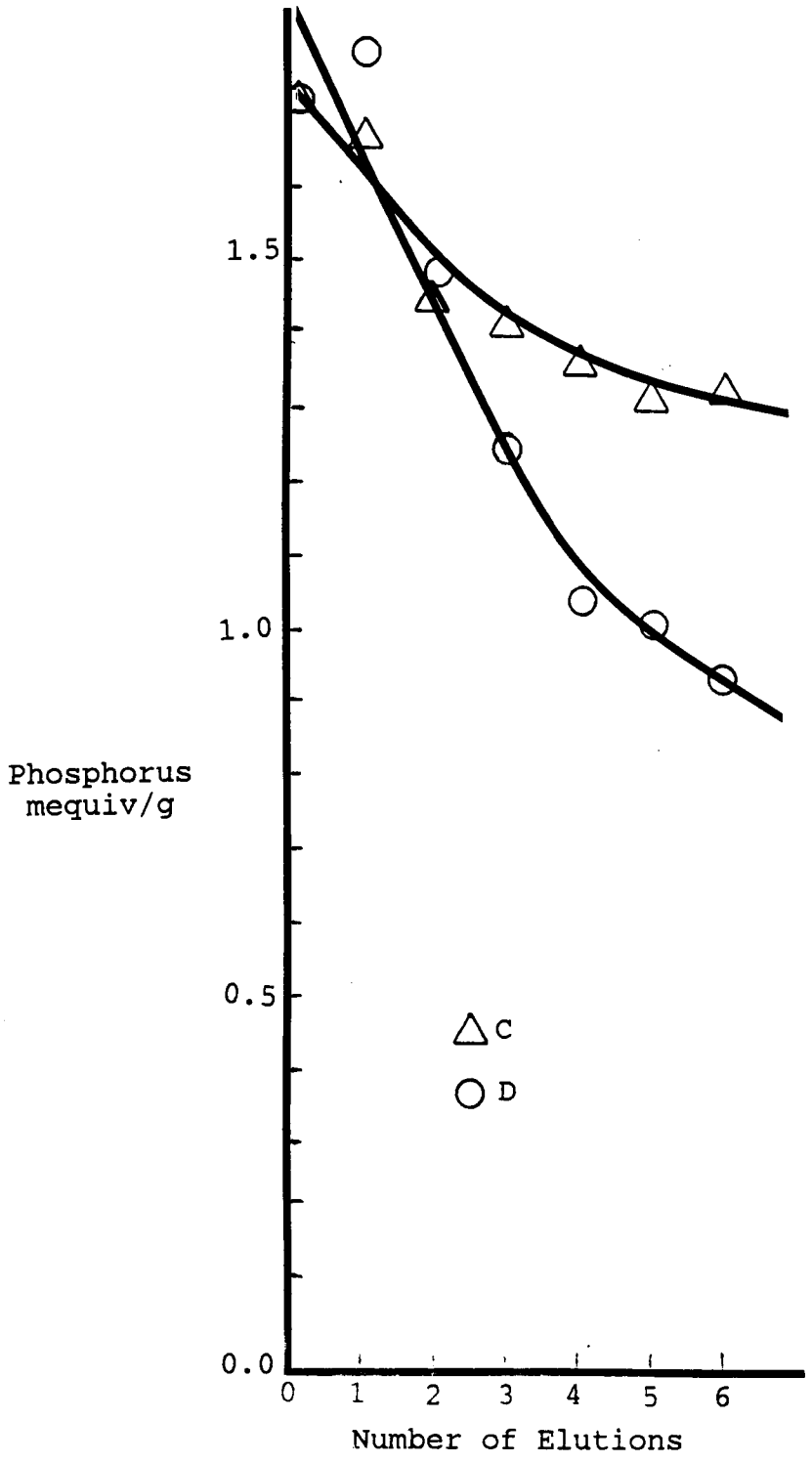


FIGURE 7

50% ETHANOL ELUTION STUDY OF MS-02-151C AND D

The CEC was determined to be 0.5M DUP based on the data presented in figures 4-7. Figure 7 shows that at 0.25M DUP, no significant difference is seen between the IPN and PAE. However at 0.5M DUP and higher there is a distinct difference in the elution rates of an IPN and a PAE. This difference has been attributed to polymer formation in the IPN.

Polymer Degree of Polymerization

The next question which needs to be answered is: what is the nature of the polymer? What is required is a determination of the degree of polymerization ($\overline{DP}$). Two separate techniques were used to determine the $\overline{DP}$ of DUP. The first technique involved a bromine number determination of unreacted double bonds. The second technique was vapor pressure osmometry (VPO). From the bromine techniques attempted, the Br_2/CCl_4 system seemed the most effective. It showed that 11% of the DUP double bonds were consumed during a 96hr polymerization. The American Standard Testing Methods (ASTM) procedure showed a 6.5% double bond consumption over the same period. Neither of these results is very encouraging. Observations of the physical properties of the DUP before and after polymerization indicate that some polymerization has taken place. DUP is a low melting solid (30-35^{o}C). However the material after polymerization remains a viscous liquid at room

temperature. This indicates that sufficient polymerization has taken place to disrupt crystallization.

Attempts at $\overline{DP}$ determinations with VPO for polymerized DUP were unsuccessful. The DUP aggregated, causing the unpolymerized DUP to give a higher $\overline{DP}$ than the polymerized DUP which does not aggregate as well. What was finally done was to use undecenyl alcohol (UA) as a model compound for DUP polymerization. Several samples of 2M UA in benzene were polymerized at 60°C for varying lengths of time. VPO analysis of each was done to determine its $\overline{DP}$. The results are given in table 7. If it is assumed that any loss in UA concentration results in the formation of dimers, then the percentage of monomer now as polymer is equal to the drop in UA concentration times two.

For MS-03-045E

$$\frac{8.822\times10^{-3} - 6.50\times10^{-3}}{8.822\times10^{-3}} \times 100 = 20.93\%$$

$20.93\% \times 2 = 41.87\%$ as dimer

Conclusion

From the evidence presented in this chapter it is clear the the concept of stabilizing extractants in polymer supports by IPN formation is feasible. Even with

TABLE 7

VPO DATA OF POLYMERIZED UNDECENYL ALCOHOL

Code Number	Pzn Time[a]	Theo M[b]	VPO M[c]	DP[d]
MS-03-045A	0hr	6.459	6.18	1.045
MS-03-045B	24hr	7.211	6.60	1.093
MS-03-045C	48hr	7.234	6.22	1.163
MS-03-045D	72hr	7.892	6.81	1.159
MS-03-045E	96hr	8.221	6.50	1.265

[a]Polymerization time at 60°C

[b]Theoretical molarity based on weight of UA added

[c]VPO determined molarity

[d]$\overline{DP}$ = Theo M/VPO M

very low $\overline{DP}$'s, the differences in the IPN and PAE elution rates are clear. However in absolute terms the performance of the IPN still falls short of what is required for applications. There are several options available for possible improvements of the performance of polymer-supported extractants. The possibilities include: 1) trapping the extractant by forming the polymer network around it (chapter 4), 2) Copolymerizing DUP in order to obtain higher $\overline{DP}$'s (chapter 5), and 3) changing the nature of the double bond in order to obtain higher $\overline{DP}$'s.

CHAPTER 4

POLYMER TRAPPED EXTRACTANTS

The concept is to form a polymer network around the metal ion extractant. Incorporating the DUP within a styrene/DVB mixture before polymerization may allow the DUP to become trapped between the polymer chains during polymerization.

Synthesis

The synthesis of polymer trapped extractants (PTE's) with DUP and DEHP was carried out by bulk polymerization of the solutions shown in table 8. Polymerization was done at 80^{o}C for 10hr. Solutions A and C went cloudy very quickly which indicates phase separation. All of the samples became solid within the first hour of the polymerization. The reactivity ratio of styrene with allylic double bonds is zero and therefore no copolymerization was expected.

Elution

The solid bulk polymers were ground into bead sized particles and swollen with a minimal amount of toluene. These swollen resins were then eluted with 50% EtOH

TABLE 8

PTE COMPOSITIONS

Code Number	Extractant	concentration[a]	wt%[b]
MS-02-177A	DUP	1.0M	46.5
MS-02-177B	DUP	0.5M	23.2
MS-02-177C	DEHP	1.0M	37.2
MS-02-177D	DEHP	0.5M	18.6

[a]Solvent is styrene/2% DVB/1% BPO

[b]Weight percent

solutions at 500mL/hr. The results of these elutions are given in figure 8. The elution rate of PTE's seems to be as fast or faster than the conventional PAE's. The difference between the DUP and DEHP initial elution rate is most likely due to simple molecular weight differences. However their final values are very nearly the same.

Porosity Study

The extractant seems to be acting as a diluent during the polymerization. Qualitatively this is supported by the phase separation seen during the polymerization. In order to determine quantitatively a porosity effect several styrene/DVB copolymers were made with varying levels of porosity. 4-Methyl-2-pentanol was used as the diluent in concentrations of 30% to 70%. The bulk copolymers were ground into bead sized particles. Using these as polymer supports PAE's were made with a 1M DUP in toluene solution. The elution results of the PAE's are given in figure 9. At the lowest porosity only a small amount of DUP was incorporated into the network. As for the 50%, 60%, and 70% porosity samples the rate of elution is proportional to the level of porosity of the supporting network.

