To the Graduate Council:

I am submitting herewith a dissertation written by Cheryl E. Duffey entitled "Metal Ion Selectivity Influences in Polymer-Supported Reagents." 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.

Spiro D. Alexandratos
Major Professor

We have read this dissertation
and recommend its acceptance:

Accepted for the Council:

Associate Vice Chancellor and
Dean of The Graduate School

METAL ION SELECTIVITY INFLUENCES IN POLYMER-SUPPORTED REAGENTS

A Dissertation

Presented for the

Doctor of Philosophy

Degree

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Cheryl E. Duffey

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To my husband Jon and my family

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ABSTRACT

The synthesis and characterization of numerous mono- and bifunctional coordinating and ion exchange resins were accomplished. A series of ethyleneimine polymers was synthesized and their abilities to complex metal ions from dilute solutions evaluated. A selective removal of Cu^{2+} ions in the presence of Fe^{3+} was noted from solutions of pH 2. Several factors were shown to influence the resin's ability to complex metal ions. An increase in the percent Cu^{2+} complexed corresponding to an increase in ligand length was observed and was attributed to the nature of the ligand. It was also noted that resins eluted with HCl exhibited greater percent Cu^{2+} complexed values than the same resins eluted with HNO_3. Introduction of a second ligand onto the ethyleneimine polymers had a profound impact on the percent M^{n+} complexed that did not follow the trends set forth by the monofunctional resins containing the same ligands.

A series of phosphorus acid/ester mono- and bifunctional resins were prepared and their ability to complex Cd^{2+}, Cu^{2+}, Pb^{2+}, Eu^{3+}, and Fe^{3+} was investigated. It was shown that as the DVB crosslinking level was increased in phosphonic acid resins, the Eu^{3+} uptake decreased. Increased accessibility was demonstrated by macroreticular (MR) resins when compared to microporous (gel) resins for the uptake of Eu^{3+} by the same resins. The polymer supports to which $-P(O)(OH)_2$ ligands were covalently bound were shown not to be inert

matrices, but exhibited a marked influence on the ligand's ability to bind the above metal ions from dilute solutions. In 0.1 N HNO_3 solutions, resin binding ability increased in the order: Phos (VBC) < Phos (STY) < Phosphoric.

In addition a series of resins was prepared in which amidoxime ligands were covalently bound to differing polymer supports. These polymer supports were shown not to be inert matrices, but exhibited a marked influence on the ligand's ability to bind Cu^{2+} and Fe^{3+} from dilute solutions. In single metal ion studies binding ability of unsulfonated resins in 0.01 N HNO_3 followed the order: AN > Benzo > AN/STY (50/50) ≈ AN/STY (75/25). A preferential complexation of Cu^{2+} over Fe^{3+} was observed with the AN resins which became more pronounced during competition studies. Sulfonation of the Benzo and AN/STY (50/50) resins increased complexation of both Cu^{2+} and Fe^{3+}, and a preferential complexation of Fe^{3+} over Cu^{2+} was observed in the competition studies with the sulfonated Benzo resin.

A series of interpenetrating polymer networks was prepared in which the microenvironment around the vinylimidazole (Vlm) ligand was altered. This altering of the microenvironment was shown to have a marked influence on the ligand's ability to bind Cu^{2+}. In single metal ion studies K_{11} values increased in the order: AA < Vlm < Vlm/AA (50/50) < Vlm/EA (50/50). When Cu^{2+} ions were put into competition with Co^{2+} ions the K_{11} values (for Cu^{2+} complexation) followed the order: AA < Vlm/AA (50/50) < Vlm < Vlm/EA (50/50).

Finally, an evaluation of the Irving-Williams series of metal ion stability

was performed using polymer-supported phosphonic acid ligands. Metal ion complexation abilities of the four polymers examined were found to follow the order: $Co^{2+} < Ni^{2+} < Zn^{2+} < Mn^{2+} < Cu^{2+} < Fe^{2+}$. This observed order is not in agreement with the Irving-Williams series of stability for small molecule complexing agents which follows the order: $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$. It was also noted that although the complexing ligand in each resin was phosphonic acid, the percent M^{2+} complexed values increased in the order: VBC/MMA < STY < VBC < Acetyl.

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CHAPTER 1

INTRODUCTION

Since the mid-1960's, when Merrifield used an insoluble crosslinked macromolecule in the synthesis of peptides, the use of polymer-supported reagents has grown tremendously.[1] Until that point, the synthesis and development of macromolecules had primarily focussed on their use as materials rather than reagents. Polymer-supported reagents are functionalized polymers which may be used as: catalysts, stoichiometric reagents, chromatographic reagents, enzyme immobilizers, ion exchangers and metal ion chelaters.[2] These polymer-supported reagents may be prepared by polymerization of monomers containing the desired functional group, or by chemical modification of a previously synthesized polymer.[3] Polymer-supported reagents may take the form of beads (via suspension polymerization),[4] membranes,[5] fibers,[6] or ground natural products such as wood or chitin.[7] They may also be soluble linear or colloidal.[8]

In theory any reagent or catalyst, organic or inorganic, may be supported on a polymer. However, no reasons exist for the use of polymeric reagents unless distinct advantages are evident.[8] Some advantages as well as disadvantages are listed below.[2,3,9]

Advantages

- Ease of separation, work-up, and isolation
- Possibility of regenerating or recycling the reagent
- Possibility of automation
- Safety in handling highly reactive, malodorous, or toxic chemicals

Disadvantages

- Additional time and cost of synthesizing the reagent
- Possibility of slow reaction rates and poor yields due to limited accessibility
- Chemical and mechanical stability may be limiting
- Capacity of polymer may be restricted

Although polymer-supported reagents may be linear or crosslinked, and in a physical form such as those listed above, they most often exist as crosslinked beads.[2] Many reviews have been written on their use as reagents and catalysts.[2,8,10-14] These beads may be prepared as **microporous** (gel) species in which vinyl monomers are polymerized in the absence of additional solvating media, **macroporous** in which the polymerization is carried out in the presence of an inert solvent which solvates both the monomers and polymer, or **macroreticular** (MR) in which the polymerization is carried out in the presence of an inert solvent which solvates the monomers but precipitates the polymer. Macroreticular resins are often termed macroporous since both techniques produce beads with pores larger than those of microporous beads.[2]

Functionalized polymers have been used successfully in many well known organic reactions as reagents and catalysts. Polymer-supported phenylphosphines have been used in the Wittig reaction (ketone or aldehyde conversion to alkenes) to alleviate the problems of separating the byproduct, triphenylphosphine oxide, from the desired alkene product. With the supported reagent, the byproduct is also supported and thus readily separated and recycled. In addition, high yields of the *cis*-alkene products are obtainable when the polymeric reagent is used due to the ability to remove the lithium salt before the addition of the carbonyl.[2,14] Polymer-supported reagents have also been used in the Mitsunobu reaction for the condensation of alcohols and acids. These reactions have been carried out using supported phenylphosphines as well as supported azodicarboxylates.[15]

Polymer-supported reagents have also been utilized as oxidizing and reducing agents in redox reactions. Supported chromic acid has been used to oxidize alcohols and alkyl halides to aldehydes and ketones.[16] Polymeric phosphinic acid has been used to reduce Hg^{2+} to Hg^{0}.[17] Along with other advantages, the dangers of the epoxidation of alkenes are eliminated with the use of polymer-supported peracids. Their small molecule analogues explode on contact.[14]

Halogenation reactions have been carried out using *N*-chloropolymaleimide and *N*-bromopolymaleimide, the polymeric analogues of *N*-chlorosuccinimide (NCS) and *N*-bromosuccinimide (NBS), respectively. When

alkylaromatic compounds were chlorinated using NCS, mixtures of alkyl- and aryl-substituted products were obtained. However, when the polymeric analogue was used under the same conditions, only the aryl-substitued products were obtained.[18] Interesting results were also obtained using the polymeric analogue of NBS. When NBS was reacted with cumene (isopropylbenzene) only α-bromocumene and α,β-dibromocumene were obtained as products. When the polymeric analogue was used both above products were absent and three unexpected products were obtained (α,β,β'-tribromocumene, β-bromo-α-methylstyrene, and α-bromomethylstyrene).[19]

Polymer-supported catalysts, organic and inorganic, are used in a variety of applications. Ion exchange resins, such as supported sulfonic acid and supported ammonium hydroxide salts, represent the earliest examples of polymer-supported catalysts. Sulfonic acid resins have been used as catalysts in condensations, dehydrations, rearrangements, and the hydrolysis of esters, peptides, and carbohydrates. Supported ammonium hydroxide salts have been used as catalysts in dehydrohalogenations, condensations, cyclizations, and esterifications. Polymeric Lewis acids such as supported $AlCl_3$ have been used in acetyl formation.[2,14] Halogenated polymer-supported metalloporphyrins have been shown to be efficient catalysts in the oxidation of hydrocarbons.[20] Polymer-supported crown ethers have been used as phase transfer catalysts as well as catalysts in decarboxylation reactions.[2]

In addition to their applications in organic chemistry, polymer-supported reagents are employed in analytical chemistry, water treatment processes, and metallurgical extractions.[2] Analytical chemistry uses polymeric reagents for chromatographic separations of molecular and ionic species, preconcentration, and purification of solvents and samples.[21]

Water treatment processes consume approximately 90% of all ion exchange materials produced.[22] In 1905 Gans used sodium aluminosilicate cation exchange materials, known as zeolites, to replace Ca^{2+} and Mg^{2+} with Na^{+}. The removal of Ca^{2+} and Mg^{2+} is referred to as softening and the term zeolite softener is often used to describe any cation exchange process. Today strong cation resins such as supported sulfonic acid are used to soften water. These resins may be used in the protonated or sodium form and function well at all pH's. Weak cation exchangers such as supported carboxylic acids may also be used but do not work well below pH 5. Either of these types of resins may be used in conjuction with strong base resins, such as supported quaternary ammonium hydroxides, or weak base resins, such as supported amines, to demineralize water. Weak base resins however, will not remove silicic and carbonic acids. Strong acid and base resins are referred to as "salt splitting" resins.[23] Ion exchange resins are also used for the treatment of waste water and pollution control where the removal of such toxic species as Cd^{2+}, Hg^{2+}, and Pb^{2+} is essential. Polymeric adsorbers are often used in conjunction

with ion exchange resins for the removal of chlorinated compounds, colorants, wetting agents, and other non-ionic organic compounds.[24]

The use of polymer-supported reagents for the separation and recovery of metals from complex ores and sea water is ever increasing. Included in the metallurgical applications of polymer-supported reagents is the separation and recovery of metals from industrial waste streams. Although these separations are of significant environmental importance, the recovery of these metals is of economic importance as well. Metals find use in areas such as the chemical industry (catalysts), traditional engineering industries (aviation, marine vessels, equipment, tools, motor vehicles), strategic energy sources, electronic industries, plating industries, electrochemical energy sources (batteries), and other applications too numerous to mention.[25] Some typical metals recovered and purified by polymer-supported reagents include uranium, thorium, gold, silver, chromium, copper, zinc, nickel, cobalt, tungsten, rare earths, platinum group metals, and the transuranic elements.[26]

A wide variety of polymer-supported functional groups have been shown to selectively remove targeted metal ions from aqueous solutions. Amino-phosphonate functional groups, supported on a macroporous polystyrene copolymer, selectively sorb uranium from other trace metal ions.[26] Platinum group metals (PGM) are selectively removed from HCl/Cl_2 leach solutions by polymer-supported isothiourea groups.[27] Polymer-supported *N*-Methyl-2-thioimidazole has been shown to quantitatively separate gold from a 1 M HCl

solution containing excess Cu^{2+}, Fe^{3+}, Mn^{2+}, and Ni^{2+}.[11] Obviously the selection of a particular ligand based upon inorganic principles is the first step in the design of ion selective polymers.[10] Equally important however are the changes in metal ion selectivity once a particular ligand is covalently bound to a polymer support.