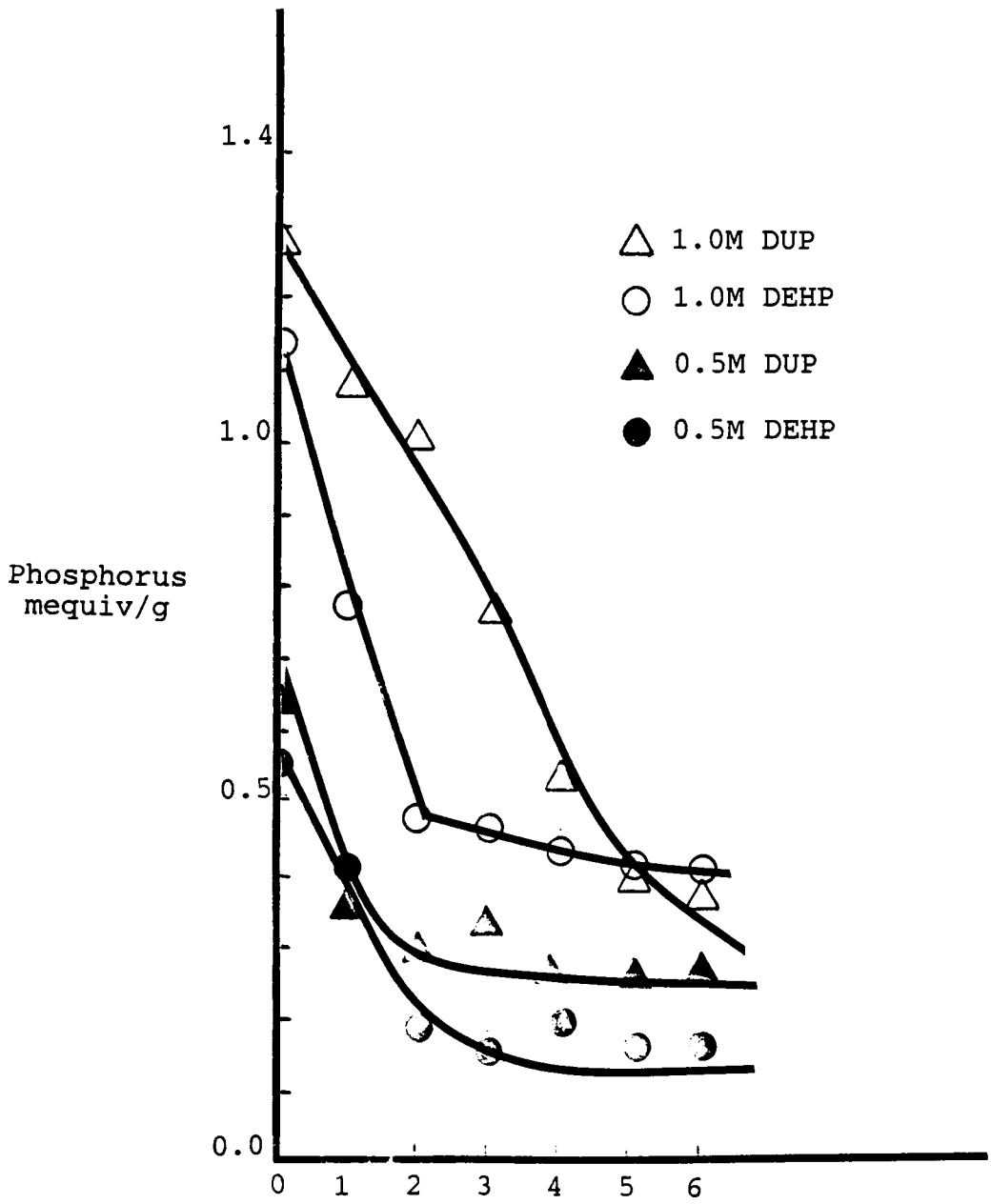


FIGURE 8

50% ETHANOL ELUTION STUDY OF PTE's

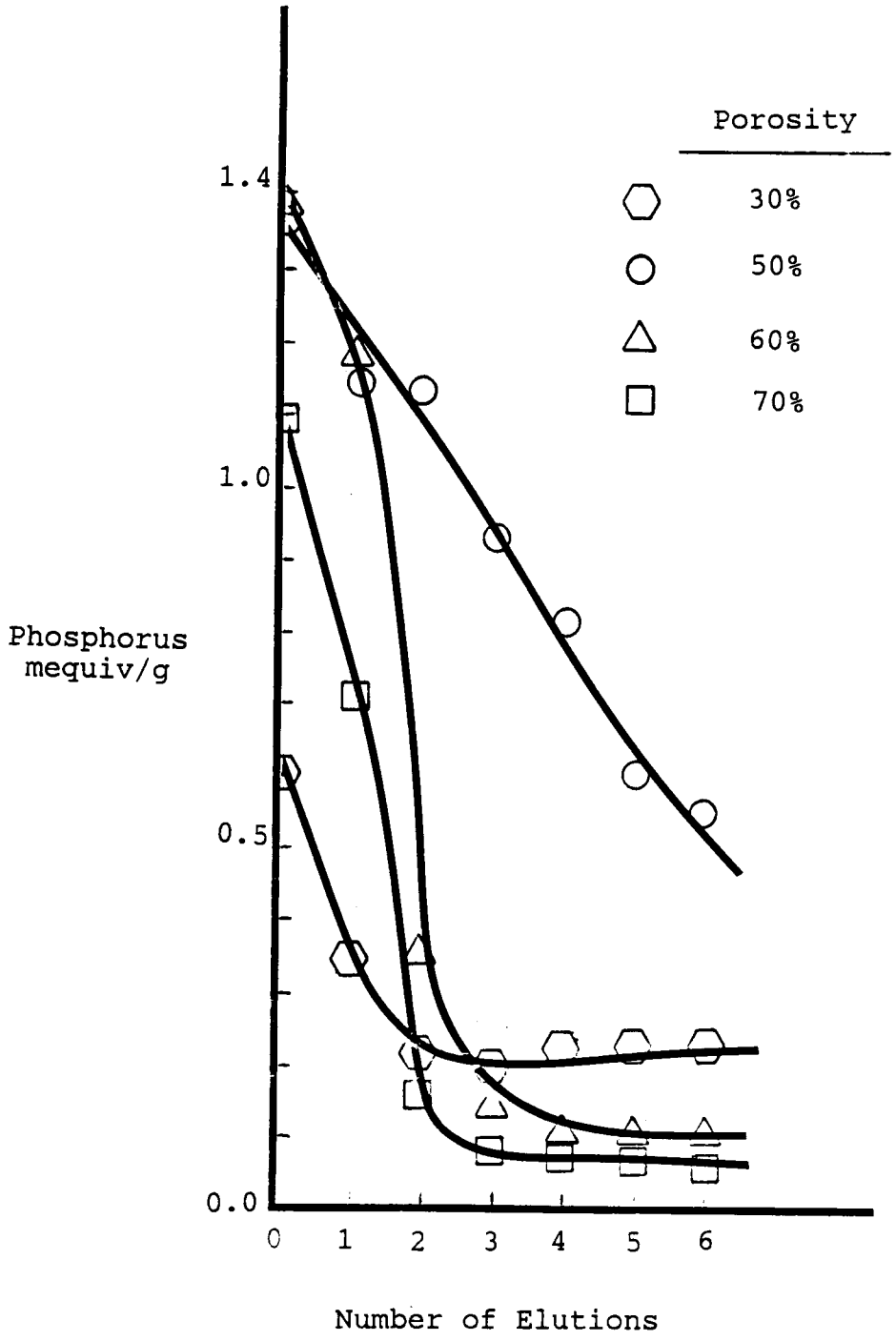


FIGURE 9

50% ETHANOL ELUTION OF POROSITY STUDY OF PAE's

Conclusion

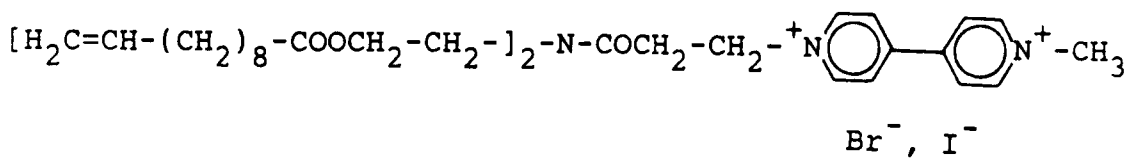
The increased elution rate of PTE's over PAE's is due to the DUP acting as a diluent during the polymerization. DUP seems to be a better diluent than 4-methyl-2-pentanol which is the standard for styrene/DVB MR copolymers. Diluent efficiency is inversely related to its polymer compatability. [119-122]. For styrene/DVB copolymers, very polar or very nonpolar diluents work best. Cyclohexanol and cyclohexane are both better diluents than cyclohexanone.[122] Molecules that contain both hydrophobic and hydrophilic groups are very good diluents. Ethylhexanoic acid is a more effective diluent than pentanol as benzyl alcohol.[120] Based on these ideas it is no suprise that DUP is a more effective diluent than 4-methyl-2-pentanol. The formation of a PTE will not aid in extractant retention.

CHAPTER 5

DUP ACRYLONITRILE COPOLYMER IPN's

In order to obtain improved extractant stability within the polymer support an increase in the degree of polymerization ($\overline{DP}$) of the polymerizable extractant is required. Vinyl groups adjacent to a methylene moiety (to be refered to in the subsequent discussion as "allylic") are known to polymerize very poorly. The results given in chapter 3 indicate a very low $\overline{DP}$.

Fendler has worked with polymerizable surfactants to make stable vesicles. One example of a polymerizable surfactant is shown below.



Fendler found that this particular surfactant would only polymerize if acrylonitrile (AN) was added as a comonomer. DUP does oligomerize slightly during homopolymerization. DUP and Fendler's surfactant both contain two allylic double bonds. If AN can cause the polymerization of

Fendler's surfactant it should increase the incorporation of the DUP into an IPN.

IPN and PAE Formation

DUP/AN copolymer PAE's and IPN's were made as shown in table 9. In each case the concentration of polymerizable double bonds was maintained at two equivalents per liter.

Elution Study

The resultant PAE's and IPN's were eluted with 50% EtOH/H_2O at a rate of 500 mL/h. The results of these elutions are given in figures 10, 11, and 12. The results indicate that the AN helps to incorporate more DUP into the IPN copolymer.

DUP/AN Bulk Copolymers

The reactivity of the allylic double bond is very low. Therefore the nature of the DUP/AN copolymer was studied by looking at its bulk copolymer properties. The bulk copolymers were formed by polymerizing DUP/AN in toluene with AIBN. The resultant solid polymers were dried to remove the toluene and eluted with 95% EtOH to remove any of the DUP that was not part of the copolymer. Table 10 gives the composition of the bulk solutions that were polymerized as well as the percentage of the DUP that

TABLE 9

DUP/AN PAE's AND IPN's[a]

Code Number	Swelling Solution[b] DUP	AN	Type[c]
MS-02-229A	0.50M	1.0M	IPN
MS-02-229B	0.50M	1.0M	PAE
MS-O2-229C	0.25M	1.5M	IPN
MS-02-229D	0.25M	1.5M	PAE
MS-O2-229E	0.10M	1.8M	IPN
MS-02-229F	0.10M	1.8M	PAE

[a]Polymer Support = 5% DVB/Styrene MR Beads

[b]Solvent = Toluene

[c]IPN's, 2(w/v)% AIBN, Polymerization at 60^{o}C for 96h

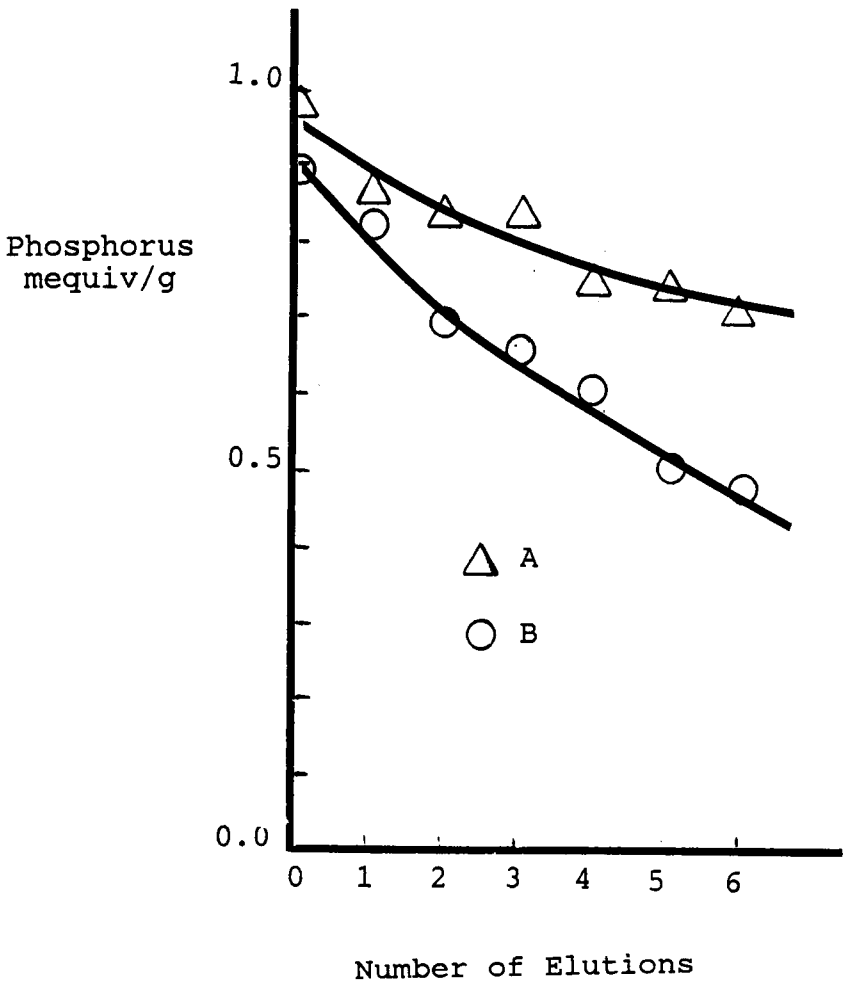


FIGURE 10

50% ETHANOL ELUTION STUDY OF MS-02-229A AND B

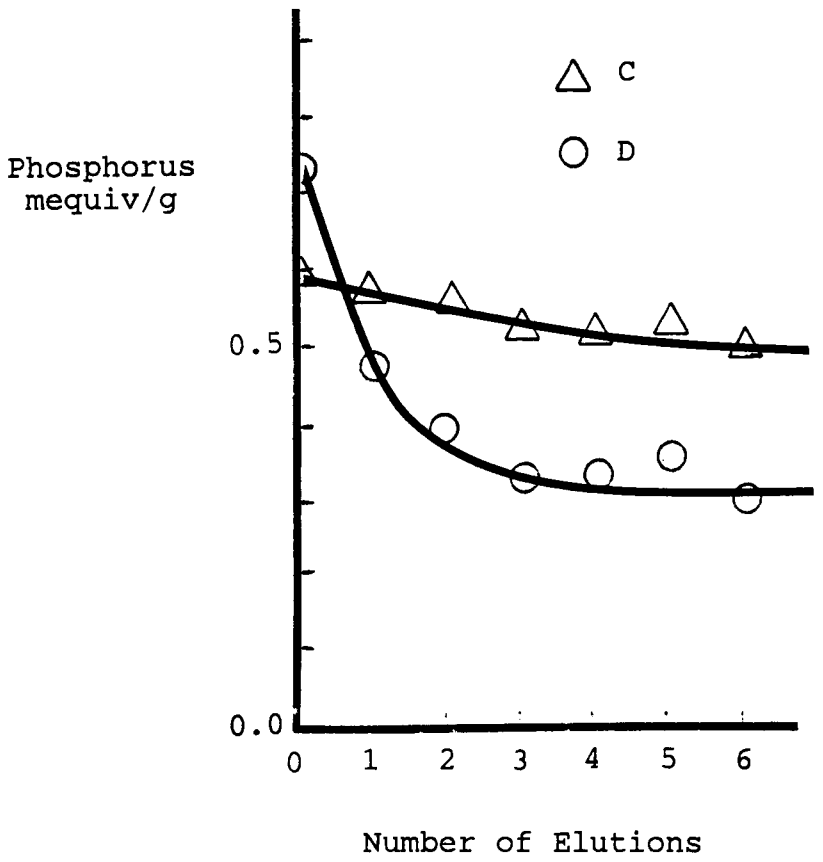


FIGURE 11

50% ETHANOL ELUTION STUDY OF MS-02-229C AND D

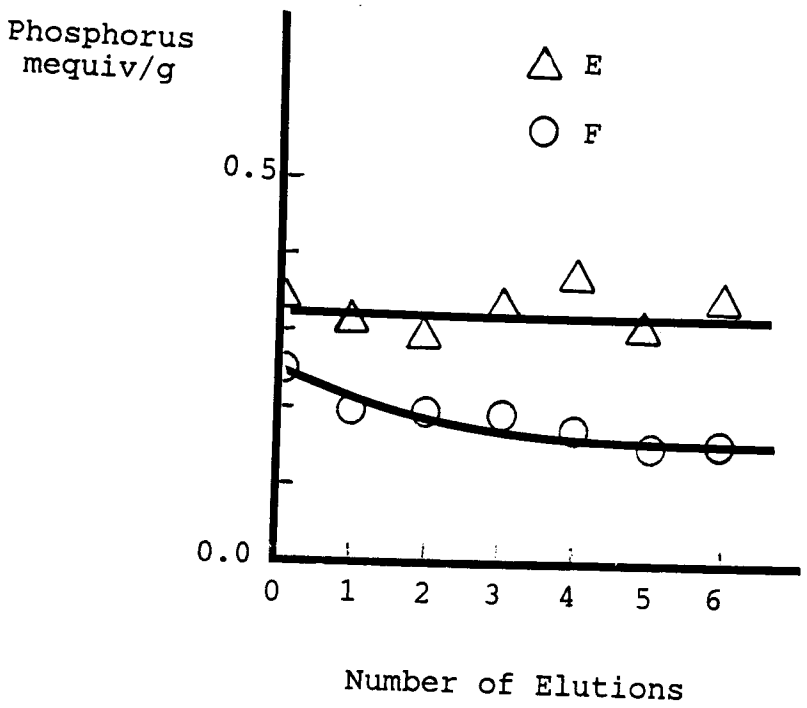


FIGURE 12

50% ETHANOL ELUTION STUDY OF MS-02-229E AND F

TABLE 10

DUP/AN BULK COPOLYMERS

Code Number	Bulk Solution[a] DUP	AN	AIBN	%DUP[b]
MS-03-072	0.25M	1.5M	2%[c]	75%
MS-03-117	0.25M	1.0M[d]	2%	5%
MS-03-122	0.25M	3.0M	2%	69%
MS-03-123	0.25M	1.5M	6%	85%

[a]Solvent = Toluene

[b]Percent DUP Remaining in the Network

[c]w/v%

[d]Also Contains 0.5M Styrene

could be removed via 95% EtOH elution.

Based on the results in Table 10 (MS-03-072) about 75% of the DUP is incorporated into the polymer network. This corresponds to the results given in figure 11. Both systems have the same chemical composition and show similar losses of DUP upon elution. These end results are independent of a solid support. If the AIBN level is raised to 6%, then 85% of the DUP can be incorporated into the network.

End Use Conditions

In the introduction (chapter 1) it was indicated that the end use of the supported metal ion extractants would be as chromatographic supports in extraction chromatography and as supported liquid membranes. In both cases a solvent is required in the support system. This solvent must have a low vapor pressure and be very insoluble in the aqueous phases that it is exposed to. Toluene is unacceptable on both counts. To avoid problems, the toluene was removed and replaced with dodecane. This was done for a PAE (0.25M DUP/1.5M AN) and an IPN (0.25M DUP/1.5M AN/2(w/v)% AIBN). Both the IPN and the PAE were then eluted with 50% EtOH. The results of this experiment are given in figure 13. In this experiment unlike those with toluene the solvent remained in the support through the entire elution sequence. Therefore the extractant

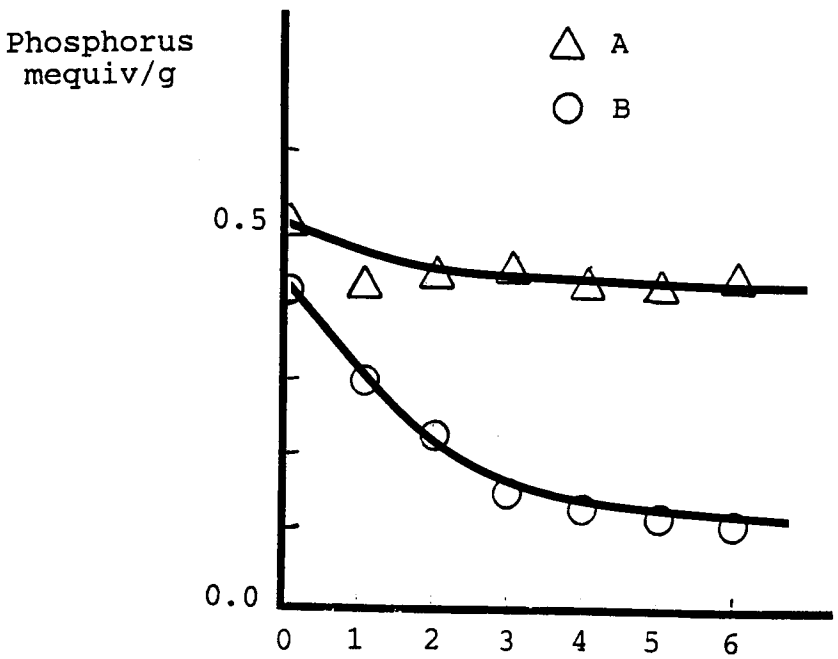


FIGURE 13

50% ETHANOL ELUTION STUDY OF MS-02-244A AND B

remained mobile within the network. This will aid in metal ion extraction and transport and also increases the rate of extractant loss from the PAE.

Conclusion

Copolymerization of DUP with AN greatly increases DUPs' incorporation into the polymer network (up to 85%). The analysis of these materials as metal ion extractants will be discussed in chapter 7.

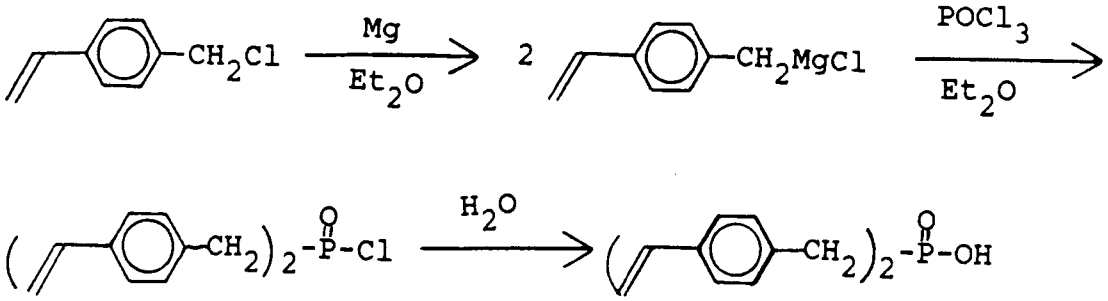
CHAPTER 6

STYRENE-BASED POLYMERIZABLE EXTRACTANTS

The DUP/AN copolymer IPN is quite stable in both bead form (chapter 5) and membrane form (chapter 7). However it is desirable to form a totally stable IPN. In order to get better IPN formation a better polymerizable unit is required. Styrene polymerizes very well by free radical initiation. This chapter presents several syntheses which have been aimed at incorporating one or two styrene rings into a phosphorus extractant.

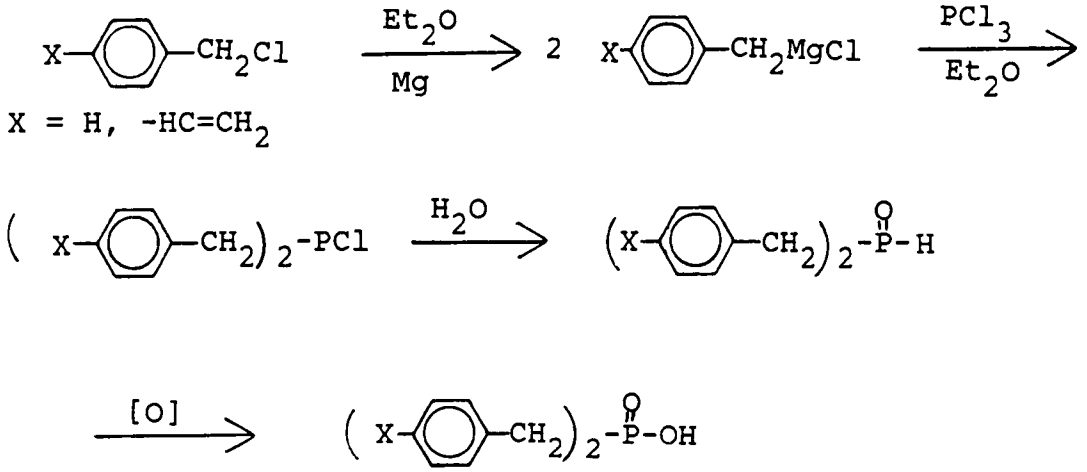
Symmetrical Extractants via Grignard Synthesis

The first steps to incorporate styrene into a phosphorus extractant followed the scheme shown below (see chapter 9 for experimental details):



The resultant divinylbenzyl phosphinic acid (DVBP) is totally insoluble in toluene and ethanol. The model reaction using benzyl chloride resulted in the formation of dibenzyl phosphinic acid (DBP). DBP is a colorless solid that is soluble in toluene. The difference in the solubility DVBP and DBP must be due to the vinyl groups.

The first consideration is possible polymerization of the DVBP during the reaction. In order to test this idea a second synthetic scheme was tried. The scheme is shown below and was followed with both vinylbenzyl chloride and benzyl chloride:



The intermediate phosphine oxide was isolated. IR and NMR spectra confirmed the presents of the P-H bond as well as the vinyl groups (IR, vinyl group at 3075 cm^{-1} and 1620 cm^{-1}, P-H at 2330 cm^{-1}, see figure 14 for NMR). Oxidation of both oxide compounds resulted in phosphinic acid

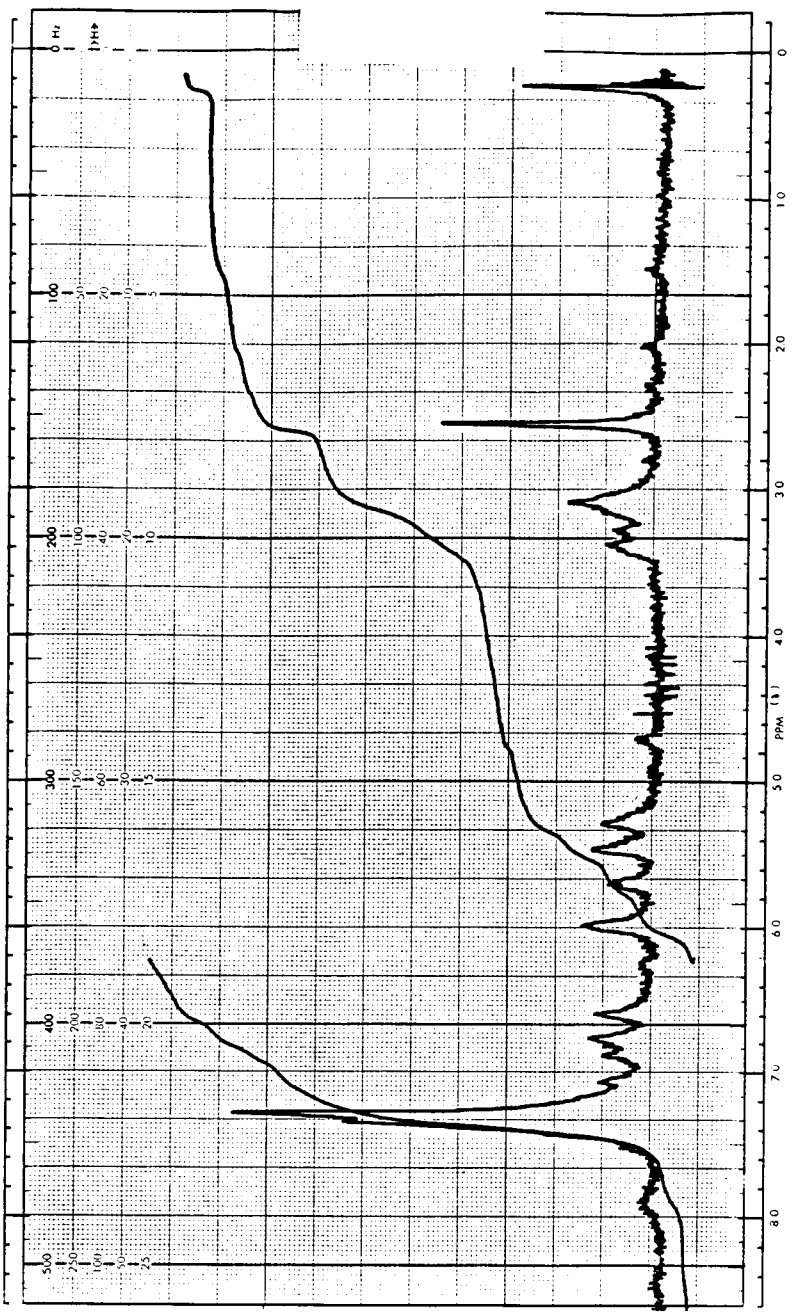


FIGURE 14

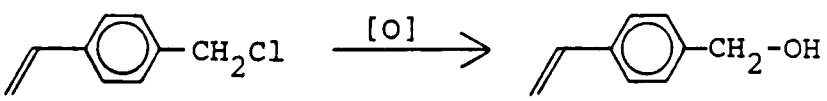
DIVINYLBENZYL PHOSPHINE OXIDE NMR, MS-03-099

formation. However, the DVBP was still insoluble while the DBP was soluble in toluene as before.

Three different methods for the oxidation step were attempted. The three oxidizing agents used were H_2O_2, KI_3, and NaOH. All three were successful in converting the secondary phosphine oxide into a secondary phosphinic acid. DVBP is not usable because of its insolubility. However, the oxidation of the model compound did add credibility to the iodine oxidation (method for primary P-H determination in the phosphinic acid resins, see part I). Also the NaOH oxidation of the secondary oxide to a secondary phosphinic acid supports the NaOH oxidation step during conditioning of resins containing secondary oxide groups (see part I).

Ester Synthesis With Vinylbenzyl Alcohol

The second approach to incorporating styrene into a phosphorus extractant involved the use of an ester synthesis. The first step was to obtain vinylbenzyl alcohol (VBA).



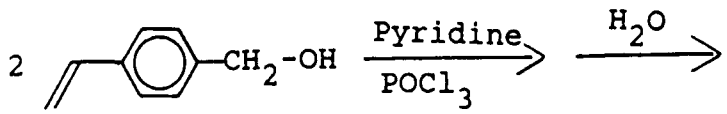
VBC VBA

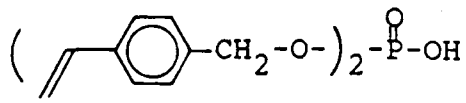
The oxidation of VBC to VBA was initially attempted via KOH/EtOH hydrolysis. The product obtained was mostly

vinylbenzyl ethyl ether with only a trace of VBA. The addition of water to the reaction mixture had no effect on the product mixture.

The industrial preparation of benzyl alcohol is done by refluxing benzyl chloride with an aqueous potassium carbonate solution[123]. A 65% yield of VBA was obtained using this procedure starting from VBC. The remainder of the product mixture was VBC (25%) and divinylbenzyl ether (7%) with 3% of the material unidentified. The product analysis was based on HPLC results.

The VBA was used as is with the assumption that the VBC and ether would not react during the following reaction:

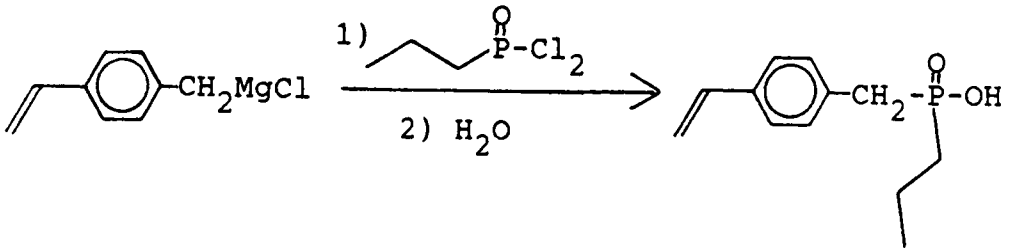




The above reaction was done using both VBA and benzyl alcohol. In all cases only the starting alcohol or benzyl chloride was isolated. Even in a control reaction where pure benzyl alcohol was used, a mixture of benzyl alcohol and benzyl chloride was isolated. The reactivity of the benzyl alcohol toward $POCl_3$ seems to parallel the reactivity of allyl alcohol as mentioned in chapter 2.

Vinylbenzyl Propyl Phosphinic Acid (VBPP)

The Grignard synthesis used to make the symmetrical extractant mentioned earlier seems to be the best way to incorporate styrene into a phosphorus extractant. However the solubility of the extractant in toluene needs to be improved. An unsymmetrical molecule should tend to crystallize less and therefore increase its solubility. With this concept in mind, one equivalent of vinylbenzyl magnesium bromide was added to propyl phosphonic dichloride as shown below:



The crude product mixture was washed with water to remove any propyl phosphonic acid. The VBPP was then converted to its sodium salt form and washed into an aqueous phase to separate it from any neutral products. Acidification of the aqueous phase caused the separation of VBPP.