This dissertation describes research aimed at understanding the factors which control metal ion selectivity in polymer-supported reagents. Influences investigated include resin porosity, type and level of crosslinking, polymer support effects, bifunctionality, ligand chain length effects, and counterion effects. Also examined were metal ion selectivity of interpenetrating polymer networks (IPN's) and polymeric influences on the Irving-Williams series of metal ion stability.

CHAPTER 2

METAL ION SELECTIVITY INFLUENCES IN ETHYLENEIMINE POLYMERS

Introduction

The removal of metal ions has become increasingly important in governmental as well as industrial sectors.[28] Technical applications include effluent treatment, analytical separations, and recovery from mining industry tailings.[29,30] Of particular hydrometallurgical interest is the removal and recovery of Cu^{2+}.[31] Due to the presence of other transition metal ions in these solutions, the successful removal of the targeted metal ion is dependent upon a high degree of selectivity from the chosen extractant. In the leaching of copper, for example, the most troublesome impurity is Fe^{3+}. The selective removal and recovery of Cu^{2+} in the presence of high concentrations of Fe^{3+} would greatly facilitate the leaching process.[32,33]

Development of a suitable metal ion extractant relies upon experimental evidence as well as inorganic principles such as valence bond theory, Pearson's hard and soft acid and base theory, the Irving-Williams series of stability, and chelate or macrocyclic effects.[10,34] Classical donor ligands such as those containing nitrogen lend themselves to the formation of stable complexes with transition as well as main group metals. Since Alfred Werner (1866-1919)

won the Nobel Prize in 1913 for his work on complex salts such as $[Co(NH_3)_6]^{3+}Cl_3^-$,[35] nitrogen containing ligands remain among the most intensively studied.[36]

It is well known that the stability of a metal ion complex is enhanced by the formation of chelate rings due to coordination between a metal ion and a multidentate ligand or ligands. This enhanced stability is termed the "chelate effect" and can be explained by thermodynamic principles.[37,38] The formation of these chelate rings is limited by steric requirements in much the same way as organic ring systems. However, in chelate rings where significant resonance effects are absent, five-membered rings show maximum stability.[39] The bidentate ligand ethylenediamine forms such five-membered rings with many transition metals. When two or three ethylenediamine ligands are coordinated to the same metal ion, complexes with tetrahedral, square planar or octahedral geometries can be obtained. These complexes contain two, two, and three five-membered rings, respectively. Multiple chelate rings may also be formed with tri-, tetra-, penta-, and hexadentate ligands.[40] Table 2.1 gives equilibrium constants for the "Irving-Williams" metal ions with ammonia, and ethylenediamine type (ethyleneimine) ligands. These values indicate that for ethyleneimine ligands, binding ability increases with an increase in ligand length (and number of nitrogens contained in the ligand) and are selective for Cu^{2+}.

Polymeric ethylenediamine type amines have been developed and studied with respect to their chelating properties.[41-44] Poly(ethyleneimine) (PEI)

Table 2.1

K_1 Values for Ethyleneimine Ligands[10]

		$NH_2(CH_2CH_2NH)_nH$		
	NH_3	n = 1	n = 2	n = 3
Mn(II)	-	5×10^2	1×10^4	1×10^5
Fe(II)	-	2×10^4	17×10^5	1×10^8
Co(II)	1×10^2	8×10^5	2×10^8	1×10^{11}
Ni(II)	5×10^2	4×10^7	6×10^{10}	1×10^{14}
Cu(II)	12×10^3	5×10^{10}	1×10^{16}	1×10^{20}
Zn(II)	2×10^2	8×10^5	1×10^9	1×10^{12}

can have a linear (LPEI) or branched (BPEI) structure, both providing a multitude of amine sites for complexation with metal ions. Although these polymers show selectivity for Cu^{2+}, recovery is limited due to their solubility in water. Several methods exist which can make these polymers insoluble, including post polymerization crosslinking with agents such as ethylene dibromide or epichlorohydrin, and grafting of the PEI polymers to a crosslinked matrix such as polystyrene.[42,43]

An alternative and more efficient method to those listed above is the incorporation of the chelating ligand into an insoluble polymer matrix. This concept of polymer-supported reagents is growing in popularity and use in separation science as well as organic synthesis.[2,10,11] Polymer-supported reagents may be synthesized by polymerization of a functionalized vinyl derivative, or by polymerization of a vinyl monomer followed by chemical conversion to the desired functional group.[28] For obvious reasons either synthetic route should consist of as few steps as possible without alteration of ligand characteristics. In addition to selectivity, the resins must exhibit high mechanical strength without compromising accessibility to the chelating sites.[42] It has been observed that accessibility is greater in resins that have undergone chemical modification than in those produced by polymerization of a functionalized monomer.[29]

Binding properties of polymer-supported ethyleneimine ligands have been studied. It has been shown that during the single step reaction of crosslinked

poly(vinylbenzyl chloride) with a given ethyleneimine, secondary crosslinking occurs which may lead to a reduction in the capacity of the resin as well as the alteration of well defined ligands.[10,45] Multistep synthetic methods have been examined which eliminate these undesirable bridging reactions, but have been limited to ligands containing three nitrogens.[1,30]

This work examines the complexing abilities of a series of polymer-supported ethyleneimine resins with metal ions from dilute solutions. The role of copolymer matrix, ligand length, anion of eluting acid, and bifunctionality are investigated and their influence on complexing ability reported.

Synthesis and Characterization

Brief descriptions of all syntheses follow. Details of these syntheses are found in the Experimental chapter.

The monofunctional imine resins used in these studies were synthesized by the reaction of a given ethyleneimine, such as ethylenediamine, with a vinylbenzyl chloride polymer support (Figure 2.1). These polymer supports were prepared by the suspension polymerization of vinylbenzyl chloride (VBC) and vinylbenzyl chloride-*co*-styrene (VBC/STY). Microporous (i.e., gel) as well as macroreticular (MR) beads were prepared with divinylbenzene (DVB) as the crosslinking agent in both. All copolymers had a particle size of 250 µm - 425 µm. The VBC beads were synthesized as gels, with crosslinking levels of 2 wt% and 20 wt% DVB, and MR's, with a crosslinking level of 5 wt% DVB.

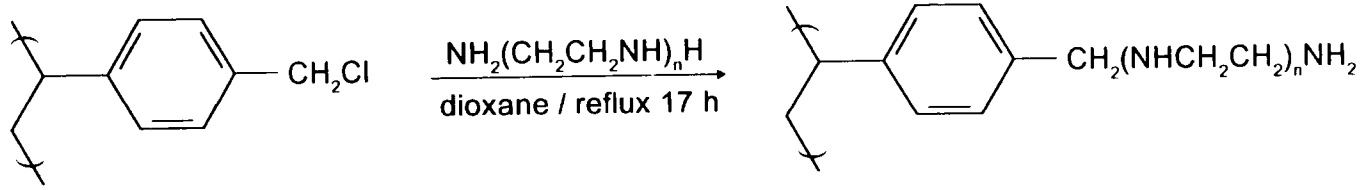


Figure 2.1. Synthesis of Ethyleneimine Resins

The VBC/STY beads were prepared only as gels with 2 wt% DVB, and monomer ratios of 50/50 wt% and 75/25 wt%.

Ethylenediamine (EDA) Resins

The EDA resins were prepared without deviation from the general procedure, i.e., beads containing VBC moieties were reacted with excess ethylenediamine in dioxane. The ethylenediamine used was obtained from Aldrich Chemical Co. and had a purity of 99%. The acid (protonated) form of the resin was obtained by elution of the functionalized beads with 1 L each: H_2O, 4 wt% NaOH, H_2O, 4 wt% HCl or HNO_3, and H_2O until a neutral drip was obtained. The base (unprotonated) form of the resin was obtained by elution of the functionalized beads with 1 L each: H_2O, 4 wt% HCl, H_2O, 4 wt% NaOH, and H_2O until a neutral drip was obtained. The resins were characterized by procedures described in detail in the Experimental chapter. The properties of the acid and base forms of the EDA resins are summarized in Tables 2.2 and 2.3 respectively.

The percent solids of the EDA resins varied as anticipated with the MR resin (CL3-012) having the lowest value, 28.34%, and the 20% DVB gel resin (CL3-078) having the highest, 77.42%. The 2% DVB gel resins from VBC eluted with HCl had solids levels of approximately 42%, whereas the one eluted with HNO_3 had a solids level of 52.71%. Base forms of the resins exhibit higher solids levels than acid forms in all cases. For example resin CL3-017 had a

Table 2.2

Characterization of EDA Resins in Acid Form

Resin	% DVB/ Porosity	Eluting Acid	% Solids (g_{dry}/g_{wet})100	Nitrogen Capacity (mequiv/g)	Chlorine Capacity (mequiv/g)
CL3-017	2%/gel	HCl	41.42	5.57[a] (10.94)[b]	-
CL3-141	2%/gel	HCl	42.88	5.94 (10.94)	-
CL4-054	2%/gel	HCl	42.16	6.26 (10.94)	-
		HCl	42.45	6.32 (10.94)	6.93
		HNO_3	52.71	7.61 (-----)	0.18
CL3-078	20%/gel	HCl	77.42	4.58 (7.22)	-
CL3-080[c]	2%/gel	HCl	58.12	3.46 (5.46)	-
CL3-012	5%/MR	HCl	28.34	4.68 (10.28)	-

[a]Experimental
[b]Theoretical
[c]From VBC/STY 50/50 wt%

Table 2.3

Characterization of EDA Resins in Base Form

Resin	% DVB/ Porosity	% Solids (g_{dry}/g_{wet})100	Nitrogen Capacity (mequiv/g)	Chlorine Capacity (mequiv/g)
CL3-017	2%/gel	51.08	6.66[a] (10.94)[b]	-
CL3-141	2%/gel	51.58	7.06 (10.94)	-
CL3-078	20%/gel	80.46	4.11 (7.22)	0.27
CL3-080[c]	2%/gel	62.73	3.70 (5.46)	0.14

[a]Experimental
[b]Theoretical
[c]From VBC/STY 50/50 wt%

solids level of 41.42% in the acid form and 51.08% in the base form. This result is expected due to the hydrophilicity of the protonated form.

Nitrogen capacities of the 2% DVB gels eluted with HCl varied from 5.57 mequiv/g to 6.32 mequiv/g. The 2% DVB gel eluted with HNO_3 had a capacity of 7.61 mequiv/g, the increase in capacity being attributed at least in part to the nitrogen of the anion. The base forms of the 2% DVB gels showed higher capacities than the acid forms; for resin CL3-017 these values were 6.66 mequiv/g and 5.57 mequiv/g, respectively. It should be noted that for all resins the experimental nitrogen capacity is considerably less than the theoretical value, e.g., for a 2% DVB gel resin from VBC the theoretical nitrogen capacity is 10.94 mequiv/g with the highest experimental capacity being 6.32 mequiv/g. This discrepancy cannot be attributed to incomplete funtionalization of the copolymer since the chlorine capacity in the base form and HNO_3 eluted form is essentially 0 mequiv/g. The most likely explanation is internal crosslinking by the ethylenediamine.[30,45] Figure 2.2 depicts possible crosslinking configurations when VBC is reacted with diethylenetriamine.

Diethylenetriamine (DETA) Resins

The DETA resins were also prepared without deviation from the general procedure. Resin CL3-037 was synthesized using diethylenetriamine from Fluka Chemical Company of unknown age and purity. The remainder of the resins were synthesized using diethylenetriamine from Aldrich Chemical Co. of

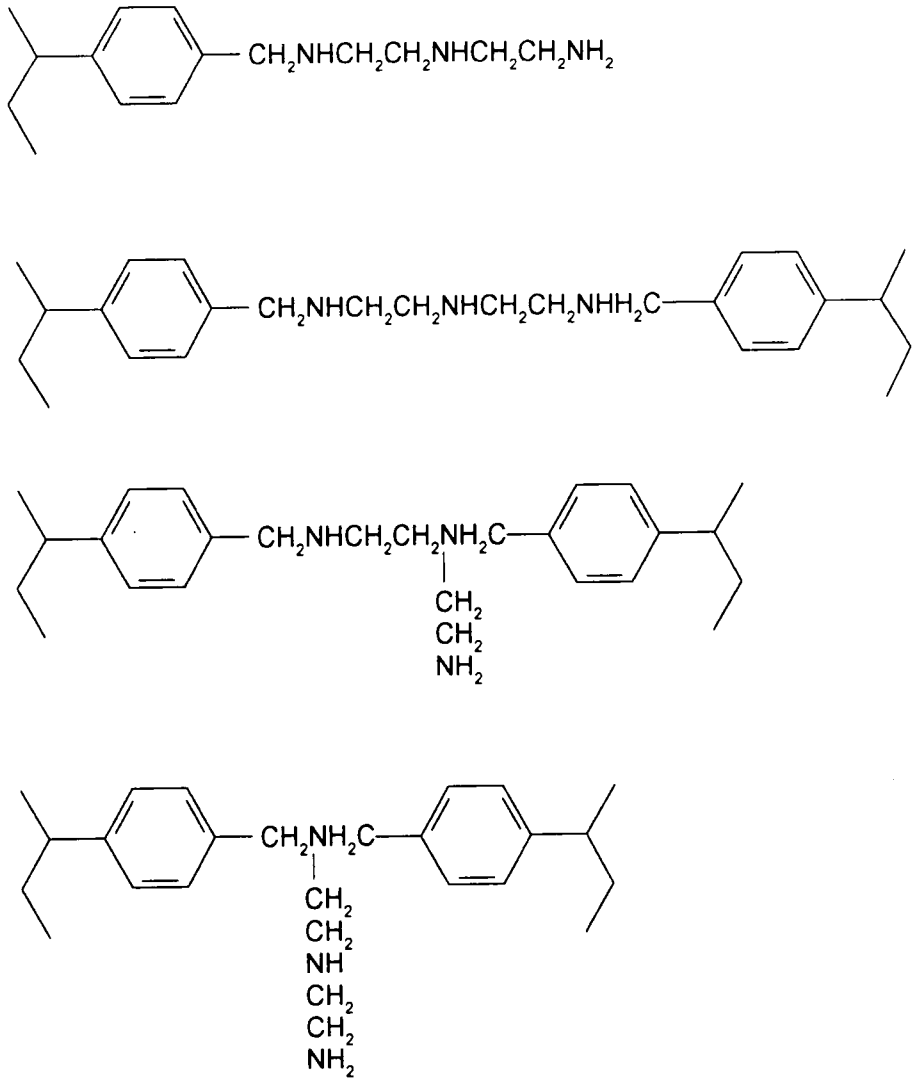


Figure 2.2. Possible Crosslinking Configurations of DETA Resins

99% purity. The properties of the acid and base forms of the DETA resins are summarized in Tables 2.4 and 2.5 respectively.

The DETA resins follow the same characterization trends as noted with the EDA resins. Again when HNO_3 is the eluting acid the solids level is a value of approximately 10% higher than its HCl counterpart. For resin CL4-055 the solids level is 39.57% for the Cl^- form and 50.54% for the NO_3^- form.

The 2% DVB gel DETA resins in the same form yield quite reproducible results, exceptions being CL3-037 made with Fluka diethylenetriamine and the first characterization of CL3-164. The latter was originally prepared in the base form and converted to the acid form by a partial conditioning, i.e., elution with 1 L each: 4 wt% HCl and H_2O until a neutral drip was obtained. The nitrogen capacity was 9.09 mequiv/g which was approximately 2 mequiv/g higher than other resins of the same type. The resin was then conditioned with the entire elution sequence and upon characterization yielded a nitrogen capacity of 7.15 mequiv/g, a value which is quite consistent with that of other resins.

Triethylenetetramine (TETA) Resins

TETA resins were prepared following the general procedure using both dioxane and water as solvents. All resins were synthesized using Aldrich technical grade triethylenetetramine of 60% purity. Impurities include tris(aminoethyl)amine, diaminoethylpiperazine, piperazinoethylethylenediamine,

Table 2.4

Characterization of DETA Resins in Acid Form

Resin	% DVB/ Porosity	Eluting Acid	% Solids (g_{dry}/g_{wet})100	Nitrogen Capacity (mequiv/g)	Chlorine Capacity (mequiv/g)
CL3-037[a]	2%/gel	HCl	43.79	8.03[b] (13.14)[c]	-
CL3-076	2%/gel	HCl	42.06	7.09 (13.14)	-
CL3-164	2%/gel	HCl	41.71	9.09 (13.14)	-
		HCl	42.06	7.15 (13.14)	-
CL4-055	2%/gel	HCl	39.57	7.34 (13.14)	-
		HNO_3	50.54	9.06 (-----)	-
CL4-074	2%/gel	HCl	39.58	7.57 (13.14)	5.76
		HNO_3	50.68	9.07 (-----)	0.24
CL3-077	20%/gel	HCl	78.59	4.67 (8.70)	-
CL3-079[d]	2%/gel	HCl	51.47	4.90 (6.60)	-

[a]Fluka
[b]Experimental
[c]Theoretical
[d]From VBC/STY 50/50 wt%

Table 2.5

Characterization of DETA Resins in Base Form

Resin	% DVB/ Porosity	% Solids (g_{dry}/g_{wet})100	Nitrogen Capacity (mequiv/g)	Chlorine Capacity (mequiv/g)
CL3-037[a]	2%/gel	50.37	9.79[b] (13.14)[c]	-
CL3-076	2%/gel	52.22	8.11 (13.14)	-
CL3-162	2%/gel	57.49	8.52 (13.14)	-
CL3-164	2%/gel	51.54	8.23 (13.14)	-
CL3-077	20%/gel	81.89	4.86 (8.70)	0.41
CL3-079[d]	2%/gel	57.77	5.07 (6.60)	0.31

[a]Fluka
[b]Experimental
[c]Theoretical
[d]From VBC/STY 50/50 wt%

as per Aldrich Customer Service. The properties of the acid and base forms of the resins are summarized in Tables 2.6 and 2.7 respectively.

Characterization properties of a given type of resin in the same form are quite consistent, and follow the same trends as those mentioned previously. Consistency exceptions are those in which the resins were generated using water as the solvent rather than dioxane. Resin CL3-016, which was synthesized using water, had a solids level of 94.01% and a nitrogen capacity of essentially 0.00 mequiv/g, whereas resins of the same type, synthesized using dioxane, had solids levels of approximately 43% and nitrogen capacities of approximately 8.25 mequiv/g. This indicates an accessibility problem exists due to the hydrophobic nature of the copolymer. The 2% DVB gel copolymer swelled to a volume approximately three times its original volume in dioxane, whereas in H_2O no volume increase was observed. An increase in nitrogen capacity (2.87 mequiv/g) was seen with resin CL3-013 which was expected due to the 50% void volume of the macroreticular copolymer. This capacity however, is substantially lower than that obtained when dioxane was used as the solvent (approximately 7.00 mequiv/g).

Tetraethylenepentamine (TEPA) Resins

TEPA resins were prepared without deviation from the general procedure. Resins CL3-038 and CL3-110 were synthesized using technical grade tetraethylenepentamine obtained from Fluka and Aldrich respectively.

Table 2.6

Characterization of TETA Resins in Acid Form

Resin	% DVB/ Porosity	Eluting Acid	% Solids (g_{dry}/g_{wet})100	Nitrogen Capacity (mequiv/g)	Chlorine Capacity (mequiv/g)
CL2-278	2%/gel	HCl	41.01	8.47[a] (14.72)[b]	-
CL3-036	2%/gel	HCl	43.09	8.25 (14.72)	-
CL4-025	2%/gel	HCl	46.62	8.18 (14.72)	-
CL3-016[c]	2%/gel	HCl	94.01	0.15 (14.72)	-
CL3-006	5%/MR	HCl	29.77	7.01 (14.20)	8.95
CL3-035	5%/MR	HCl	33.52	6.91 (14.20)	8.56
CL3-013[c]	5%/MR	HCl	36.77	2.87 (14.20)	-

[a]Experimental
[b]Theoretical
[c]H_2O used as solvent during functionalization

Table 2.7

Characterization of TETA Resins in Base Form

Resin	% DVB/ Porosity	% Solids $(g_{dry}/g_{wet})100$	Nitrogen Capacity (mequiv/g)	Chlorine Capacity (mequiv/g)
CL2-278	2%/gel	48.34	9.69[a](14.72)[b]	0.00
CL3-140	2%/gel	47.96	10.35 (14.72)	-

[a]Experimental
[b]Theoretical

Attempts were made to isolate the tetraethylenepentamine by vacuum distillation with no success. All other TEPA resins were synthesized from tetraethylenepentamine which was isolated from the Aldrich pentahydrochloride salt. Reaction of the hydrochloride salt with NaOH followed by extraction into dioxane yielded tetraethylenepentamine of a greater purity than those of the distilled reagents. Properties of the acid and base forms of the TEPA resins are summarized in Tables 2.8 and 2.9, respectively.

The resin generated using Fluka tetraethylenepentamine, CL3-038, had nitrogen capacities (acid and base forms) which were approximately 1.0 mequiv/g lower than resins generated using Aldrich reagents. This may be due to decomposition of the tetraethylenepentamine since the age of the reagent was unknown. The resin synthesized using the technical grade Aldrich amine, CL3-110, had properties reasonably close to those of CL3-217, which was synthesized using the amine from the hydrochloride salt (solids levels of 53.34% and 52.44%, respectively, and nitrogen capacities of 9.75 mequiv/g and 9.25 mequiv/g, respectively). It is possible that nitrogen-containing impurities present in the technical grade tetraethylenepentamine are incorporated into the resin, thus contributing to the total nitrogen capacity.

Pentaethylenehexamine (PEHA) Resin

The PEHA resin was prepared without deviation from the general procedure. Resin CL3-039 was synthesized using Fluka technical grade

Table 2.8

Characterization of TEPA Resins in Acid Form

Resin	% DVB/ Porosity	Eluting Acid	% Solids (g_{dry}/g_{wet})100	Nitrogen Capacity (mequiv/g)	Chlorine Capacity (mequiv/g)
CL3-038[a]	2%/gel	HCl	40.83	6.60[b] (15.75)[c]	-
CL4-019[d]	2%/gel	HCl	44.51	8.12 (15.75)	-
		HCl	44.31	7.52 (15.75)	5.03
		HNO_3	53.43	9.00 (-----)	0.14

[a]Fluka
[b]Experimental
[c]Theoretical
[d]Tetraethylenepentamine isolated from the HCl salt

Table 2.9

Characterization of TEPA Resins in Base Form

Resin	% DVB/ Porosity	% Solids (g_{dry}/g_{wet})100	Nitrogen Capacity (mequiv/g)	Chlorine Capacity (mequiv/g)
CL3-038[a]	2%/gel	50.58	8.22[b] (15.75)[c]	-
CL3-110	2%/gel	53.34	9.75 (15.75)	-
CL3-217[d]	2%/gel	52.44	9.25 (15.75)	-

[a]Fluka
[b]Experimental
[c]Theoretical
[d]Tetraethylenepentamine isolated from the HCl salt

pentaethylenehexamine of unknown age. The properties of the acid and base forms of the PEHA resin are summarized in Tables 2.10 and 2.11, respectively.

Bifunctional Resins

The bifunctional resins containing ethyleneimine and phosphonic acid moieties were synthesized by the same general procedure shown in Figure 2.3. VBC beads were reacted with triisopropyl phosphite in a two fold excess of toluene to yield the phosphonate ester which was approximately 50% functionalized. The ester functionality was then hydrolyzed to the phosphonic acid by reflux in concentrated HCl. The resulting phosphonic acid resin was reacted with the appropriate amine in dioxane which yielded the bifunctional resin. The DETA/Isopropylphosphonate diester resin was generated as above excluding the HCl hydrolysis.

The bifunctional resin containing triethylenetetramine and sulfonic acid moieties was synthesized from a VBC/styrene (STY) copolymer with a monomer ratio of 75/25. The reaction of the copolymer with triethylenetetramine followed the general procedure. The resin was then reacted with chlorosulfonic acid in ethylene dichloride to yield the bifunctional resin. The synthesis is shown in Figure 2.4. Properties of all bifunctional resins in acid form are summarized in Table 2.12.