The VBPP was dried and excess HCl removed by ethanol azeotrope as before. The titration of the VBPP showed a single end point which corresponded to 81 to 85% purity on various synthesis (a sample NMR is given in figure 15). A mass spectrum of the product indicated that ethanol was present.[124] The mass spectrum was done by direct

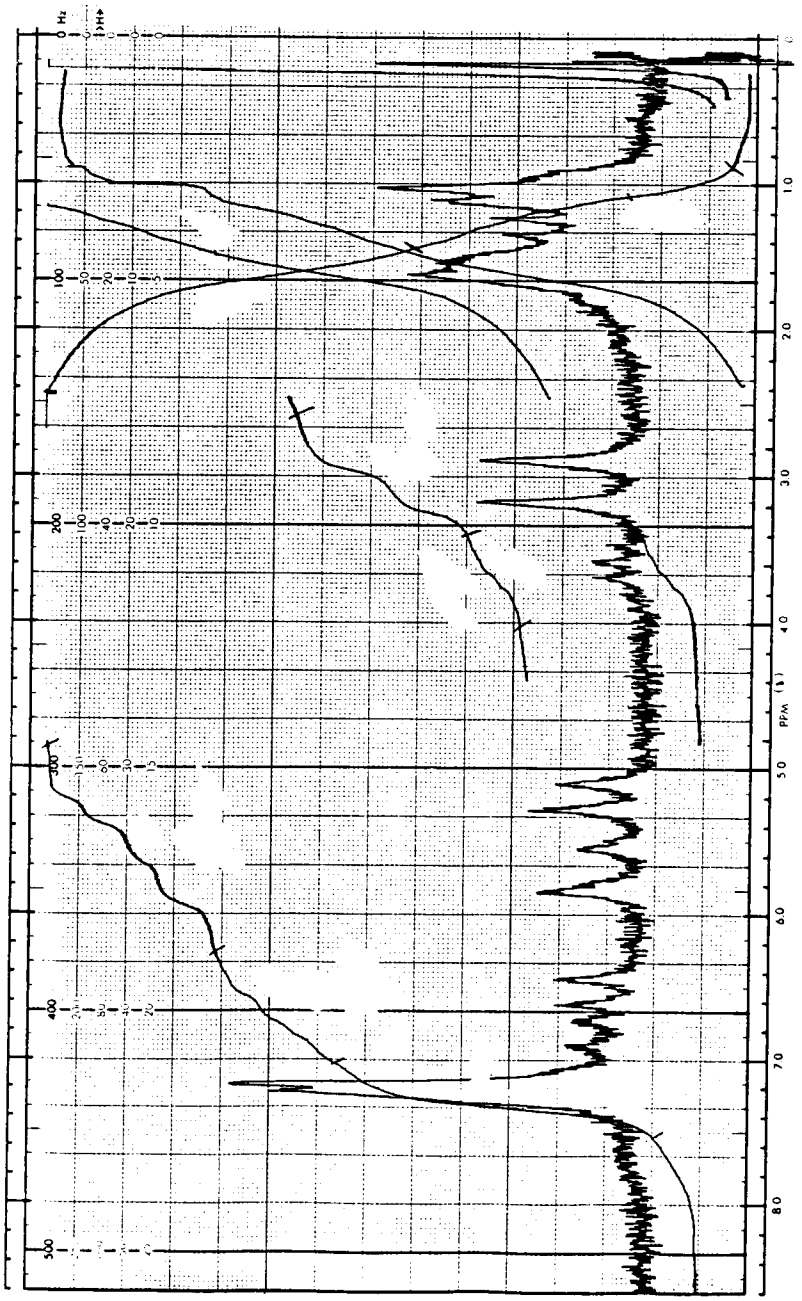


FIGURE 15

VBPP NMR, MS-03-142

insertion. Two different peaks were found. The first GC peak was a low molecular weight solvent peak (mass units, 31, 36, 45, and 46, EtOH = 46). The second was VBPP (mass units, 91, 115, 118, 119, 197, 210, 225, and 226, VBPP = 224). If a 1:1 complex between the VBPP and the ethanol was formed then the capacity should be 83%. The azeotroping process was repeated using methanol, ethanol and isopropanol. After each process a sample was titrated to determine its purity. The results of these titrations are given in table 11. VBPP seems to form a 1:1 complex with methanol and ethanol. The complex formation of VBPP with isopropanol is less than 1:1. This is most likely due to the steric hindrance of the isopropyl group.

The VBPP was used in its ethanol complex form to make IPN's and bulk copolymers. Table 12 gives the composition of the various swelling solutions.

The CEC (see chapter 3) for VBPP homopolymers is well below 0.1M. What may be more meaningful is to develop the concept of a total CEC. The concentration of VBPP required to obtain total entanglement is 0.5M based on MS-03-147A-D given in table 12. VBPP does not have the ability to crosslink. However, sufficient entanglements are seen in spite of the lack of crosslinks.

Copolymerizing VBPP with acrylonitrile, styrene, or styrene/divinyl benzene has the same effect as having a

TABLE 11

VBPP/ALCOHOL 1:1 COMPLEXES

Alcohol	Theoretical % Purity[a]	Experimental % Purity[b]
Methanol	87.5	85.4
Ethanol	82.9	81.1
Isopropanol	78.9	81.8

[a]Based on a 1:1 Complex

[b]NaOEt Titration

TABLE 12

VBPP IPN's AND BULK COPOLYMERS[a]

Code Number	VBPP	Type[b]	AN	STY	DVB	%Drop[c]
MS-03-147A	1.0M	IPN				0%
MS-03-147A	1.0M	PAE				94%
MS-03-147B	0.5M	IPN				0%
MS-03-147B	0.5M	PAE				93%
MS-03-147C	0.25M	IPN				35%
MS-03-147C	0.25M	PAE				93%
MS-03-147D	0.1M	IPN				43%
MS-03-147D	0.1M	PAE				80%
MS-03-147E	0.25M	IPN	1.75			3%
MS-03-147E	0.25M	PAE	1.75			93%
MS-03-147E[d]	0.25M	BULK	1.75			
MS-03-147F	0.25M	IPN		1.75		4%
MS-03-147F	0.25M	PAE		1.75		90%
MS-03-147F[e]	0.25	BULK		1.75		
MS-03-147G	0.25	IPN		1.25	0.25	0%
MS-03-147G	0.25	PAE		1.25	0.25	85%
MS-03-147G[f]	0.25	BULK		1.25	0.25	

[a]Solvent = Toluene

[b]IPN's and Bulk Copolymers Contained 2(w/v)% AIBN

[c]% VBPP Loss with 500 mL 95% Ethanol Wash Over 2h

[d]Solid Block Copolymer

[e]Viscous Liquid

[f]Solid Block Copolymer

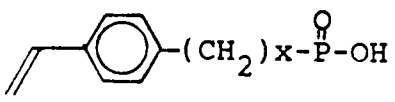
higher VBPP concentration. VBPP is a marked improvement over DUP/AN IPN's in terms of IPN stability.

The metal ion extraction ability of VBPP and VBPP IPN's will be discussed in detail in chapter 7. However for the current synthetic discussion it is important to note the mercury (II) extraction ability of VBPP greatly decreases when comparing a liquid—liquid extraction to an IPN equilibrium extraction. This drop has been attributed to loss of local extractant mobility.

In order for mercury (II) extraction to take place two VBPP units must come together. If the network is too tight then the extraction ability of the IPN will decrease.

Spacer Chain Styrenic Phosphorus Extractant

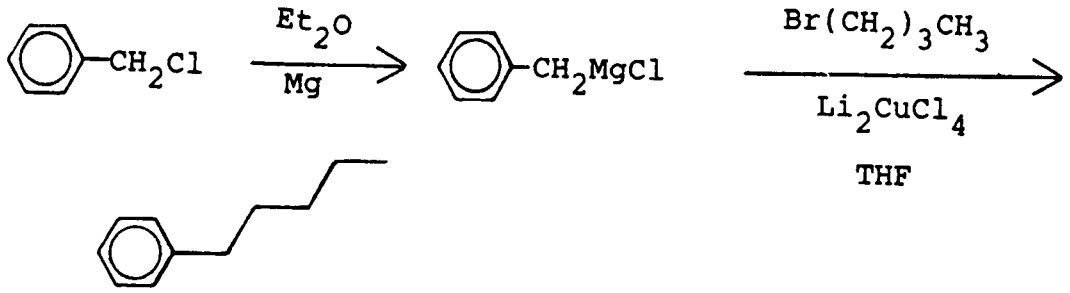
Flexibility needs to be built into a styrene based polymerizable extractant. If the VBPP molecule could simply be extended, as shown below, the flexibility may be obtained.



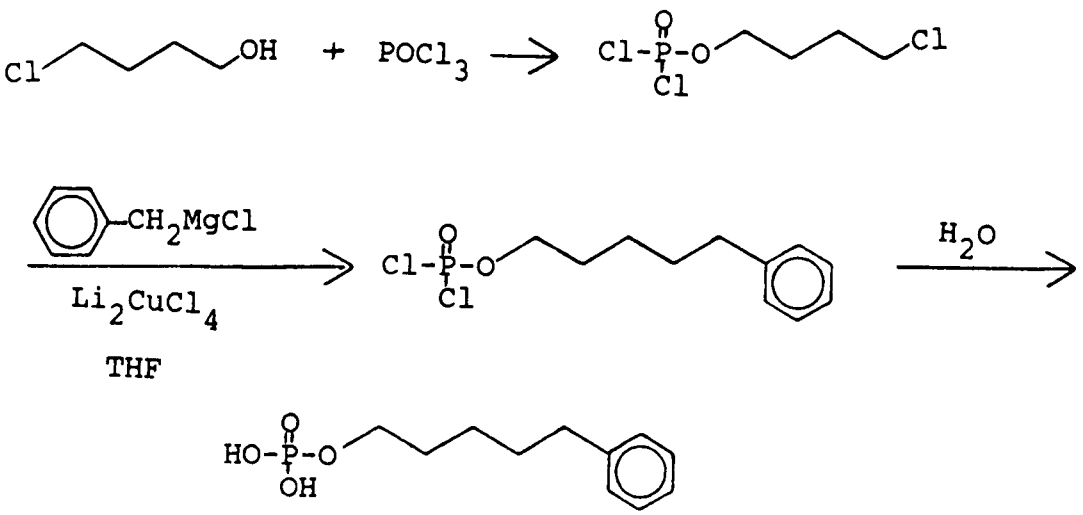
x = 1, VBPP
x = 5, Desired product

Two synthetic routes were attempted to form a styrene/phosphorus extractant with a spacer chain. Both

of these methods relied on a Grignard halide coupling reaction.[125] The first model reaction is shown below:



The product was identified by NMR (see figure 16). The singlet peak at 2.95 ppm is most likely due to a methyl group on the benzene ring caused by rearrangememt of the Grignard reagent. The first synthetic scheme is shown below using a benzyl Grignard as a model:



The reaction was attempted without the double bond to avoid unnecessary difficulties at this point. The coupling reaction was unsuccessful due to the high reactivity of the P-Cl bond. The benzylic Grignard was found to be

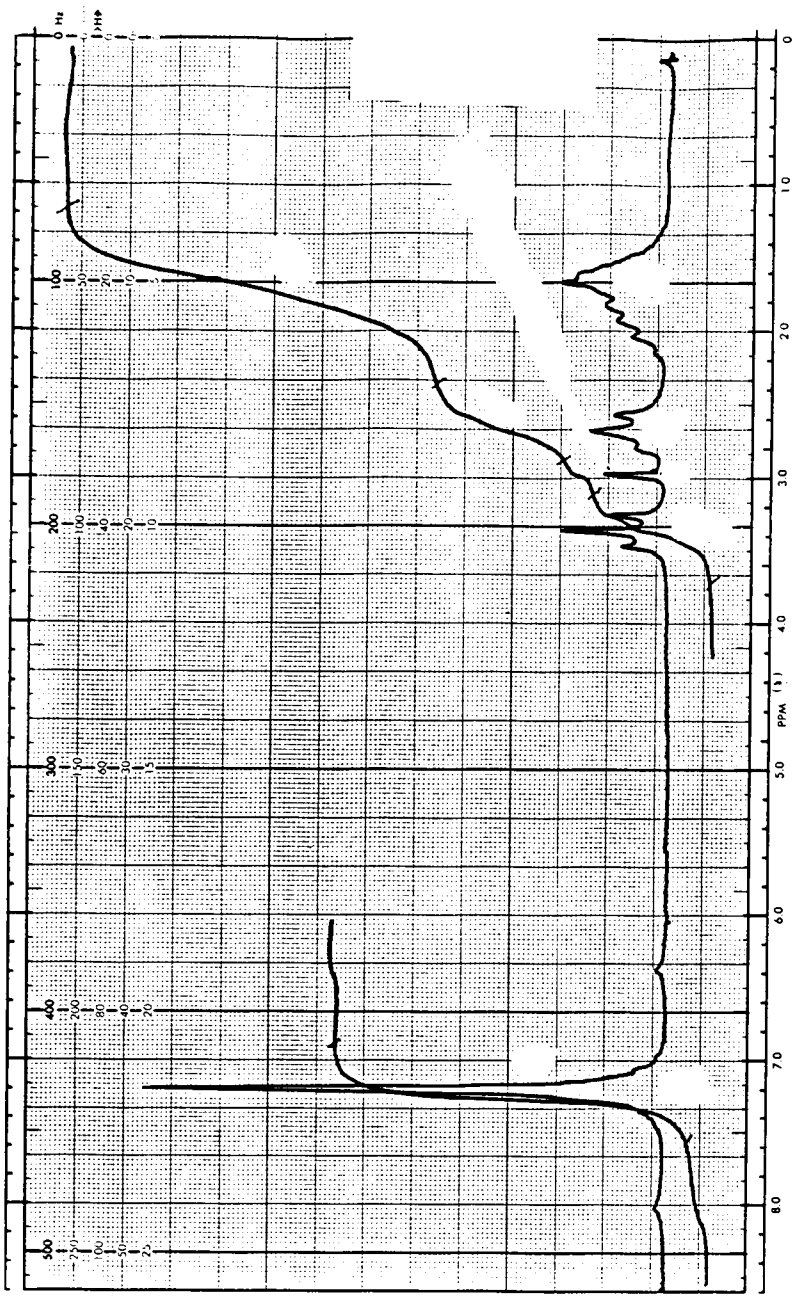
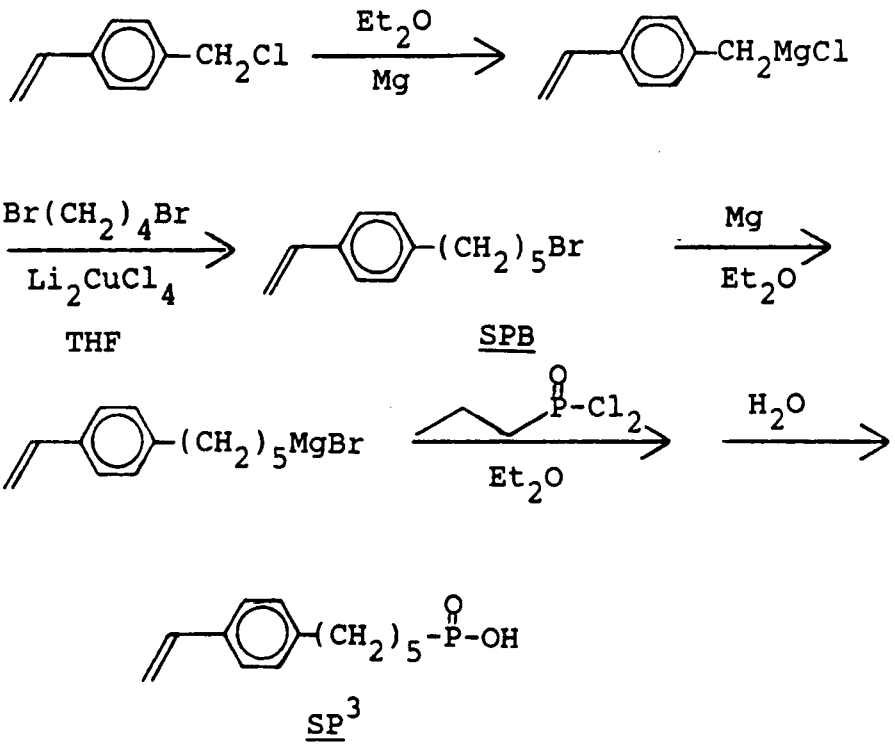


FIGURE 16

1-PHENYL-5-BROMO PENTANE NMR, MS-03-267

attached to the phosphorus rather than the aliphatic chain.