The trends for the nitrogen capacities and solids levels of the bifunctional resin are the same as those of the monofunctional resins, i.e., greater when

Table 2.10

Characterization of PEHA Resin in Acid Form

Resin	% DVB/ Porosity	Eluting Acid	% Solids (g_{dry}/g_{wet})100	Nitrogen Capacity (mequiv/g)	Chlorine Capacity (mequiv/g)
CL3-039[a]	2%/gel	HCl	48.06	7.93[b] (16.56)[c]	-

[a]Fluka
[b]Experimental
[c]Theoretical

Table 2.11

Characterization of PEHA Resin in Base Form

Resin	% DVB/ Porosity	% Solids $(g_{dry}/g_{wet})100$	Nitrogen Capacity (mequiv/g)	Chlorine Capacity (mequiv/g)
CL3-039[a]	2%/gel	52.47	9.90[b] (16.56)[c]	0.00

[a]Fluka
[b]Experimental
[c]Theoretical

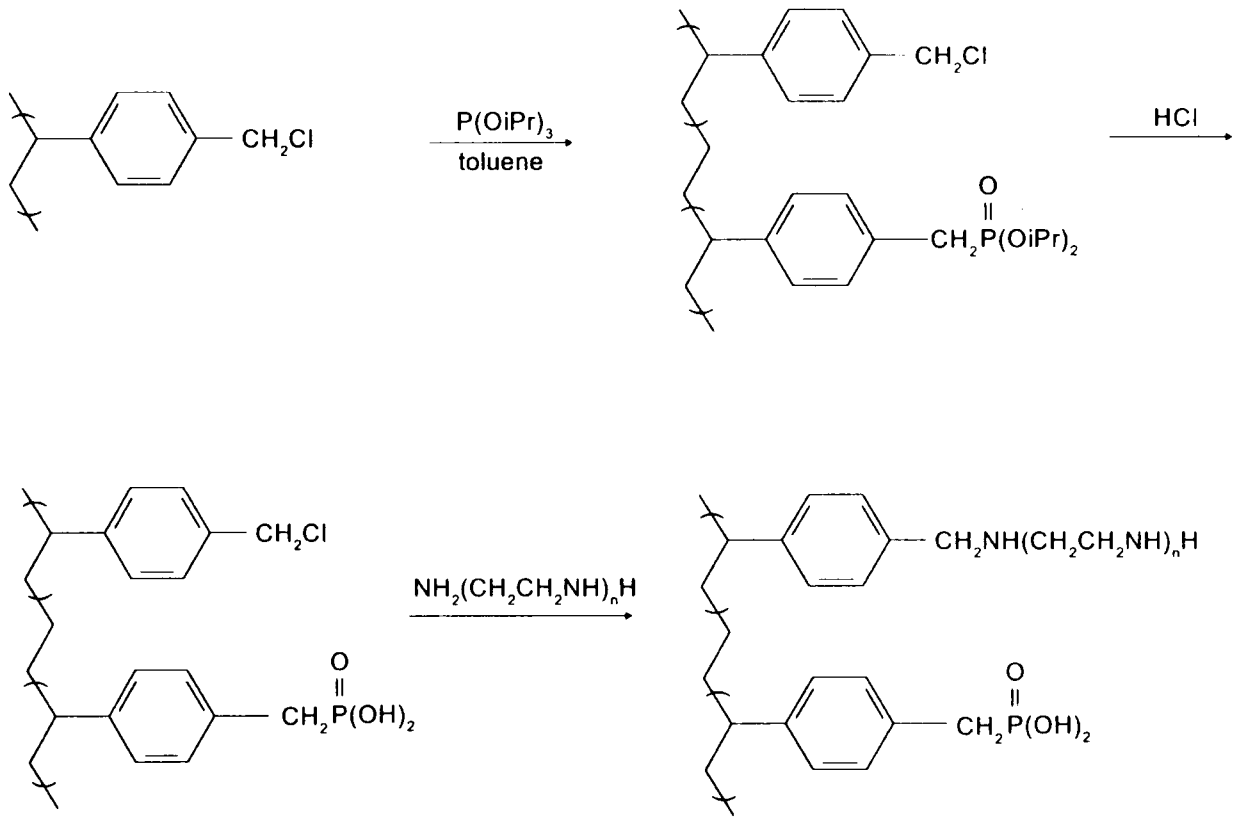


Figure 2.3. Synthesis of Ethyleneamine/Phosphonic Acid Bifunctional Resin

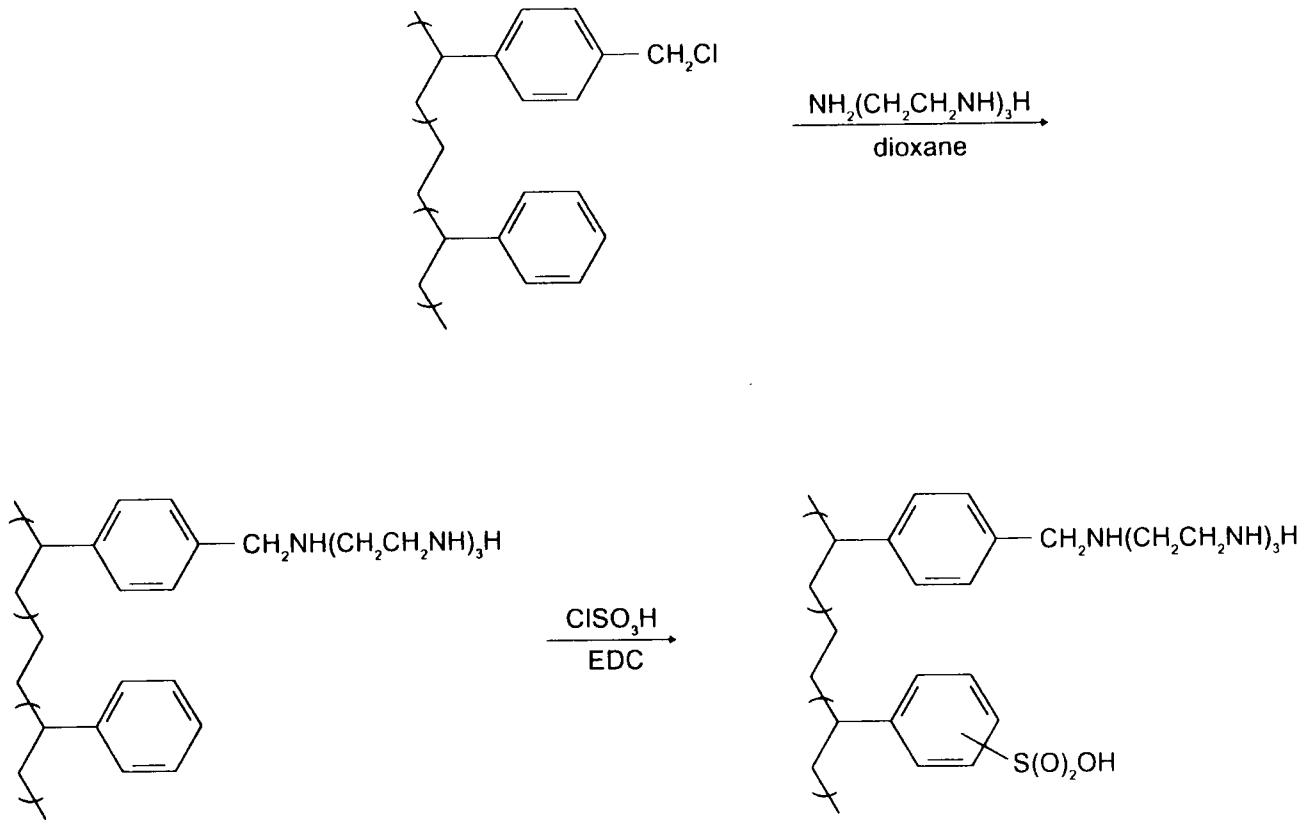


Figure 2.4. Synthesis of TETA/Sulfonic Acid Bifunctional Resin

Table 2.12

Characterization of Bifunctional Resins in Acid Form

Resin	Functional Groups	Eluting Acid	% Solids (g_{dry}/g_{wet})100	Nitrogen Capacity (mequiv/g)	Phosphorus Capacity (mequiv/g)
CL3-174	DETA/ Phos. acid[a]	HCl	58.65	4.35	2.28
CL3-201	DETA/ Phos. acid	HCl	50.16	5.45	1.88
		HCl	51.06	5.76	2.00
		HNO_3	57.89	6.28	1.89
CL4-122	DETA/ Phos. acid	HCl	45.47	6.11	1.39
CL4-123	EDA/ Phos. acid	HCl	54.98	4.01	2.30
		HNO_3	59.21	4.72	2.32
CL4-133	DETA/ Phos. ester[b]	HCl	34.30	3.72	1.76
CL2-274	TETA/ Sulfonic acid	HCl	41.99	7.13	-

[a]Phosphonic acid
[b]Isopropylphosphonate diester

NO_3^- is the anion. However, the differences accompanied by a change in anion are less in the bifunctional case. One explanation for these observed differences may be the interaction between the amine and phosphonic acid ligands. Solid-state ^{31}P NMR spectra of the bifunctional resins show the effect the presence of an amine has on the chemical shift of the phosphorus of the phosphonic acid. Resin CL3-063, a 100% phosphonic acid resin, exhibits a peak position of 30.24 ppm, while the EDA and DETA bifunctional resins exhibit peak positions of 24.00 and 23.44 ppm, respectively. Similar results have been reported with bifunctional resins having phosphonic acid and benzyltrimetylammonium groups.[46] This upfield shift in peak position is not observed with the DETA/isopropyl ester resin (30.28 ppm), which is consistent with the lack of interaction between the amine and ester ligands.

When determining percent functionality of the amine and phosphorus moieties, the total nitrogen capacity is divided by the number of nitrogens in the amine to yield a ligand capacity in mmol/g. This method is only valid when HCl, not HNO_3, is the eluting acid. The ligand capacity may then be compared directly to the phosphorus capacity. Resin CL4-122 had a total nitrogen capacity of 6.11 mequiv/g, a ligand capacity of 2.04 mmol/g (DETA), and a phosphorus capacity of 1.39 mequiv/g. Thus, resin CL4-122 contains approximately 60% DETA and 40% phosphonic acid ligands.

Metal Ion Studies

Complexing abilities of the amine resins were investigated using acidic metal salt solutions of low concentration. In the studies examining a single metal ion, 10^{-4} N metal salt solutions in either 0.01 N or 0.1 N acid were used. In all cases, the anion of the metal salt was consistent with the anion of the acid. In the studies involving ion competition, a solution which was 10^{-4} N $FeCl_3$ and 10^{-5} N $CuCl_2$ in 0.01 N HCl was used. The results are reported as "percent M^{n+} complexed" and in terms of the distribution coefficient "D".

$$D = \frac{\textit{mequiv } M^{n+} \textit{ complexed / g dry polymer}}{\textit{mequiv } M^{n+} \textit{ free / mL solution}}$$

It should be noted that small differences in the percent M^{n+} complexed can result in large differences in the corresponding distribution coefficients.

The complexing abilities of the resins with Cu^{2+}, Fe^{3+}, Cd^{2+}, Pb^{2+}, and Eu^{3+} ions were determined as follows. An amount of polymer corresponding to one milliequivalent of ligand (based on the total nitrogen capacity divided by the number of nitrogens in the ligand) was accurately weighed and the matrix equilibrated with the appropriate acid. The resin was then contacted with 10 mL of a metal ion solution for 30 min or 24 h, as indicated. The systems were considered at equilibrium after 24 h, as no additional metal ion uptake was observed for longer contact times. The concentrations of metal ions in the

resulting solutions were determined by atomic absorption/emission spectrometry (Perkin-Elmer model 3100), from which the percent M^{n+} complexed values and distribution coefficients were calculated.

Results of the complexation studies using EDA, DETA, TETA, TEPA, and PEHA resins with Cu^{2+} and Fe^{3+} are listed in Tables 2.13 - 2.21. The chloride system (same anion of metal salt and acid) results are given in odd numbered tables and the nitrate system results are given in even numbered tables. Unless indicated, all resins are 2% DVB crosslinked, and of gel porosity.

For a given amine ligand of the same crosslinking level and porosity, complexation ability is dependent upon several variables. For example, purity of the reagents used to functionalize the copolymers had a marked effect on the metal ion uptake. Unless indicated all resins were generated using Aldrich reagents. The results obtained when using resins generated from Fluka reagents, i.e., DETA (CL3-037), TEPA (CL3-038), and PEHA (CL3-039), are listed but are not considered reliable due to unknown age and purity of the reagents. Although all TETA resins and TEPA resin CL3-110 were generated using new Aldrich reagents, these results are not used in ligand length comparisons due to the reagents being of technical grade. Further investigation is needed to ascertain if other moieties are being incorporated into the resins in addition to those of interest. Another variable is the form of the resin after conditioning. Large differences in apparent metal ion uptake have been

Table 2.13

Metal Ion Uptake from $CuCl_2$ and/or $FeCl_3$ in 0.01 N HCl by EDA Resins

Resin	Eluted Form	Solvent Exchange	Cu^{2+}	Fe^{3+}	Ion Competition 10:1	
					Fe^{3+}	Cu^{2+}
Kinetics Studies: 30 min Contact Time						
CL3-012[a]	Acid (HCl)	(1)[b]	6.82[c](1.73)[d]	9.22 (2.40)	9.22 (2.40)	9.73 (2.54)
CL3-017	Acid (HCl)	(1)	2.50 (0.705)	4.10 (1.18)	5.76 (1.68)	1.64 (0.456)
Equilibrium Studies: ≥24 h Contact Time						
CL3-012[a]	Acid (HCl)	(1)	35.3 (12.9)	14.4 (3.96)	16.1 (4.53)	37.6 (14.2)
CL3-017	Acid (HCl)	(1)	6.68 (1.96)	7.41 (2.19)	5.76 (1.68)	1.64 (0.457)
CL3-078[e]	Acid (HCl)	(1)	3.61 (0.863)	7.75 (1.94)	6.26 (1.54)	8.51 (2.14)
CL3-017	Base	(1)	100.0 (∞)	41.4 (23.2)	43.1 (25.0)	100.0 (∞)
CL3-078[e]	Base	(1)	35.1 (11.2)	85.9 (126)	70.5 (49.5)	78.8 (76.9)
CL3-080[f]	Base	(1)	97.2 (633)	94.5 (315)	94.5 (315)	100.0 (∞)

Table 2.13 (continued)

Resin	Form	Solvent Exchange	Cu^{2+}	Fe^{3+}	Ion Competition 10:1	
					Fe^{3+}	Cu^{2+}
CL3-017	Base	(2)	6.54 (2.25)	0.00 (0.00)	0.00 (0.00)	18.0 (7.05)
CL3-078[e]	Base	(2)	3.86 (0.824)	3.91 (0.834)	3.91 (0.834)	10.5 (2.40)
CL3-080[f]	Base	(2)	9.44 (1.89)	0.26 (0.048)	2.09 (0.387)	17.4 (3.83)
CL3-141	Base	(2)	3.57 (1.29)	0.00 (0.00)	0.00 (0.00)	16.3 (6.75)

[a]MR, 5%DVB
[b](1) 4 x 0.01 N HCl (2) 1 x 1.0 N HCl, 2 x H_2O, 3 x 0.01 N HCl
[c]Percent M^{n+} complexed
[d]Distribution coefficient
[e]20% DVB
[f]From VBC/STY 50/50 wt%

Table 2.14

Metal Ion Uptake from $Cu(NO_3)_2$ and/or $Fe(NO_3)_3$ in 0.01 N HNO_3 by EDA Resins

Resin	Eluted Form	Solvent Exchange	Cu^{2+}	Fe^{3+}
		Equilibrium Studies: ≥24 h Contact Time		
CL3-141	Acid (HCl)	(1)[a]	27.1[b](11.1)[c]	10.3 (3.39)
CL3-141	Acid (HCl)	(1)	30.2 (13.2)	8.36 (2.78)
CL3-141	Acid (HCl)	(1)	41.2 (20.3)	-
CL4-054	Acid (HCl)	(1)	24.2 (9.89)	-
CL4-054	Acid (HCl)	(1)	23.3 (9.61)	-
CL4-054	Acid (HNO_3)	(1)	13.7 (4.04)	-

[a](1) 4 x 0.01 N HNO_3
[b]Percent M^{n+} complexed
[c]Distribution coefficient

Table 2.15

Metal Ion Uptake from $CuCl_2$ and/or $FeCl_3$ in 0.01 N HCl by DETA Resins

Resin	Eluted Form	Solvent Exchange	Cu^{2+}	Fe^{3+}	Ion Competition 10:1	
					Fe^{3+}	Cu^{2+}
Equilibrium Studies: ≥24 h Contact Time						
CL3-037[a]	Acid (HCl)	(1)[b]	95.0[c](503)[d]	7.06 (2.03)	5.14 (1.45)	100.0 (∞)
CL3-076	Acid (HCl)	(1)	63.0 (39.7)	6.26 (1.55)	4.76 (1.17)	71.7 (59.1)
CL3-077[e]	Acid (HCl)	(1)	9.30 (1.62)	4.76 (0.790)	3.26 (0.534)	14.8 (2.75)
CL3-037[a]	Base	(1)	100.0 (∞)	32.8 (15.9)	58.5 (46.0)	100.0 (∞)
CL3-076	Base	(1)	100.0 (∞)	77.4 (91.6)	77.4 (91.6)	100.0 (∞)
CL3-077[e]	Base	(1)	95.1 (309)	84.2 (85.4)	73.9 (45.6)	100.0 (∞)
CL3-079[f]	Base	(1)	100.0 (∞)	91.1 (169)	77.4 (56.6)	100.0 (∞)
CL3-037[a]	Base	(2)	91.8 (367)	0.00 (0.00)	0.00 (0.00)	100.0 (∞)
CL3-076	Base	(2)	51.4(27.7)	0.00 (0.00)	0.00 (0.00)	78.8 (76.9)
CL3-077[e]	Base	(2)	13.4 (2.48)	1.63 (0.266)	6.35 (1.09)	30.5 (7.05)

Table 2.15 (continued)

Resin	Form	Solvent Exchange	Cu^{2+}	Fe^{3+}	Ion Competition 10:1	
					Fe^{3+}	Cu^{2+}
CL3-162	Base	(2)	36.6 (16.4)	0.00 (0.00)	0.00 (0.00)	42.2 (20.8)
CL3-162	Base	(2)	46.1 (24.3)	0.09 (0.026)	0.09 (0.026)	58.0 (39.0)
CL3-076	Base	(2)	51.4 (28.2)	0.09 (0.025)	1.77 (0.480)	71.2 (66.0)
CL3-164	Base	(2)	46.8 (24.1)	1.77 (0.492)	0.09 (0.025)	58.0 (37.6)
CL3-162	Acid (HCl)	(1)	38.5 (17.9)	-	-	-
CL4-074	Acid (HCl)	(1)	81.4 (109)	-	-	-
CL4-055	Acid (HCl)	(1)	77.6 (85.7)	-	-	-
CL4-074	Acid (HCl)	(1)	70.3 (60.6)	-	-	-

[a]Fluka
[b](1) 4 x 0.01 N HCl (2) 1 x 1.0 N HCl, 2 x H_2O, 3 x 0.01 N HCl
[c]Percent M^{n+} complexed
[d]Distribution coefficient
[e]20% DVB
[f]From VBC/STY 50/50 wt%

Table 2.16

Metal Ion Uptake from $Cu(NO_3)_2$ and/or $Fe(NO_3)_3$ in 0.01 N HNO_3 by DETA Resins

Resin	Eluted Form	Solvent Exchange	Cu^{2+}	Fe^{3+}
	Equilibrium Studies: ≥24 h Contact Time			
CL3-162	Base	(2)[a]	31.3[b](13.0)[c]	-
CL3-164	Acid (HCl)	(1)	67.2 (48.2)	-
CL3-164	Acid (HCl)	(1)	57.5 (32.5)	10.2 (2.73)
CL3-162	Acid (HCl)	(1)	49.2 (24.0)	-
CL4-055	Acid (HCl)	(1)	76.0 (78.3)	-
CL4-055	Acid (HNO_3)	(1)	46.8 (17.0)	-
CL4-074	Acid (HCl)	(1)	80.9 (106)	-
CL4-074	Acid (HNO_3)	(1)	47.1 (17.7)	-

[a](1) 4 x 0.01 N HNO_3 (2) 1 x 1.0 N HNO_3, 2 x H_2O, 3 x 0.01 N HNO_3
[b]Percent M^{n+} complexed
[c]Distribution coefficient

Table 2.17

Metal Ion Uptake from $CuCl_2$ and/or $FeCl_3$ in 0.01 N HCl by TETA Resins

Resin	Eluted Form	Solvent Exchange	Cu^{2+}	Fe^{3+}	Ion Competition 10:1	
					Fe^{3+}	Cu^{2+}
Kinetics Studies: 30 min Contact Time						
CL2-278	Acid (HCl)	(1)[a]	43.9[b](16.5)[c]	12.5 (3.02)	14.3 (3.51)	56.9 (27.8)
CL3-006[d]	Acid (HCl)	(1)	9.33 (3.10)	10.9 (3.68)	10.9 (3.63)	17.0 (6.18)
CL2-274[e]	Acid (HCl)	(1)	45.3 (14.7)	16.0 (3.39)	16.0 (3.39)	71.5 (4.46)
Equilibrium Studies: ≥24 h Contact Time						
AT[f]	Acid (HCl)	(1)	90.7 (172)	42.8 (13.1)	43.19 (13.3)	100.0 (∞)
AT[f]	Acid (HCl)	(1)	90.5 (172)	-	-	-
CL3-278	Acid (HCl)	(1)	100.0 (∞)	16.0 (4.02)	14.3 (3.51)	100.0 (∞)
CL3-006[d]	Acid (HCl)	(1)	100.0 (∞)	17.2 (3.65)	19.9 (4.37)	100.0 (∞)
CL2-274[e]	Acid (HCl)	(1)	94.6 (308)	21.3 (4.71)	27.5 (6.61)	100.0 (∞)
CL4-025	Acid (HCl)	(1)	96.5 (557)	-	-	-

Table 2.17 (continued)

Resin	Eluted Form	Solvent Exchange	Cu^{2+}	Fe^{3+}	Ion Competition 10:1	
					Fe^{3+}	Cu^{2+}
CL2-278	Base	(1)	100.0 (∞)	-	70.5 (56.9)	100.0 (∞)
CL3-140	Base	(2)	85.2 (151)	0.00 (0.00)	0.00 (0.00)	100.0 (∞)

[a](1) 4 x 0.01 N HCl (2) 1 x 1.0 N HCl, 2 x H_2O, 3 x 0.01 N HCl
[b]Percent M^{n+} complexed
[c]Distribution coefficient
[d]MR, 5% DVB
[e]Sulfonated TETA
[f]Andrzej Trochimcuk's resin

Table 2.18

Metal Ion Uptake from $Cu(NO_3)_2$ and/or $Fe(NO_3)_3$ in 0.01 N HNO_3 by TETA Resins

Resin	Eluted Form	Solvent Exchange	Cu^{2+}	Fe^{3+}	Ion Competition 10:1	
					Fe^{3+}	Cu^{2+}
Kinetics Studies: 30 min Contact Time						
CL2-278	Acid (HCl)	(1)[a]	46.2[b](18.1)[c]	2.30 (0.497)	0.00 (0.00)	68.2 (45.3)
CL2-274[d]	Acid (HCl)	(1)	46.2 (15.2)	4.30 (0.794)	0.33 (0.058)	75.0 (54.5)
Equilibrium Studies: ≥24 h Contact Time						
AT[e]	Acid (HCl)	(1)	82.6 (85.6)	50.7 (18.5)	38.0 (10.7)	100.0 (∞)
CL3-278	Acid (HCl)	(1)	100.0 (∞)	4.28 (0.944)	0.33 (0.069)	100.0 (∞)
CL2-274[d]	Acid (HCl)	(1)	93.0 (230)	22.1 (4.94)	18.8 (4.05)	100.0 (∞)