The second synthetic scheme involved using the coupling reaction first followed by a second Grignard step as shown below:



The acronym SP^3 stands for styrylpentyl propyl phosphinic acid. The above synthetic pathway has been carried out. However, the success rate and yields are very low. The first difficulty is in the purification of the styrylpentyl bromide (SPB). Purification of SPB requires a vacuum distillation. SPB comes over between 93 and 100°C at 0.17 torr. Hydroquinone is added as a free radical inhibitor.

However, if the distillation flask is heated too quickly, polymerization will take place in the distillation flask. Yields of about 50% SPB have been obtained.

The conversion of SPB into SP^3 is done by a second Grignard step (see figure 17 for product NMR). The yield of this reaction is only 26.6%. The styrylpentyl magnesium bromide does not form very well and its reactivity toward propyl phosphonic dichloride is low. With only low yields of SP^3 at this point only one elution experiment has been done.

An IPN and PAE were made with 0.25M SP^3 in toluene. The 50% ethanol elution results are given in figure 18. The elution of SP^3 (0.25M) parallels the elution results of the VBPP (0.25) mentioned earlier. The SP^3 showed a 39% drop while the VBPP showed a 34% drop. It can be concluded that the spacer chain between the styrene and the phosphinic acid groups has little effect on the polymerization reaction.

Further Studies

At the time of this writing no metal ion extraction studies on SP^3 IPN's have been done. The idea of increasing metal ion complexing ability by incorporating more flexibility into the molecule is yet to be substantiated. However if the idea proves to be correct, a higher yield

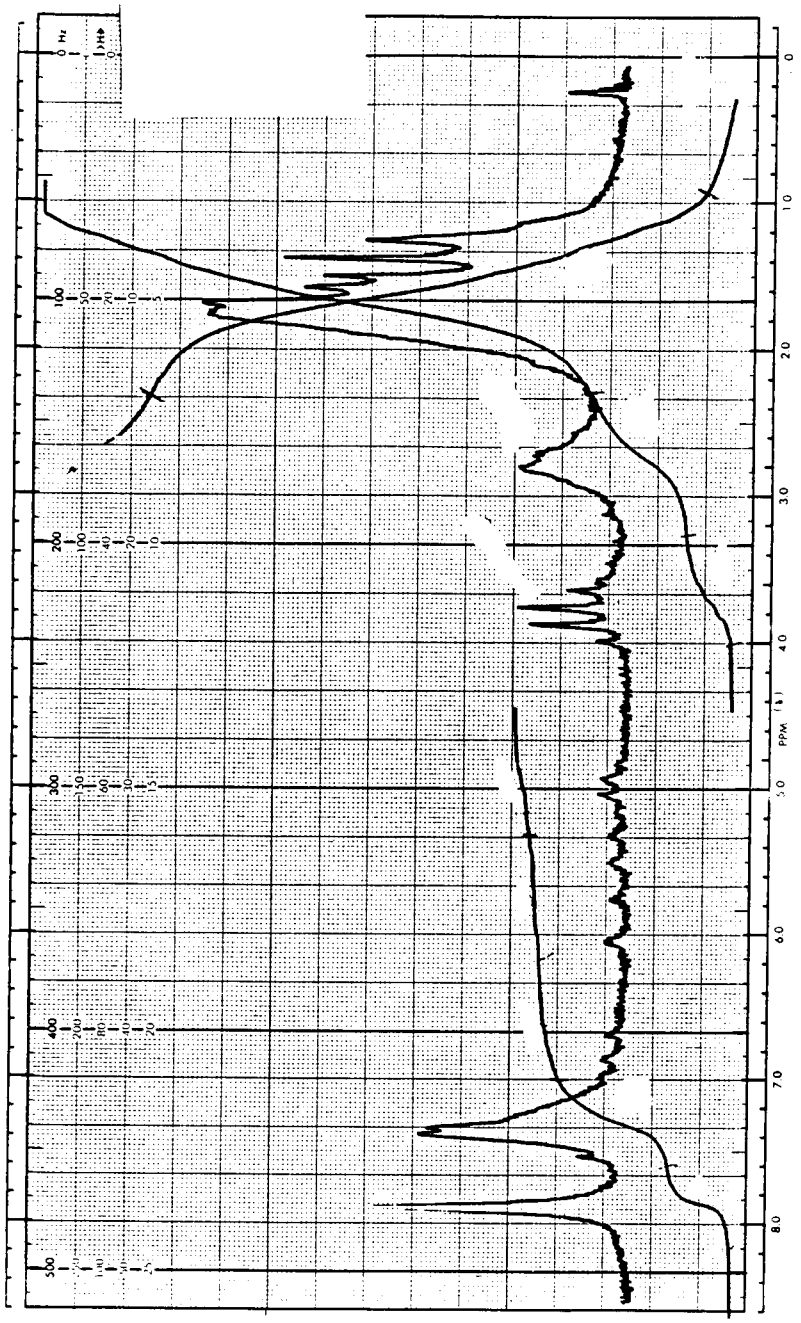


FIGURE 17

SP^3 NMR, MS-04-001

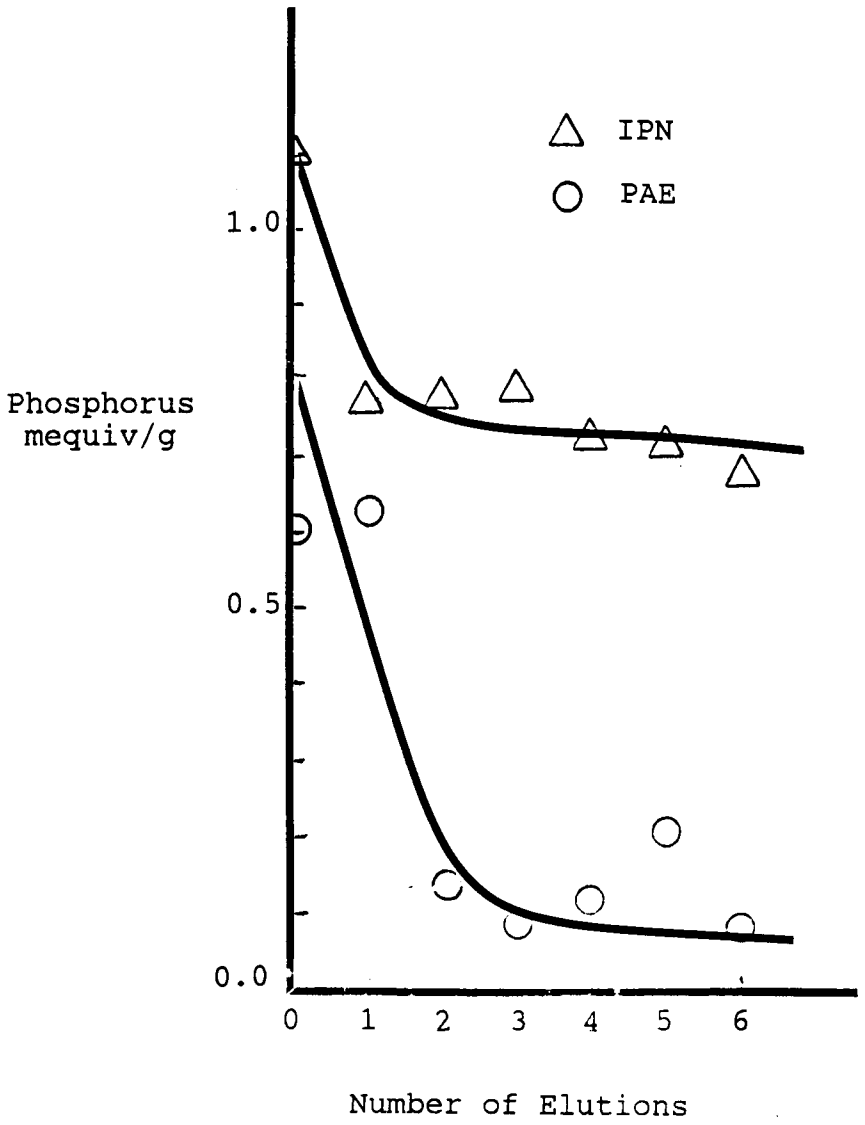
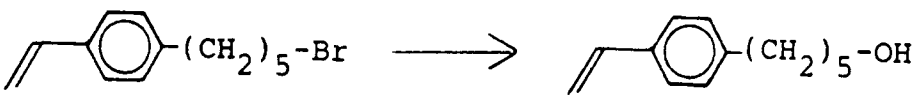


FIGURE 18

50% ETHANOL ELUTION STUDY OF MS-04-052

synthesis or an alternate approach to a flexible molecule is required.

The major drawback to the SP^3 synthesis is the second Grignard step. It may be possible to avoid this reaction if the following reaction can be accomplished:



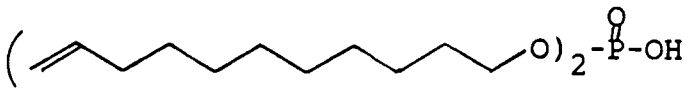
The reaction has been attempted by the following: 1) KOH/ethanol, 2)sodium carbonate in water and, 3) KOH/dioxane. All three of these methods yielded only small amounts of the alcohol. The KOH/ethanol yielded mostly the ethyl ether while the other two methods gave back the starting bromide. If styrylpentyl alcohol or a similar molecule could be obtained, then simple addition to $POCl_3$ or propyl phosphonic dichloride would result in a phosphoric acid.

It may also be possible to increase chain flexibility by copolymerizing VBPP with other monomers. Copolymerization of VBPP has only briefly been studied. If an appropriate swelling solvent can be incorporated into a copolymer IPN, more flexibility may result.

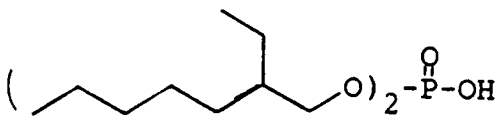
CHAPTER 7

METAL ION EXTRACTION STUDIES

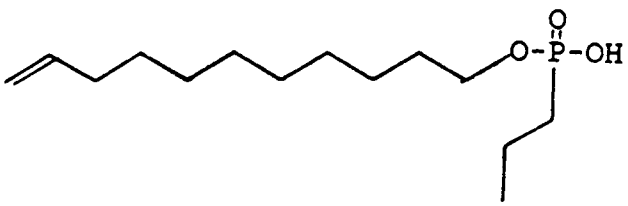
This chapter includes metal extraction studies with DUP, DEHP, UHPP, and VBPP as liquid ion exchangers and IPN's. The structure of each is given below:



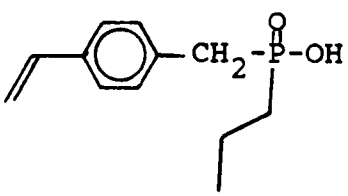
DUP



DEHP



UHPP



VBPP

The metal ion studied was mercury (II) due to its simple titrimetric analysis (see chapter 9 for details) and the importance of its recovery due to its toxicity.[126]

DUP as a Liquid Extractant and an IPN

The mercury (II) extraction ability of DUP was compared to DEHP. All of the extraction experiments were done under equilibrium conditions. The liquid—liquid extraction of mercury (II) by DUP and DEHP is given in table 13. The results of table 13 show that DUP is a very good extractant for mercury. The next consideration is how does IPN formation effect the extraction ability of DUP. The DUP/AN IPN's were studied for their mercury (II) extraction ability. The results are given in table 14.

A comparison of tables 13 and 14 indicates that as long as the DUP concentration is 0.25M or greater, IPN formation does not affect its extraction ability.

UHPP as a Liquid Extractant

Undecenyl propyl phosphonic acid (UHPP) contains only one double bond and does not form effective IPN's. However, one experiment with UHPP showed extractive ability.

UHPP was able to extract 97.1% of mercury (II) at an R_i = 1.0 under normal emulsion—type extraction conditions. A second extraction using the quiet interface technique showed 94.2% extraction of mercury (II) at an R_i = 1.0, indicating that UHPP has the ability to act as an extractant.

TABLE 13

MERCURY (II) LIQUID—LIQUID EXTRACTION

Code Number	Extractant[a]	R_i	% Loading
MS-02-181A	DUP	1.0	96.3
MS-02-181B	DEHP	1.0	44.5

[a]Solvent = Toluene

TABLE 14

DUP/AN IPN's AS MERCURY (II) EXTRACTANTS

Code number	DUP/AN	R_i	%Loading
MS-02-229A	0.50M/1.0M	1.0	96.7
MS-02-229B	0.25M/1.5M	1.0	96.3
MS-02-229C	0.10M/1.8M	1.0	71.0

AN as a Coordinating Agent

DUP extracts mercury (II) equally well with or without acrylonitrile (AN). However, it may be possible for the AN to assist in other extraction experiments. To test this idea AN was added to DEHP in a mercury extraction experiment. The DEHP/AN (0.25M/1.5M) solution was able to extract 58.2% of the available mercury at an R_i = 1.0. DEHP alone was able to extract 44.5% of the available mercury under the same conditions. AN does have some coordinating ability.

VBPP

VBPP was first studied as a liquid extractant and then as an IPN. The extraction results of mercury (II) with VBPP given in table 15, demonstrate the need for adding the spacer chain between the styrene and the phosphorus group as was discussed in chapter 6. When VBPP is polymerized to form IPN's it tends to immobilize a good portion of its phosphorus groups, making them inaccessible for mercury extraction. The addition of comonomers to the VBPP was an attempt at adding local flexibility to the polymer chains. The allyl alcohol was partially successful and gave a small increase in the mercury extraction ability of the IPN.

TABLE 15

VBPP AS AN EXTRACTANT FOR MERCURY (II)

Code Number	[VBPP][a]	Form	R_i	% Absorbed
MS-03-181		Liquid	1.23	82.8
MS-03-171C	0.1M	IPN	1.0	33.4
MS-03-184A	0.25M	IPN	1.0	47.4
MS-03-184B	0.5M	IPN	1.0	42.1
MS-03-199A[b]	0.25M	IPN	1.0	16.5
MS-03-199B[c]	0.25M	IPN	1.0	37.4
MS-03-199C[d]	0.25M	IPN	1.0	56.8
MS-03-199D	0.25M	IPN	1.0	20.8

[a]VBPP concentration in toluene swelling solution

[b]1.75M styrene as comonomer

[c]1.75M acrylonitrile as comonomer

[d]1.75M allyl alcohol as comonomer

Conclusion

At this point there seems to be a balance required between metal ion extraction ability and IPN stability. If the IPN forms too tightly, its metal ion extraction ability will decrease.

CHAPTER 8

HIGH STABILITY SUPPORTED LIQUID MEMBRANES

The supported liquid membranes that were discussed in chapter 1 were effective for metal ion separations. The only drawback to these membranes is their short lifetime due to losses of the extractants from the membrane. The information presented in the previous chapters for PAE's and IPN's on polystyrene beads can be carried over to PAE and IPN formation on polymer membranes.

Polymer Support

The porosity study on polystyrene supports indicated that the level of porosity controls the rate of extractant loss. The membrane support that has been used is a macroporous polypropylene membrane (Celgard 2500, Celanese) with a porosity level of 45% based on volume. Most of the PAE and IPN work on styrene beads was with a 50% porosity network. Assuming that the differences in the chemical nature of the two supports are unimportant, the two supports should act in a similar manner.

Membrane Elution Study

IPN's and PAE's of DUP were made using Celgard 2500 membranes. These membranes were then eluted with 500mL of 50% ethanol for 12 hours. This process was done twice. A sample of the membranewas taken after each wash and dried for phosphorus elemental analysis. The results of these elution experiments are given in table 16, and are in agreement with the results for DUP PAE's and IPN's given in chapter 3. The 0.1M IPN and PAE show no difference while the 1.0M IPN and PAE have a considerably different elution rate. This is the expected behavior based on the CEC determination of 0.5M DUP (see chapter 3).

Dodecane as a Solvent

A supported liquid membrane has three components: 1) the solid support, 2) the metal ion extractant and, 3) the solvent. The function of the solvent is to keep the extractant mobile and prevent the aqueous phases from mixing. The aqueous phase solubility and the vapor pressure of this solvent need to be low. The membranes are made using an extractant solution in toluene. The toluene works well in the membrane formation process but is unacceptable as a solvent for membrane transport experiments. The high membrane surface area combined with toluene's high vapor pressure cause a rapid evaporation of the toluene solvent. Toluene is also slightly water

TABLE 16

ELUTION STUDY OF MEMBRANE IPN's AND PAE's WITH DUP

Code Number	Type	[DUP][a]	Initial P[b]	1st[c]	2nd[d]
MS-02-155B	IPN	1.0M	2.06	0.80	0.47
MS-02-155C	PAE	1.0M	2.07	0.14	0.13
MS-02-155D	IPN	0.1M	0.46	0.05	0.05
MS-02-155E	PAE	0.1M	0.40	0.04	0.08

[a]DUP concentration in toluene swelling solution, IPN's contain 2(w/v)% AIBN, polymerization at 60°C for 96 hours

[b]Initial phosphorus elemental analysis in mequiv/g

[c]Phosphorus capacity after one elution

[d]Phosphorus capacity after two elutions.

soluble and would dissolve out of the membrane during use. To avoid these problems, the toluene was removed after membrane formation and replaced with dodecane.

Membrane Transport Experiments

Membrane transport is studied by measuring the drop in ion concentration on the feed side and/or the rise in concentration on the strip side. A typical membrane setup is diagramed in figure 19.

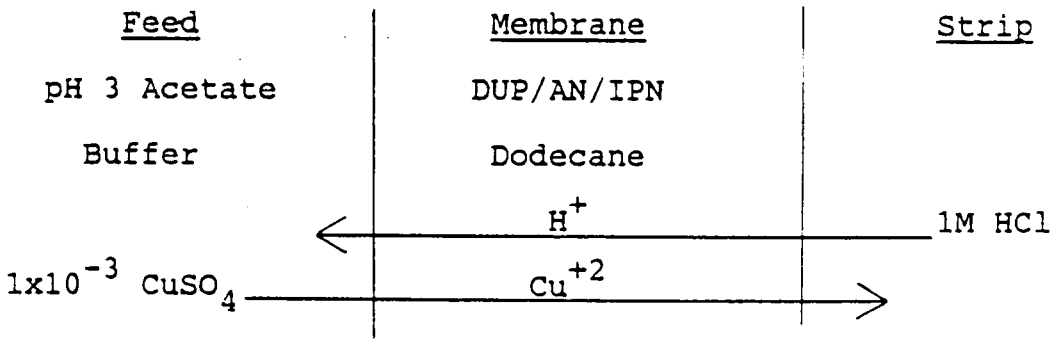


FIGURE 19
MEMBRANE TRANSPORT DIAGRAM Cu^{+2}

Two ions have been studied. Eu^{+3} has been studied by radio tracer techniques at Argonne National Laboratory (P. R. Danesi and E. P. Horwitz) and Cu^{+2} has been studied using a copper selective electrode at the University of Tennessee. The theoretical treatment of membrane transport will be used as it was presented in chapter 1. All of the Eu^{+3} results will be discussed first, followed by the Cu^{+2} results and ongoing experiments.

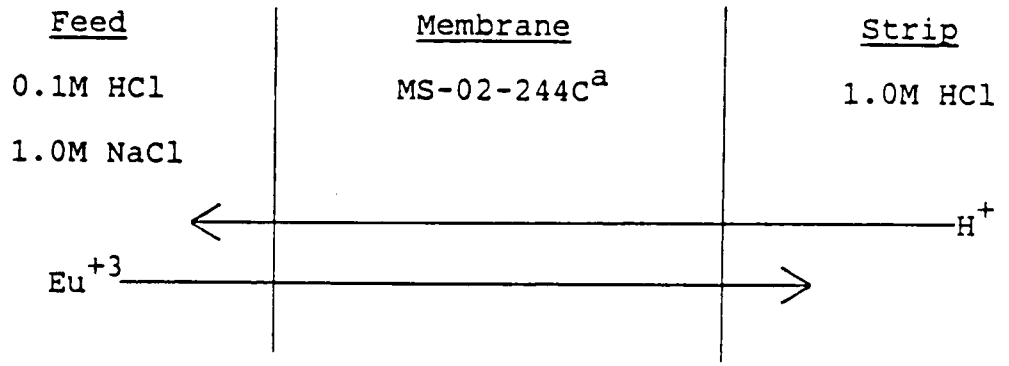
DUP IPN Membranes for Eu^{+3} Transport

The preliminary experiments conducted by Argonne National Laboratory indicated that DUP was at least as good if not better than DEHP for Eu^{+3} transport.[126] However, even in its IPN form it lost its selectivity as did the DEHP membrane in about six days. This problem has been associated with two possible causes. The first is the loss of extractant by aqueous phase solubility as has been discussed earlier. The second is thought to be hydration of the membrane. The metal ion brings with it waters of hydration. A certain percentage of this water is left within the membrane after transport. As the water level builds up it forms water channels through the pores of the membrane. These channels allow salt transport. Once salt transport is seen the membrane is no longer able to selectively separate metal ions.

The choice of dodecane over aromatic solvents helps to retard this process but does not eliminate it. The copolymerization of DUP with AN should help to eliminate both possible causes. DUP/AN forms a much better IPN as has already been discussed. Also the fact that AN is less polar than a phosphorus acid should help minimize, if not eliminate, the hydration problem.

Europium (III) Transport by DUP/AN IPN Membranes

The Eu^{+3} transport experiments were set up according to figure 20.



[a]MS-02-244C = 0.25M DUP/1.5M AN, IPN reswollen with dodecane

FIGURE 20
MEMBRANE TRANSPORT DIAGRAM Eu^{+3}

The apparatus used in the experiments is shown in figure 21. The experiment was conducted using a radio tracer amount of Eu^{+3}. The Eu^{+3} was followed by monitoring its loss from the feed solution and its buildup in the strip solution. By determining both of these rates it was determined that build up of Eu^{+3} in the membrane was not taking place. The rate of loss of the Eu^{+3} from the feed solution was plotted using Ficks Law (see chapter 1).

$$\ln(C/C_o) = -PTQ/V$$

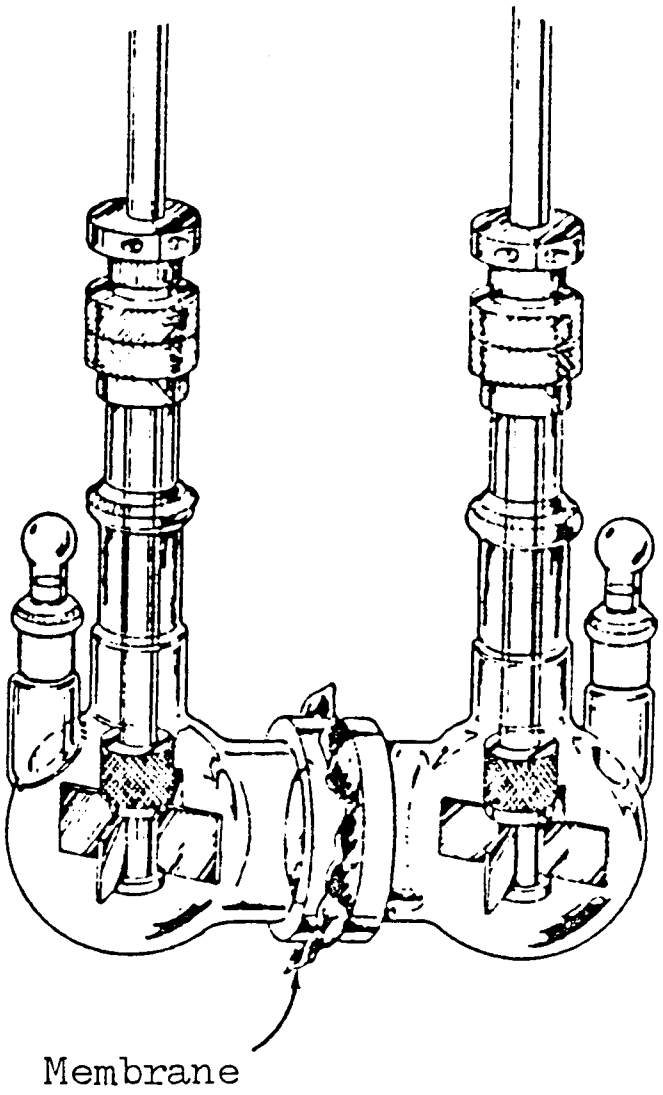


FIGURE 21

APPARATUS FOR EUROPIUM TRANSPORT EXPERIMENTS

The Eu^{+3} experiment was done each day with new solutions. Some selected data are presented in figure 22. The permeability coefficient (P) was calculated for each day. Some of these values are given in table 17.

A plot of P vs. days of operation gives a slope of -0.007. A DEHP PAE membrane gives a slope of -0.031 for the same plot. The DEHP fails in six days under these conditions while the DUP/AN IPN membrane is still operating at 80% of its original efficiency after 60 days of operation.

Copper Transport Through Supported Liquid Membranes

Copper transport is followed by the use of a copper selective electrode (Orion). The copper transport experiments are conducted in the same manner as the Eu^{+3} transport experiments discussed earlier.