[a](1) 4 x 0.01 N HCl
[b]Percent M^{n+} complexed
[c]Distribution coefficient
[d]Sulfonated TETA
[e]Andrzej Trochimcuk's resin

Table 2.19

Metal Ion Uptake from $CuCl_2$ and/or $FeCl_3$ in 0.01 N HCl by TEPA Resins

Resin	Eluted Form	Solvent Exchange	Cu^{2+}	Fe^{3+}	Ion Competition 10:1	
					Fe^{3+}	Cu^{2+}
Equilibrium Studies: ≥24 h Contact Time						
CL3-038[a]	Acid (HCl)	(1)[b]	75.9[c](41.3)[d]	7.06 (1.03)	7.06 (1.03)	98.5 (905)
CL3-038[a]	Acid (HCl)	(1)	74.4 (37.9)	-	-	-
CL3-038[a]	Base	(1)	100.0 (∞)	56.8 (20.1)	53.4 (18.2)	100.0 (∞)
CL3-110	Base	(2)	93.1 (259)	0.00 (0.00)	0.00 (0.00)	100.0 (∞)
CL3-217[e]	Base	(2)	85.7 (111)	-	-	-
CL4-019[e]	Acid (HCl)	(1)	98.8 (1220)	-	-	-

[a]Fluka
[b](1) 4 x 0.01 N HCl (2) 1 x 1.0 N HCl, 2 x H_2O, 3 x 0.01 N HCl
[c]Percent M^{n+} complexed
[d]Distribution coefficient
[e]From hydrochloride salt

Table 2.20

Metal Ion Uptake from $Cu(NO_3)_2$ and/or $Fe(NO_3)_3$ in 0.01 N HNO_3 by TEPA Resins[a]

Resin	Eluted Form	Solvent Exchange	Cu^{2+}	Fe^{3+}
	Equilibrium Studies: ≥24 h Contact Time			
CL3-217	Base	(2)[b]	74.7[c](54.5)[d]	-
CL4-019	Acid (HCl)	(1)	99.3 (2340)	10.7 (1.95)
CL4-019	Acid (HCl)	(1)	97.9 (751)	-
CL4-019	Acid (HCl)	(1)	97.5 (639)	-
CL4-019	Acid (HCl)	(1)	99.6 (3870)	-
CL4-019	Acid (HNO_3)	(1)	99.0 (1270)	-

[a]From hydrochloride salt
[b](1) 4 x 0.01 N HNO_3 (2) 1 x 1.0 N HNO_3, 2 x H_2O, 3 x 0.01 N HNO_3
[c]Percent M^{n+} complexed
[d]Distribution coefficient

Table 2.21

Metal Ion Uptake from $CuCl_2$ and/or $FeCl_3$ in 0.01 N HCl by PEHA Resins[a]

Resin	Eluted Form	Solvent Exchange	Cu^{2+}	Fe^{3+}	Ion Competition 10:1	
					Fe^{3+}	Cu^{2+}
Equilibrium Studies: ≥24 h Contact Time						
CL3-039	Acid (HCl)	(1)[b]	99.0[c](1270)[d]	5.14 (0.708)	5.14 (0.708)	100.0 (∞)
CL3-039	Base	(1)	100.0 (∞)	84.2 (88.0)	51.7 (17.7)	100.0 (∞)
CL3-039	Base	(2)	96.8 (497)	0.00 (0.00)	0.00 (0.00)	100.0 (∞)

[a]Fluka
[b](1) 4 x 0.01 N HCl (2) 1 x 1.0 N HCl, 2 x H_2O, 3 x 0.01 N HCl
[c]Percent M^{n+} complexed
[d]Distribution coefficient

observed when comparing the results for a given resin in the acid (protonated) form and in the base (unprotonated) form. These large differences occurred when the matrices of the resins were equilibrated by standard procedures, i.e., solvent exchange four times with the appropriate acid. For example, the EDA resin CL3-017 showed a percent Cu^{2+} complexed of 6.68 in the acid form and 100 .0 in the base form from a 0.01 N HCl solution. This, coupled with final pH values of 2.01 and 7.28, respectively, and a cloudiness of the resulting solution, suggests that for the base form of the resin, the matrix was not equilibrated and the ligand was being protonated. When the solvent exchange sequence for the base form of the same resin was modified to 1 x 1.0 N HCl, 2 x H_2O, 3 x 0.01 N HCl, the percent Cu^{2+} complexed was 6.54 which is consistent with the value shown by the acid form of the resin. From this point, results which were obtained from resins in the base form will not be included in discussions.

A difference in metal ion uptake was also observed for the same resin conditioned using HCl versus HNO_3. For example, DETA resin CL4-074 showed percent Cu^{2+} complexed values, from $Cu(NO_3)_2$ in 0.01 N HNO_3, of 80.9 and 47.1 for the HCl and HNO_3 eluted forms, respectively. Irreproducible results for metal ion complexation from nitrate systems are attributed to the incomplete removal of excess chloride ions from the matrix of the polymer.

Copolymer Influence

Metal ion uptake can be influenced by limited accessibility into the

polymer bead. Methods exist which may assist in alleviating accessibility problems. These methods include: increasing the porosity of the polymer, decreasing the crosslinking level, and incorporation of additional functional groups, such as sulfonic acid, within the polymer.[47]

The EDA resins showed an increase in all percent M^{n+} complexed with an increase in porosity (Table 2.13). This increase was most pronounced in the equilibrium studies at contact times of ≥ 24 h. The percent Cu^{2+} complexed values were 6.68 and 35.3 for the gel and MR resins, respectively. The increase in the percent Fe^{3+} complexed in the equilibrium studies was less pronounced, with values of 7.41 and 14.4 for the gel and MR resins, respectively. In the kinetic studies, 30 min contact time, only slight increases in metal ion uptake were observed when the porosity was increased from gel to MR. Increasing the crosslinking level of the EDA resins from 2% to 20% decreased the percent Cu^{2+} complexed slightly from 6.68 to 3.61.

Increasing the crosslinking levels in the DETA resins from 2% to 20% had a dramatic effect on the resin's ability to complex Cu^{2+}, but little if any effect on the complexation of Fe^{3+}, (Table 2.15). The percent Cu^{2+} complexed dropped from an average value of 73.1 for the 2% resin to 9.30 for the 20% resin, whereas the drop in percent Fe^{3+} complexed was from 6.26 to 4.76. At this point these results cannot be solely attributed to accessibility problems. Inter-ligand cooperation may be present which would decrease when the level of crosslinking was increased.[45]

The kinetic studies reveal a different trend in the ability of the TETA resins to complex Cu^{2+}, (Table 2.17). Here, an increase in porosity from gel to MR decreases the percent Cu^{2+} complexed from 43.9 to 9.33, respectively. Again, the effects are not as great for the percent Fe^{3+} complexed which decreases only slightly from 12.5 to 10.9. The equilibrium studies indicate there is no advantage to increasing the porosity, as both the gel and MR resins had a percent Cu^{2+} complexed of 100.0. The percent Fe^{3+} increased an insignificant amount from 16.0 to 17.2 for the gel and MR resins, respectively.

It should be noted that when comparing percent M^{n+} complexed values in the kinetics and equilibrium studies, it is apparent that the Fe^{3+} approaches equilibrium faster than does the Cu^{2+} under the same conditions. This is consistent with the results of Grinstead's work on the picolylamine resins.[33]

The addition of sulfonic acid groups to resins containing ion selective ligands often enhances the attraction of metal ions into the polymer bead.[47] However, sulfonation of the TETA resins had only slight effects on the percent Cu^{2+} complexed. In the kinetics studies this value went from 43.9 to 45.3 for the unsulfonated and sulfonated resins, respectively. There was a slight decrease in the values at equilibrium from 100.0 to 94.6. In both the kinetic and equilibrium studies, an increase in the percent Fe^{3+} complexed was observed for the sulfonated resin, from 12.5 to 16.0, and from 16.0 to 21.3, respectively.

General Selectivity Trends

The results in Tables 2.13 through 2.21 indicate that for the imine resins examined there is a tendency of preferential complexation of Cu^{2+} ions over Fe^{3+} ions. Even in solutions containing a 10:1 excess of Fe^{3+} ions in direct competition with Cu^{2+} ions, the resins exhibit a selective affinity for the Cu^{2+} ions. Only in the complexation by EDA resins is this trend not observed, the exception being the equilibrium studies with the MR resin. With exception of the sulfonated TETA polymer, all resins designated "CL" showed percent Fe^{3+} complexed values of less than 20.0, while percent Cu^{2+} complexed values ranged from 63.0 to 100.0.

It has been suggested that selectivity is controlled by Cu^{2+}'s ability to form stable complexes of coordination number "4", while Fe^{3+} prefers to form complexes of coordination number "6".[32,45] The results herein indicate that the imine's selective affinity for Cu^{2+} ions cannot be based solely upon coordination number theories. No increase in percent Fe^{3+} complexed was observed with an increase in the number of nitrogens contained in the ligand. Even in the pentamine and hexamine studies the percent Fe^{3+} complexed values were only 10.7 and 5.14, respectively. Also, as mentioned previously, the possibility of inter-ligand cooperation exists where even ligands containing fewer nitrogens, DETA for example, can provide a coordination number of "6".[45]

Bifunctionality Effects

Although the imine/sulfonic acid polymer is considered bifunctional, the following discussions are limited to the imine/phosphonic acid and the imine/phosphonate ester bifunctional resins. Comparisons to 100% phosphonic acid polymers are also made, the synthesis and characterization of these resins being discussed in Chapter 3 of this dissertation.

As mentioned in the synthesis and characterization section of this chapter, the bifunctional resins consist of an approximate 1:1 ratio of imine ligand to phosphorus containing ligand. The milliequivalent of ligand used in the bifunctional studies was based on the total nitrogen capacity in order to make accurate comparisons with the monofunctional imine resins. The results of the metal ion complexation studies with Cu^{2+} and Fe^{3+} ions by the bifunctional resins are listed in Table 2.22.

The introduction of phosphonic acid ligands to the EDA resins had little effect on the resin's ability to complex Cu^{2+} ions from nitrate systems. The monofunctional imine and bifunctional rerins exhibited percent Cu^{2+} complexed values of 29.2 ± 6.5 (standard deviation, n = 5) and 26.3, respectively. Differences in percent Cu^{2+} complexed values were more dramatic when phosphonic acid ligands were incorporated into the DETA resins. The value for the monofunctional imine resin and the bifunctional resin were 70.4 ± 8.9 (standard deviation, n = 4) and 40.9 ± 4.15 (standard deviation, n = 3), respectively. The bifunctional value was also significantly lower than that of the

Table 2.22

Equilibrium Studies (≥24 h) of Metal Ion Uptake of Cu^{2+} and/or Fe^{3+} in 0.01 N Acid by Amine/Phosphorus Bifunctional Resins

Resin	Functional Groups	Eluted Form	Cu^{2+}	Fe^{3+}	Ion Competition 10:1	
					Fe^{3+}	Cu^{2+}
			$CuCl_2$ and/or $FeCl_3$ in HCl			
CL3-174	DETA/Phos[a]	Acid (HCl)	40.1[b](9.50)[c]	55.3 (17.5)	55.3 (17.5)	44.7 (11.5)
			$Cu(NO_3)_2$ and/or $Fe(NO_3)_3$ in HNO_3			
CL3-174	DETA/Phos	Acid (HCl)	35.5 (7.80)	59.9 (21.2)	58.2 (19.8)	36.0 (7.97)
CL3-201	DETA/Phos	Acid (HCl)	45.6 (15.1)	52.1 (19.7)	-	-
CL3-201	DETA/Phos	Acid (HCl)	41.5 (13.8)	-	-	-
CL3-201	DETA/Phos	Acid (HNO_3)	31.8 (7.76)	-	-	-
CL4-133	DETA/Isopr	Acid (HCl)	82.0 (55.6)	-	-	-
CL4-123	EDA/Phos	Acid (HCl)	26.3 (7.14)	-	-	-
CL4-123	EDA/Phos	Acid (HNO_3)	17.3 (3.88)	-	-	-

[a]Phos: Phosphonic acid Isopr: Isopropylphosphonate diester
[b]Percent M^{n+} complexed
[c]Distribution coefficient

monofunctional phosphonic acid value of 98.5. Table 2.23 summarizes M^{n+} complexed values for both monofunctional resins as well as the bifunctional resin with Cd^{2+}, Cu^{2+}, Fe^{3+}, Pb^{2+} and Eu^{3+}. With the exception of Fe^{3+}, the bifunctional values were less than or equal to the values for the monofunctional resins. For complexation with Fe^{3+}, the bifunctional value of 56.0 ± 3.9 (standard deviation, n = 2) was less than the monofunctional phosphonic acid value of 95.2, but greater than the monofunctional DETA value of 10.2.