The majority of the copper transport experiments were of an exploratory nature. They were designed to obtain conditions that would allow copper transport and good functioning of the copper selective electrode. The copper electrode is affected by pH, ionic strength and temperature. The copper measurements were taken only on the feed side where the pH was controlled with buffers (the electrode cannot operate below a pH of two). The ionic strength of the feed solution (about 1.0M) was kept very

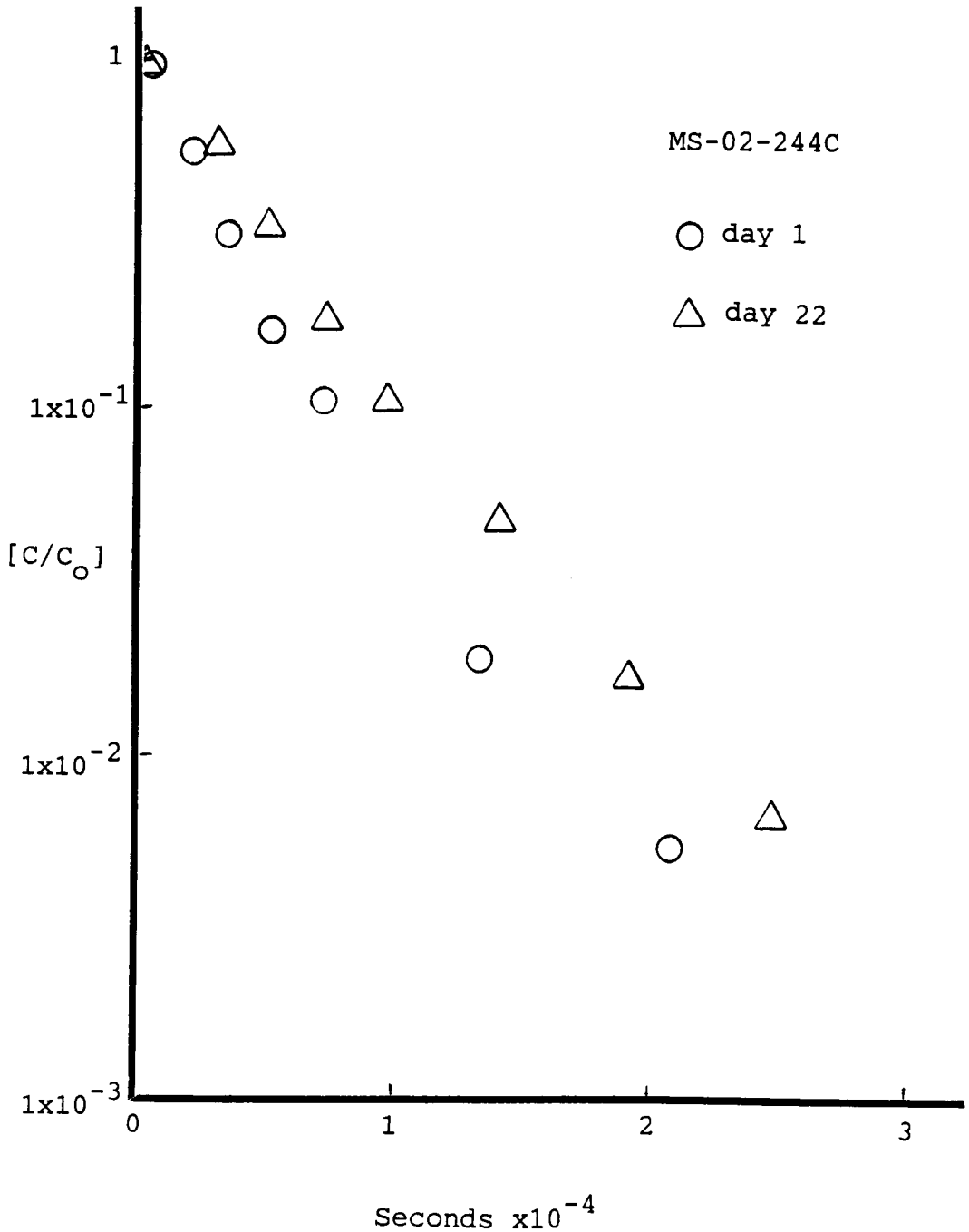


FIGURE 22

FICKS LAW PLOT OF EUROPIUM TRANSPORT DATA

TABLE 17

PERMEABILITY COEFFICIENTS FOR EUROPIUM (III) TRANSPORT THROUGH MS-02-244C[a]

Number of operating days	Permeability Coefficient
1	1.2×10^{-3}
3	0.9×10^{-3}
7	1.1×10^{-3}
9	0.9×10^{-3}
15	0.9×10^{-3}
22	1.06×10^{-3}
29	0.84×10^{-3}
36	0.83×10^{-3}

[a]Results form Argonne National Laboratory

high in relation to the overall copper concentration ($1x10^{-3}M$). The temperature was controlled by placing the apparatus in a thermostated water bath at $30^{o}C$. The first membrane systems tried are given in table 18.

The LiOAc/HOAc buffer was the only system that was able to transport the copper. However the LiOAc/HOAc is a harsh system to have in contact with the membrane. This caused the 0.25M DUP PAE to fail after just one day of operation. Several different membranes were studied under these conditions to see if the membrane lifetime could be increased. The results of these additional experiments are given in table 19. The data from table 19 indicates that the LiOAc/HOAc is removing most if not all of the extractant from the membrane by the second day of operation. A phosphorus elemental analysis of MS-03-238 after two days of contact with the LiOAc/HOAc buffer gave a value of 0.26 mequiv/g. This is considerably less than the expected value of about 2.0 mequiv/g.

A change in the buffer system to pH3 (0.018M LiOAc/0.98M HOAc) decreased the rate of membrane decomposition. The results using the pH3 buffer system are given in table 20. The results of table 20 support the idea that membrane failure is due to extractant losses from the membrane. The attempt to revive MS-03-258 by reswelling it with dodecane was unsuccessful.

The length of effective use time is directly related

TABLE 18

COPPER TRANSPORT VIA SUPPORTED LIQUID MEMBRANES[a]

Code Number	Type	Extractant	Feed[b]	Transport
MS-03-210	PAE	0.25M DEHP	c	NO
MS-03-212	PAE	0.25M DEHP	d	NO
MS-03-214	IPN	0.25M DUP/1.5M AN	e	NO
MS-03-219	PAE	0.25M DEHP	f	YES[g]

[a] Strip solution is 1M HNO_3

[b] Contained 1 x 10^{-3}M $CuSO_4$

[c] 1M $NaNO_3$/0.01MHNO_3

[d] KOAc/HOAc

[e] HOAc/LiOAc/$LiNO_3$

[f] LiOAc/HOAc

[g] Transport on the first day only

TABLE 19

COPPER TRANSPORT USING LiOAc/HOAc AS THE FEED SOLUTION[a]

Code Number	Type	Extractant	Transport
MS-03-224	PAE	1.0M DEHP	1 DAY
MS-03-234	PAE	0.5M DEHP	NO
MS-03-235	PAE	0.75M DEHP	NO
MS-03-239	PAE	1.0M DUP	1 DAY
MS-03-243	IPN	1.0M DUP	1 DAY
MS-03-247	IPN	0.25M DUP/1.5M AN	NO

[a]0.5M LiOAc/0.5M HOAc, Strip = 1M HNO_3, 1 X 10^{-3}M $CuSO_4$

TABLE 20

COPPER TRANSPORT USING pH 3 BUFFER AS THE FEED SOLUTION[a]

Code Number	Type	Extractant	Transport
MS-03-250	PAE	1.0M DEHP	6 DAYS[b]
MS-03-255	PAE	0.25M DEHP	2 DAYS
MS-03-258	IPN	0.25M DUP/1.5M AN	1 DAY
MS-03-263[c]	IPN	0.25M DUP/1.5M AN	NO
MS-03-268	IPN	0.5M DUP/3.0M AN	6 DAYS[b]

[a]Strip = 1M HNO_3

[b]Still functional after six days

[c]MS-03-263 is MS-03-258 after being resoaked with dodecane

to the extractant level in the membrane swelling solution. This is true for both DEHP PAE's and DUP/AN IPN's.

The last feed buffer system that was studied was a sulfate/bisulfate buffer. The pH of this buffer was between 4.2 and 4.6. The sulfate buffer system is gentler on the copper selective electrode than are the acetate systems. The acetate systems cause the electrode readings to drift. The results of membrane copper transport experiments using the sulfate buffer system are given in table 21. Qualitatively the results given in table 21 show no real differences between DUP and DEHP or PAE's and IPN's.

Permeability Coefficient of Copper Transport

Permeability coefficients are calculated based on Ficks Law for copper losses from the feed solution. Selected permeability coefficients are given in table 22 for membrane transport experiments that were successful for at least four days. At this point the conclusions that can be drawn concerning copper transport are very limited. However, it can be said that the DUP systems are acting similarly to the DEHP systems and that at reasonably high extractant levels IPN formation does not greatly affect the copper transport rate

TABLE 21

COPPER TRANSPORT USING SULFATE BUFFER AS THE FEED SOLUTION[a]

Code Number	Type	Extractant	Transport
MS-03-278	PAE	1.0M DEHP	4 DAYS
MS-03-283	IPN	0.5M DUP/3.0M AN	1 DAY
MS-03-284	IPN	1.0M DUP/3.0M AN	1 DAY
MS-03-285	IPN	1.0M DUP/6.0M AN	1 DAY
MS-03-291	IPN/PAE	b	4 DAYS
MS-03-292	IPN/PAE	c	4 DAYS
MS-04-012	IPN	0.25M DUP/1.5M AN	1 DAY
MS-04-024	PAE	O.5M DUP	2 DAYS[d]
MS-04-025	PAE	O.25M DUP	1 DAY

[a] Strip = 1.0M HNO_3

[b] MS-03-283 reswollen with 0.5M DEHP

[c] 1M DUP IPN reswollen with 1M DUP

[d] System leaked after two days, not membrane failure

TABLE 22

PERMEABILITY COEFFICIENTS FOR SELECTED MEMBRANE COPPER TRANSPORT EXPERIMENTS

Code Number	See Table	Day	P[a]
MS-03-250	20	1	2.7×10^{-3}
		2	1.3×10^{-3}
		3	2.8×10^{-3}
		4	2.7×10^{-3}
		5	2.0×10^{-3}
MS-03-268	20	1	4.7×10^{-4}
		2	4.9×10^{-4}
		3	3.2×10^{-4}
		4	6.9×10^{-4}
MS-03-278	21	1	3.8×10^{-4}
		2	2.2×10^{-4}
		3	1.9×10^{-4}
		4	1.4×10^{-4}
MS-03-292	21	1	9.6×10^{-5}
		2	7.8×10^{-5}
		3	1.4×10^{-4}
		4	6.4×10^{-5}
		5	4.0×10^{-5}

[a]Permeability coefficient

Conclusions and Continuing Work

From the Eu^{+3} experiments it can be concluded that DUP/AN IPN membranes are far more stable than DEHP PAE membranes. They are also able to transport metal ions at comparable rates.

The copper transport experiments are not nearly as clear at this point. There still needs to be much additional work to develop a system that will transport copper ions and be able to distinguish between PAE and IPN membrane stability.

CHAPTER 9

EXPERIMENTAL

Allyl/Diallyl Phosphoric Acid

The synthesis of allyl and diallyl phosphoric acid was attempted by the addition of allyl alcohol to $POCl_3$. $POCl_3$ (3.73g, 0.024mol) and pyridine (9.52g, 0.12mol) in diethyl ether (40mL) were placed in a flame dried round bottom flask (250mL). Allyl alcohol (3.49g) in diethyl ether (45mL) was added over two hours. The temperature was maintained below 15°C with an ice bath. The reaction mixture was allowed to come to room temperature and quenched with 1N HCl (43mL). The phases were separated and the organic phase was washed with 1N HCl/4N NaCl to remove the excess pyridine. The acidic product was washed into an aqueous phase with 1N NaOH. Reacidification of the aqueous phase caused the product to phase separate. The yields of this reaction were very low.

Allyl/Aliphatic Phosphoric Acid

A solution of 30.66g (0.20mol) of $POCl_3$ and 79.0g (1.0mol)of pyridine and 500mL diethyl ether (some reactions were run neat) was placed in a flame dried round bottom flask equipped with a thermometer, overhead

stirrer, and addition funnel containing one (11.62g, 0.20mol) or two (23.23g, 0.40mol) equivalents of allyl alcohol. The alcohol was added to the round bottom flask over 8 to 13 hours. The temperature was uncontrolled and went up to 35°C. The mixture was allowed to sit for about 10 hours at which point a second addition was made. The second alcohol was added over four hours in a ratio of one or two equivalents of alcohol to $POCl_3$. The alcohols used were propanol and 2-ethylhexanol. The reactions were terminated and worked up as described for the allyl and dially phosphoric acid. The trace amount of material isolated was very impure.

Allyl/Aliphatic Phosphoric Acid by Reverse Addition

The only difference between this synthesis and the one above is that now the aliphatic alcohol is added first. Product yields of about 50% were obtained (^1H NMR, allylic at 6.0, 5.5, and 4.7ppm, and aliphatic at 4.1, 1.5, and 1.1ppm).

Macroporous Support Synthesis

Suspension polymerization is used to synthesize the support network in the form of beads having approximately 1-mm diameter. An aqueous phase consisting of 0.96g of gelatin, 11.90g of poly(diallyldimethylammonium chloride)(Calgon Corp.), and 6.33g of boric acid in 316.5mL

of H_2O adjusted to pH 10.3 with 50% NaOH, is poured into a 1-L round bottom flask equipped with a condenser, nitrogen purge, thermometer, temperature control device (Instruments for Research and Industry; Cheltenham,PA), and an Eberbach Con-Torque stirrer. The organic phase (134.95g of styrene (Aldrich), 13.55g of divinylbenzene (55.4% DVB isomers, remainder as ethylstyrene isomers, Dow Chemical Co.), 1.50g of benzoyl peroxide, and 150g of 4-methyl-2-pentanol (Aldrich) is then added to the flask; The suspension is set at a stir rate of 185 rpm, followed by heating to 80°C over a 2h period and holding at 80°C for 10h. The pentanol is removed from the polymer beads by steam distillation over 6h. Upon cooling , they are water washed, dried , and sieved. A yield of about 80% (-20 +60 beads) is obtained.

DUP Synthesis

A solution of 40.93g of $POCl_3$ (0.28 mol) in 110.7g of pyridine (1.4 mol) and one liter of anhydrous diethyl ether is poured into a flame dried 2-L round bottom flask equipped with thermometer, overhead stirrer, and addition funnel containing 250mL of a 2.35M 10-undecen-1-ol/ether solution. The alcohol solution is added over a period of 5h in order to maintain a temperature of 25-30°C. Stirring is continued for 16h, followed by the addition of 350mL of 3.42N H_2SO_4 (HCl may also be used) over 2h. The

ether phase is then taken on to the copper purification step.

Purification: $Cu(DUP)_2$ Formation

The ether phase is washed with 160mL of 2N NaOH in saturated $NaNO_3$ and then with saturated $NaNO_3$ until the washings are neutral. After the DUP is converted to its sodium salt form, 400mL of 1N $CuSO_4$ is added and the mixture is shaken for 5min. After the phases are separated, most of the ether is removed by evaporation under vacuum and the viscous liquid is added to 2L of acetone. When the acetone solution is cool with an ice bath, a blue precipitate forms ($Cu(DUP)_2$), which is collected, washed with cold acetone, and air dried at 25°C for 24h.

Purification: Reacidification of $Cu(DUP)_2$

The $Cu(DUP)_2$ is dissolved in 300mL of ether and washed four times with 100mL 4N HCl. The ether is removed, and the thick viscous liquid (which crystallizes with time) is dissolved in 200mL of 100% ethanol, which is removed at 35°C under vacuum. This process is repeated until the DUP is free of HCl odor. Pure DUP (mp 33.0-34.8°C) can thus be obtained in 75% yield based on $POCl_3$ (IR, H_2C=CH- at 3080cm^{-1} and =POOH at 1020 and 1240cm^{-1}).

Sodium Ethoxide Titration

A weighed amount of phosphorus acid (approximately two millimoles) is dissolved in 50mL of 100% EtOH and titrated with 0.1N NaOEt.

Phosphorus Elemental Analysis

The procedure used is the same as was discussed in part I, chapter 6.

PAE Synthesis

The swelling solutions discussed through part II are placed in contact with either macroporous polystyrene beads or macroporous polypropylene membranes (Celgard 2500, Celanese). The PAE's are obtained after the support is allowed to swell for 24h.

IPN Synthesis

Polymerization of extractants containing double bonds is accomplished by heating PAE's that contain AIBN (generally 2(w/v)%). Bead form IPN's are obtained by placing the vial of resin in an oil bath at 60^{o}C for 96h. Membrane IPN's are obtained by placing the PAE membrane between two glass plates and sealing the edges. The membrane is then heated in an oven at 60^{o}C for 96h.

PTE Synthesis

Into a 10g batch of monomer (9.33g of styrene. 0.570g of 55.4% DVB solution (for 3% crosslinking), and 0.0978g of benzoyl peroxide as initiator) is placed enough DUP to give a 0.5 or 1M solution (3.017g and 8.519g, respectively); 5.938g of DEHP is added to 10g of the monomer mixture of the 1M DEHP/PTE. The solutions are heated in an oil bath over 2h to 80^{o}C, where they are held for 10h. When cooled, the polymers are ground by using a micromill (Lab Apparatus Co., Cleveland, OH) to obtain a -20+40 mesh cut of fairly spherical particles. Prior to elution, the particles are swollen in a minimum amount of toluene in order to simulate the PAE's.

Bulk Copolymers

4-Methyl-2-pentanol is added to a styrene/DVB/benzoyl peroxide solution (35.98g, 3.63g (5% crosslinking), and 0.40g respectively) in ratios of 30, 50, 60, and 70wt%. Each solution (20.0g) is placed in a vial and polymerized under the same conditions as a PTE (all of the monomer is converted to polymer). The solid polymer is washed with ethanol to remove the 4-methyl-2-pentanol, dried, and ground as were the PTE's.

Elution Studies

The polymers are suction filtered to remove the excess toluene solution, rinsed with 25% ethanol, and placed in a glass frit funnel. A sample is taken for phosphorus elemental analysis prior to any elution in order to determine the initial capacity. The polymers are then eluted with various solutions, as mentioned earlier, at a rate of 500mL or 1L per hour with samples taken each hour for phosphorus elemental analysis in order to determine the rate of extractant losses.

Bromine Number

A weighed sample of DUP or polymerized DUP is contacted with an excess of 0.1N Br_2 in CCl_4. After 17h in the dark, excess KI is added and the solution is titrated with 0.1N $Na_2S_2O_3$ until colorless.

Vapor Phase Osmometry

VPO experiments were done using a Wescan model 232A molecular weight apparatus. The sample solutions were made at approximately 0.006M in H_2O saturated CCl_4 based on the monomer weight for both DUP and undecenyl alcohol samples. The experimental molarities were obtained by comparison with triphenylmethane standard solutions.

Mercury Liquid-Liquid Extraction

Solutions of DUP and DEHP (0.1M) in toluene (10.0mL) are shaken with 100mL of 0.01N mercuric nitrate for 17h. A 50mL aliquot from the aqueous phase is taken and titrated for Hg (II) to determine the %Hg (II) absorbed.

Mercury Solid-Liquid Extraction

A sample of polymer containing a total of 1mequiv of active sites is shaken with 100mL of mercuric nitrate for 17h. A 50mL aliquot from the aqueous phase is taken and titrated for Hg (II) to determine the %Hg (II) absorbed.

Volhard Titration for Hg (II)

An aliquot of known volume is added to 5mL of 6N HNO_3 and 5mL of saturated ferric ammonium sulfate solution. Titration with 0.05M NH_4SCN is to the first permanent burnt orange end point.

DVBP via $POCl_3$

Magnesium (14.87g, 0.605mol) is added to a 1L round bottom flask equipped with a condenser, addition funnel, overhead stirrer, and nitrogen purge. The entire system is flame dried and 700mL ether is added to the magnesium in the round bottom flask. A solution of 83.85g of vinylbenzyl chloride (VBC, 0.55mol) in 100mL ether is

added over about 1h. The Grignard formation is initiated by heating the round bottom flask. The addition rate is controlled so that good reflux of the ether is maintained. After the addition is complete the mixture is heated at reflux for 1h to improve the yield of the VBC Grignard reagent. The Grignard reagent is then added to a 1L round bottom flask equipped in a similar manner containing 38.34g $POCl_3$ (0.25mol), 19.78g pyridine (0.25mol) in 400mL ether over 6h. The reaction was terminated by adding 500mL of ice to the addition funnel and allowing it to melt. The entire mixture is transferred to a 4L beaker and 500mL of concentrated HCl added. The precipitated product is collected by suction filtration. Spectra was not taken due to the intractable nature of the product.

DVBP via PCl_3

The VBC Grignard reagent is prepared as above using 6.09g of magnesium (0.25mol), and 41.92g of VBC (.275mol) in a total of 250mL ether. The Grignard reagent is added to a second round bottom equipped as above containing 17.20g of PCl_3 (0.125mol) in 250mL of ether over 1.5h and refluxed for an additional 0.5h. The reaction mixture is then cooled to $0^{o}C$ and 50mL of 5% HCl is added. The ether phase is washed with 2% HCl and then the ether is removed to yield the crude phosphine oxide (yellow waxy solid). The solid is then treated with an excess of KI_3/pyridine,

NaOH or H_2O_2 to yield DVBP upon HCl/ether work up followed by removal of the ether. The benzyl model compounds were synthesized in the same manner. Spectra was not taken due to the intractable nature of the product.

Vinylbenzyl Alcohol

A mixture of 100g of VBC, and 50g sodium carbonate in 500mL of H_2O is placed in a round bottom flask equipped with a reflux condenser. The mixture is refluxed for 17h and extracted with ether which is then dried over $MgSO_4$ and the ether removed to yield VBA.

VBPP

A VBC Grignard reagent (0.4mol based on Mg) is added to a round bottom equipped as in the DVBP syntheses containing 64.38g of propylphosphonic dichloride (0.40mol) in 400mL ether over 7h. The reaction mixture is allowed to set for 17h and then 200mL 4% HCl is added. The mixture is added to a separatory funnel and the ether phase washed with 0.5N HCl. The ether phase is then washed with 200mL of 2N NaOH followed by 100mL of H_2O. The two aqueous phases are combined and acidified by slowly adding 50mL of concentrated HCl. Extraction of the aqueous phases with ether, followed by removal of the ether, and ethanol azeotroping as in the DUP synthesis yields VBPP (yield = 25%, ^1H NMR, phenyl at 7.2ppm, vinyl

at 6.6 and 5.5ppm, benzyl at 3.0ppm, and propyl at 1.6 and 1.0ppm).

Styrylpentyl Bromide (SPB)

A VBC Grignard reagent (0.1mol based on Mg) is added to a round bottom flask equipped as in the DVBP synthesis containing 21.59g of 1,4-dibromobutane (0,1mol), 10mL of Li_2CuCl_4 solution (0.4239g LiCl, 1.7274g $CuCl_2$-$2H_2O$, diluted to 100mL with THF), and 100mL THF over 20min. The addition rate is regulated so that the temperature can be maintained between 5 and 10°C with an ice bath. The reaction is terminated by the addition of 3.5mL of methanol. The mixture is extracted with toluene/water followed by removal of the toluene form the organic phase to yield the crude SPB. SPB is purified by vacuum distillation between 115 and 125°C at 0.12torr. Hydroquinone is added as an inhibitor (yield = 50%, ^1H NMR, phenyl at 7.2ppm, benzyl at 3.3ppn, alpha-bromo at 2.6ppm, and ailphatic at 1.6ppm).

Styrylpentyl Propyl Phosphinic Acid (SP^3)

SPB (26.86g, 95.62mequiv based on bromine capacity) is added to a round bottom flask, equipped as in the DVBP synthesis, containing 2.11g on ether (86.93mequiv) in 60mL ether in order to form the SPB Grignard reagent. The SPB Grignard reagent is then added to a second round bottom

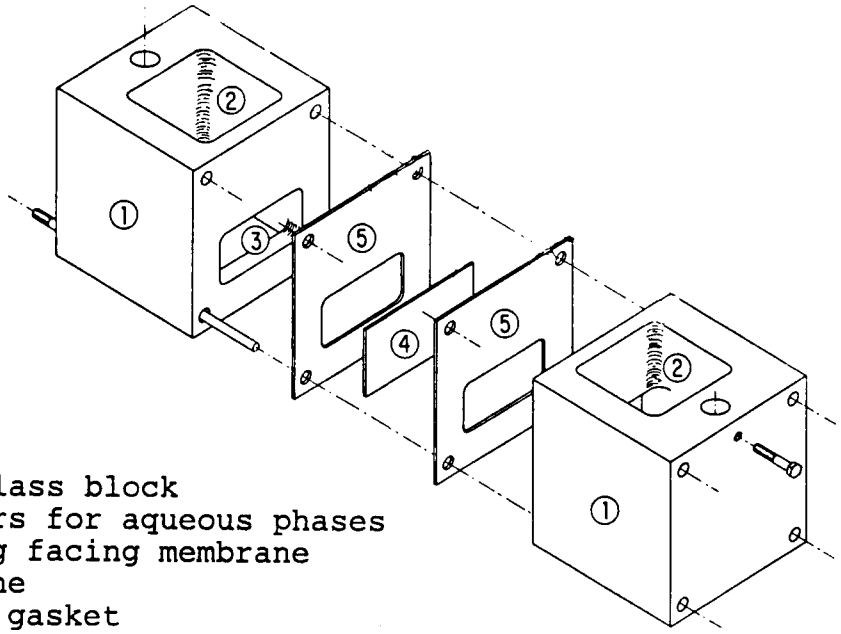
flask equipped as in the DVBP containing 13.98g of propylphosphonic dichloride in 150mL ether over 4h. The mixture is allowed to set for 16h and then terminated by the addition of 60mL 1N HCl. SP^3 is purified and isolated in the same manner as VBPP (yield = 25%, ^1H NMR, phenyl at 7.3ppm, vinyl at 6.6 and 5.5ppm, and $-CH_2-P$ at 2.8ppm).

Membrane Preparation

Standard Celgard 2400 membranes are treated with a minimal amount of swelling solution and placed between glass plates. The edges are sealed and the system heated at 60°C for 96h. The membranes are then treated with a minimal amount of dodecane. The excess dodecane is removed from the membrane surface with filter paper. The membrane is then placed in the appparatus and contacted with the aqueous phases as soon as possible.

Copper Transport Experiments

The membrane apparatus is shown in figure 23. Once the membrane is in position with the proper feed and strip solutions, both chamber are stirred at 256rpm. The motor is a 1/20 hp motor with a speed of 173rpm. The drive shaft has a 2.5 inch pulley that is connected by belt to the two stir shafts which have 1.5 inch pulleys. The membrane chamber is made from plexiglas blocks with teflon sheets on either side of the membrane. The outer plates



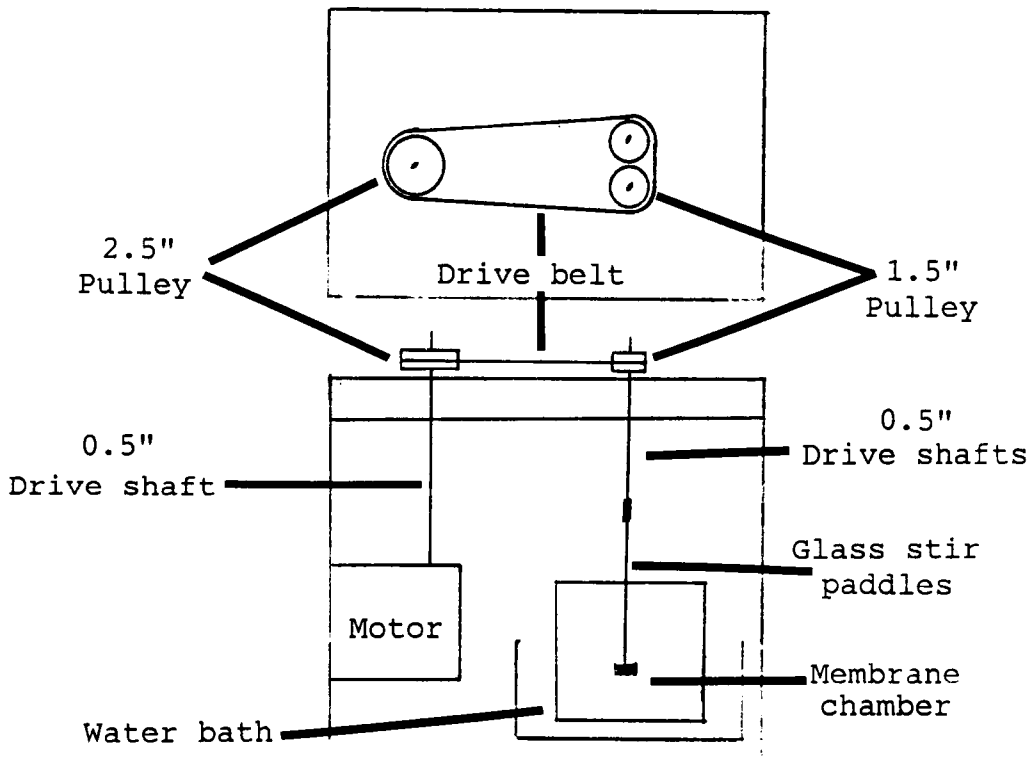


FIGURE 23

APPARATUS FOR COPPER TRANSPORT EXPERIMENTS

are either brass or aluminum plates. The apparatus is maintained at 30°C using a thermowatch (Instruments for Research and Industry; Cheltenham, PA.) connected to a water bath with heating tape.

Copper measurements are taken on the feed side using a copper selective electrode in conjunction with a double junction reference electrode (Orion) at regular intervals. The data is then interpreted by the use of Ficks law.

IR and NMR

IR's were recorded using a Perkin-Elmer 1330 IR spectrophotometer (samples run neat on NaCL plates) and the NMR's were done using a Varian T-60A NMR spectrometer (solvent = CCl_4/TMS).

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