Introduction of isopropylphosphonate diester ligands to the DETA resins seemed to increase the resins ability to complex Cu^{2+} ions somewhat. The percent Cu^{2+} complexed values for the monofunctional and ester bifunctional resins were 70.4 ± 8.9 (standard deviation, n = 4) and 82.0, respectively. This value for the monofunctional resin may be low due to the inclusion of inconsistent initial results in the average. Most recent results for the monofunctional DETA resins yield values of 76.0 and 80.9, which indicate the differences in the complexing abilities of the monofunctional and ester bifunctional resins may negligible.

Anion Effects

As mentioned previously, differences arise in the resin's ability to complex metal ions depending on the anion of the eluting acid. The results of comparisons between HCl and HNO_3 as the eluting acid are summarized in Table 2.24. For each type of resin, with the exception of the TEPA resin, the

Table 2.23

Comparison of Metal Ion Uptake Using DETA, Phosphonic Acid, and DETA/Phosphonic Acid Resins

Functional Group(s)	Cd^{2+}	Cu^{2+}	Fe^{3+}	Pb^{2+}	Eu^{3+}
			0.01 N HNO_3		
DETA	10.1[a](2.69)[b]	*70.4 (66.3)	10.2 (2.73)	19.4 (5.77)	-
Phos[c]	98.7 (3350)	98.5 (3030)	95.2 (895)	98.0 (2240)	-
DETA/Phos	0.00 (0.00)	*40.9 (12.2)	*56.0 (20.5)	9.69 (1.94)	-
			0.1 N HNO_3		
DETA	0.00 (0.00)	2.20 (0.539)	7.36 (1.51)	4.29 (1.08)	12.6 (3.47)
Phos	37.9 (32.4)	25.2 (17.9)	98.3 (3090)	59.0 (34.1)	99.3 (7320)
DETA/Phos	0.00 (0.00)	2.20 (0.406)	76.0 (57.1)	4.29 (0.809)	3.97 (0.748)
			2 N HNO_3		
DETA	-	-	0.00 (0.00)	-	-
Phos	-	-	91.6 (506)	-	-
DETA/Phos	-	-	60.4 (29.5)	-	-

[a]Percent M^{n+} complexed, *Indicates average values
[b]Distribution coefficient
[c]Phos: Phosphonic acid

Table 2.24

Metal Ion Uptake from $Cu(X)_2$ in 0.01 N HX, Comparison of Eluting Acid

Eluting Acid	X =	
	NO_3	Cl
	EDA	
HCl	*29.2[a]± 6.5 (12.8)[b]	6.68 (1.96)
HNO_3	13.7 (4.04)	-
	DETA	
HCl	*70.4 ± 8.9 (66.3)	*73.1 ± 7.1 (73.8)
HNO_3	47.1 (17.7)	-
	TEPA	
HCl	*98.6 ± 0.9 (19.1)	98.8 (1220)
HNO_3	99.0 (1270)	-
	EDA/Phosphonic Acid	
HCl	26.3 (7.14)	-
HNO_3	17.3 (3.88)	-
	DETA/Phosphonic Acid	
HCl	*40.9 ± 4.2 (12.2)	40.1 (9.50)
HNO_3	31.8 (7.76)	-

[a]Percent M^{n+} complexed,
[b]Distribution coefficient

*Indicates average of n values:
n = 5 EDA
n = 4 DETA
n = 4 DETA(Cl)
n = 4 TEPA
n = 3 DETA/Phos

percent Cu^{2+} complexed from $Cu(NO_3)_2$ in 0.01 N HNO_3 was greater when the eluting acid was HCl than when the eluting acid was HNO_3. For example, when the DETA resin was eluted with HCl, the average percent Cu^{2+} complexed was 70.4 ± 8.9 (standard deviation, n = 4) and when eluted with HNO_3, the value was 47.1. This trend was followed for the monofunctional as well as bifunctional resins, again the exception being the TEPA resin. The percent Cu^{2+} complexed values for the TEPA resin eluted with HCl and HNO_3 were 98.6 ± 0.9 (standard deviation, n = 4) and 99.0 respectively.

It should be noted that when chloride was the anion of the metal salt, matrix acid, and eluting acid, the percent Cu^{2+} complexed values were comparable to those values obtained in the nitrate system with HCl as the eluting acid. The exception to this was the EDA resin which exhibited a percent Cu^{2+} complexed from the nitrate system of 29.2 ± 6.5 (standard deviation, n = 5) and 6.68 from the chloride system.

These results indicate that early inconsistencies in percent Cu^{2+} complexed values from nitrate systems may be attributed to varying amounts of chloride remaining in the resins after matrix equilibrium. Metal ion studies using DETA resin CL4-055 in chloride and nitrate eluted forms, contacted with 10^{-4} N $AgNO_3$ in 1 N HNO_3, yielded percent Ag^{+} complexed values of 74.6 and 16.5, respectively. These values, and the observation of a cloudy resulting contact solution, indicate the exchange of anions is not complete (and thus the matrix not equilibrated) by conventional solvent exchange methods.

Ligand Effects

Table 2.25 summarizes the imine resin's ability to complex M^{n+} depending on the number of nitrogens contained within, or length of, the ethyleneimine ligand. For the monofunctional resins under identical conditions, the percent Cu^{2+} complexed increases with an increase in length of the ligand. As the number of nitrogens contained in the ligand increases from two to three to five (EDA, DETA, and TEPA), the percent Cu^{2+} complexed from the nitrate system with HCl as the eluting acid, increases from 29.2 ± 6.5 (standard deviation, n = 5) to 70.4 ± 8.9 (standard deviation, n = 4) to 98.6 ± 0.9 (standard deviation, n = 4). For the same system with HNO_3 as the eluting acid, these values increase from 13.7 to 47.1 to 99.0 (Table 2.24). This increase in percent Cu^{2+} complexed with increase in ethyleneimine length was also observed with the bifunctional resins. Other metal ions examined (Cd^{2+}, Fe^{3+}, Pb^{2+}, and Eu^{3+}) did not follow the same trend.

Since all previous metal ion studies were performed using one milliequivalent of ligand, control studies were conducted to ensure that the increase in percent Cu^{2+} complexed could be attributed to an increase in ligand length and not to the total number of nitrogens contained within a resin sample. For these studies one milliequivalent of nitrogen was used as opposed to the standard one milliequivalent of ligand, and the results are given in Table 2.26. The percent Cu^{2+} complexed from 0.01 N HNO_3 was 3.47 and 37.4 for the DETA and TEPA resins, respectively. These results, in addition to those

Table 2.25

Comparison of Metal Ion Uptake Using EDA, DETA, and TEPA Resins

Functional Group(s)	Cd^{2+}	Cu^{2+}	Fe^{3+}	Pb^{2+}	Eu^{3+}
			0.01 N HNO_3		
EDA	0.00[a](0.00)[b]	*29.2 (12.8)	*9.33 (3.09)	2.76 (0.846)	-
DETA	10.1 (2.69)	*70.4 (66.3)	10.2 (2.73)	19.4 (5.77)	-
TEPA	3.18 (0.535)	*98.6 (1900)	10.7 (1.95)	3.63 (0.613)	-
			0.1 N HNO_3		
EDA	0.00 (0.00)	1.46 (0.441)	0.00 (0.00)	1.43 (0.431)	3.59 (1.11)
DETA	0.00 (0.00)	2.20 (0.539)	7.36 (1.51)	4.29 (1.08)	12.6 (3.47)
TEPA	7.59 (1.34)	4.37 (0.744)	5.81 (1.00)	11.0 (2.01)	1.16 (0.191)

[a]Percent M^{n+} complexed, *Indicates average values
[b]Distribution coefficient

Table 2.26

Comparison of Metal Ion Uptake from $CuCl_2$ or $Cu(NO_3)_2$ in 0.01 N Acid Using 1.0 mequiv Nitrogen

Resin	Functional Group	Porosity	% Cu^{2+} Complexed	D[a]
		0.01 N HCl		
CL3-012	EDA	MR	13.6	7.26
CL3-006	TETA	MR	63.7	119
		0.01 N HNO_3		
CL3-162	DETA	gel	3.47	2.68
CL3-217	TEPA	gel	37.4	55.1

[a]Distribution coefficient

discussed above for one milliequivalent of ligand, confirm that the increase in percent Cu^{2+} complexed can be attributed to an increase in the length of the ligand.

Conclusions

A series of imine resins has been prepared which may be used for the selective removal of Cu^{2+} ions in the presence of Fe^{3+} ions. Although internal crosslinking is evident, its influence on the complexation of metal ions from dilute solutions is negligible. Several factors have been shown to influence the imine resin's ability to complex metal ions. These include (but certainly are not limited to) the nature of the ligand, anion of the eluting acid, introduction of second ligand, and copolymer structure. An increase in the percent Cu^{2+} complexed corresponding to an increase in ligand length was observed and is attributed to the nature of the ligand. Resins eluted with HCl exhibited greater percent Cu^{2+} complexed values than the same resins eluted with HNO_3. Bifunctionality has a profound impact on the percent M^{n+} complexed that does not follow the trends set forth by monofunctional resins with the same ligands. These factors may be used in the tailoring of imine resins for the selective removal of targeted metal ions from aqueous solutions.

CHAPTER 3

METAL ION SELECTIVITY INFLUENCES IN PHOSPHORUS ACID/ESTER POLYMERS

Introduction

Phosphorus chemistry has expanded exponentially since the isolation of phosphorus from urine in 1669 by Hennig Brandt. Phosphorus is the eleventh most abundant element in earth's crustal rocks and forms innumerable organophosphorus compounds.[48] One such compound, triphenylphosphine, is used in the Wittig reaction for the conversion of ketones or aldehydes to alkenes. Georg Wittig was awarded the Nobel prize in 1979 for the development of this reaction.[49] Phosphorus oxoacids outnumber those of any other element, and their derivatives and salts are second in number only to those of silicon.[50] These oxoacids and derivatives have come to be used in solvent extraction chemistry due to their ability to coordinate metal ions through the phosphoryl oxygen or ion exchange with an acidic proton.[51-54]

Organophosphorus acids are used industrially in solvent extraction mainly as the monobasic ester derivatives. These acids are of intermediate acidity and exhibit less aqueous solubility than do carboxylic and organosulfonic acids. Examples are di-2-ethylhexylphosphoric acid (DEHPA), 2-ethylhexyl-phosphonic acid mono-2-ethylhexyl ester, and di-2,4,4-trimethylpentylphosphinic

acid. These acids show selectivity series of: Zn > Ca > Cu > Mg > Co > Ni, Zn > Cu > Ca > Co > Mg > Ni, and Zn > Cu > Co > Mg > Ca > Ni, respectively at pH 3. It should be noted that the order of such selectivity series is dependent upon pH.[51,53]

Organophosphorus esters and phosphine oxides are also used in solvent extraction as solvating extractants. These extractants are able to compete with water for solvation sites on the metal ion. Extraction power increases in the order: $(RO)_3PO < (RO)_2RPO < (RO)R_2PO < R_3PO$ and reflects increasing basicity of the phosphoryl oxygen. Aqueous solubility increases in the reverse order. Examples include tri-n-butylphosphate (TBP), and tri-n-octylphosphineoxide (TOPO). TBP and TOPO have been shown to remove arsenic, antimony, and bismuth from sulfuric acid copper solutions. Mixed extraction systems are also used commercially, the most popular being DEHPA/TOPO for the extraction of uranium from phosphoric acid.[53]

Although liquid-liquid extraction provides a versatile and simple method for the removal of metal ions, a major concern is the loss of the extractant to the aqueous phase by solubility and entrainment. This can cause economical as well as environmental problems which may be alleviated by the use of polymer-supported extractants.[55] Bregman and Murata introduced polymer-supported phosphonous (the tautomer of phosphinic acid) and phosphonic acids in 1952 as cation exchangers.[56] Mono- and bifunctional phosphinic, and phosphonic acid/ester polymer-supported extractants have been the subject of

much investigation in our group and the topic of several papers.[47,57-64] Previous work has compared the extraction ability of phosphinic and/or phosphonic acid ligands with ligands such as sulfonic and carboxylic acid.[58,64] Other variables studied have been pH, ionic strength, and initial metal ion concentration.[63] Enhanced ionic recognition by bifunctional ion exchange/redox,[57] ion exchange/precipitation,[60] and ion exchange/coordination[61] resins has also been examined.

This work examines the complexing abilities of a series of polymer-supported phosphonic/phosphoric acid resins with metal ions from dilute solutions. The role of crosslinking level, crosslinking type, porosity, bifunctionality, and the way in which the $-P(O)(OH)_2$ ligand is attached to the polymer backbone are investigated and their influence on complexing ability reported.

Synthesis and Characterization

Brief descriptions of all syntheses follow. Details of these syntheses are found in the experimental chapter.

Phosphinic and Phosphonic Acid from Polystyrene (STY)

Polystyrene microporous (gel) resins at divinylbenzene crosslinking levels of 2%, 5%, and 12% were reacted with phosphorus trichloride and aluminum chloride (1.2 : 1 mole ratio $AlCl_3$: styrene) followed by hydrolysis to yield the

phosphinic acid resins (Figure 3.1). The phosphonic acid (STY) resin was obtained by nitric acid oxidation of the phosphinic acid resin. This synthesis is also depicted in Figure 3.1. Both types of resins were characterized by procedures described in the experimental chapter and the properties summarized in Table 3.1.

The percent solids of both types of resins varied as anticipated with an increasing solids level with an increase in crosslinking level. The percent solids of the phosphonic acid (STY) resins were less than those of the corresponding phosphinic resins. The phosphonic acid (STY) and phosphinic acid resins, both crosslinked with 5% DVB, exhibited solids levels of 52.03% and 65.58%, respectively. This lowering of the solids level may be due to degradation of the polymer during the nitric acid oxidation.

Phosphorus and acid capacities also varied as expected i.e., decreasing with an increase in crosslinking level. Acid capacities were approximately the same as the phosphorus capacities for the phosphinic resins. For example, the phosphorus capacity for the 5% DVB phosphinic acid resin was 5.61 mequiv P/g and the corresponding acid capacity was 5.48 mequiv/g. Acid capacities for the phosphonic acid (STY) resins were approximately twice that of the phosphorus capacities. For example, the phosphorus capacity for the 12% DVB phosphonic acid (STY) was 3.76 mequiv P/g and the corresponding acid capacity was 7.46 mequiv/g.

The phosphinic acid resins exhibited ^{31}P NMR chemical shifts of

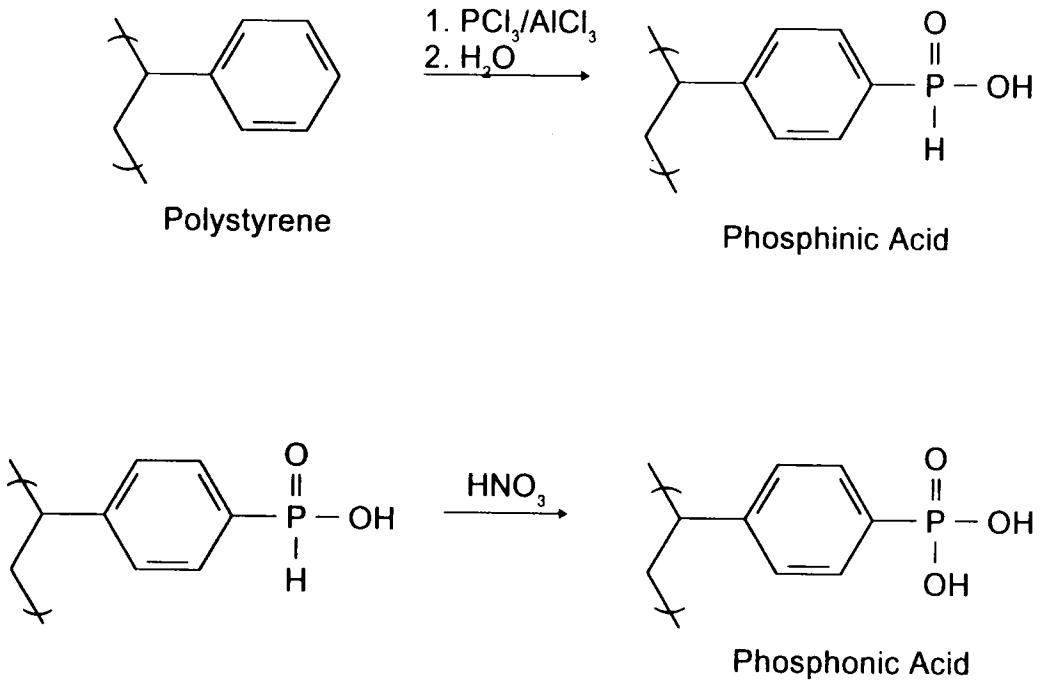


Figure 3.1. Phosphinic and Phosphonic Acid Syntheses

Table 3.1

Characterization of Monofunctional Phosphorus Acid/Ester Resins

Type	Crosslinking	%Solids (g_{dry}/g_{wet})100	Phosphorus Capacity (mequiv/g)	Acid Capacity (mequiv/g)	^{31}P NMR Chemical Shift (δ)
		Microporous (Gel)			
Phosphonic (VBC)	2% DVB	54.18	4.90	9.62	30.24
Phosphonic (VBC)	5% DVB	65.32	4.66	9.15	30.57
Phosphonic (VBC)	8% DVB	70.63	4.37	8.43	-
Phosphonic (VBC)	12% DVB	73.62	4.03	7.17	-
Phosphonic (VBC)	16% DVB	76.84	3.33	6.45	30.66
Phosphonic (VBC)	5% TMPTMA	59.72	4.95	8.70	-
Phosphonic (VBC)	12% TMPTMA	64.48	4.56	7.37	-
Phosphonic (STY)	2% DVB	36.60	4.88	9.92	21.11
Phosphonic (STY)	5% DVB	52.03	4.95	9.57	21.40
Phosphonic (STY)	12% DVB	65.95	3.76	7.46	21.40
Phosphinic	5% DVB	65.58	5.61	5.48	25.94
Phosphinic	12% DVB	73.54	4.48	4.34	25.62

Table 3.1 (continued)

Type	Crosslinking	%Solids (g_{dry}/g_{wet})100	Phosphorus Capacity (mequiv/g)	Acid Capacity (mequiv/g)	^{31}P NMR Chemical Shift (δ)
β-Ketophosphonic	2% DVB	53.82	3.70	7.52	23.77
Phosphoric	2% DVB	66.57	2.42	4.56	-1.02
Isopropyl Ester	2% DVB	81.13	3.52	-	-
		Macroporous (MR)			
Phosphonic (VBC)	2% DVB	29.69	4.73	9.48	-
Phosphonic (VBC)	5% DVB	34.02	4.59	8.60	-
Phosphonic (VBC)	8% DVB	32.62	4.06	8.56	-
Phosphonic (VBC)	12% DVB	31.19	3.44	6.28	-
Phosphonic (VBC)	16% DVB	28.66	2.52	5.12	-

25.94 ppm and 25.62 ppm for the 5% and 12% crosslinked resins, respectively. This indicates the level of DVB crosslinking does not influence the electronic environment about the phosphorus. Also, a single peak is observed in each spectrum indicating the presence of only one type of phosphorus on the resin (Figure 3.2). The phosphonic acid (STY) resins exhibited ^{31}P NMR chemical shifts of 21.11 ppm, 21.40 ppm, and 21.40 ppm for the 2%, 5%, and 12% DVB crosslinked resins, respectively. Again, a single peak is observed and apparently the level of crosslinking does not influence the phosphorus chemical shift. The ^{31}P NMR spectrum of phosphonic acid (STY) is shown in Figure 3.3.

Phosphonic Acid/Ester from Poly(vinylbenzyl chloride) (VBC)

Poly(vinylbenzyl chloride) microporous (gel) and macroreticular (MR) beads at DVB crosslinking levels of 2%, 5%, 8%, 12% and 16% were reacted with excess triisopropyl phosphite to yield the isopropyl ester resins. The esters were then hydrolyzed using concentrated HCl (Figure 3.4). VBC gel copolymers crosslinked with 5% and 12% trimethylolpropane trimethacrylate (TMPTMA) were also functionalized to phosphonic acid resins using the procedure described above. The resins were characterized by methods described in the experimental chapter and the properties are summarized in Table 3.1.

Percent solids for the gel resins varied as anticipated, increasing with increasing crosslinking level. This trend was observed in resins crosslinked

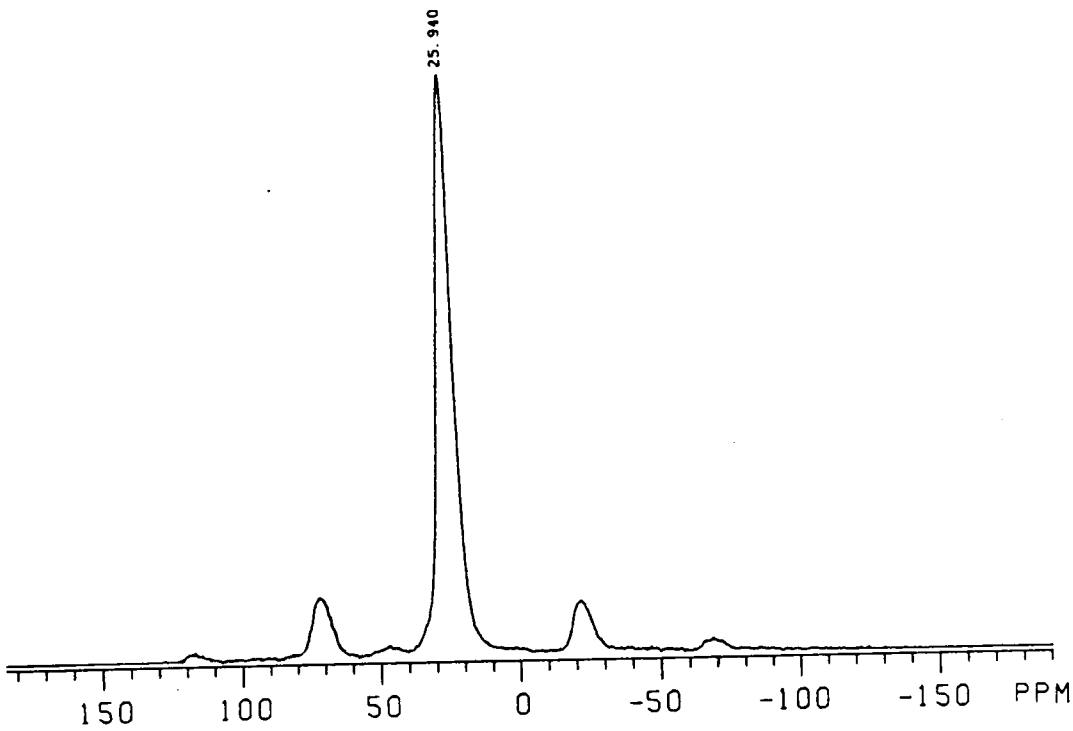


Figure 3.2. ^{31}P NMR Spectrum of Phosphinic Acid

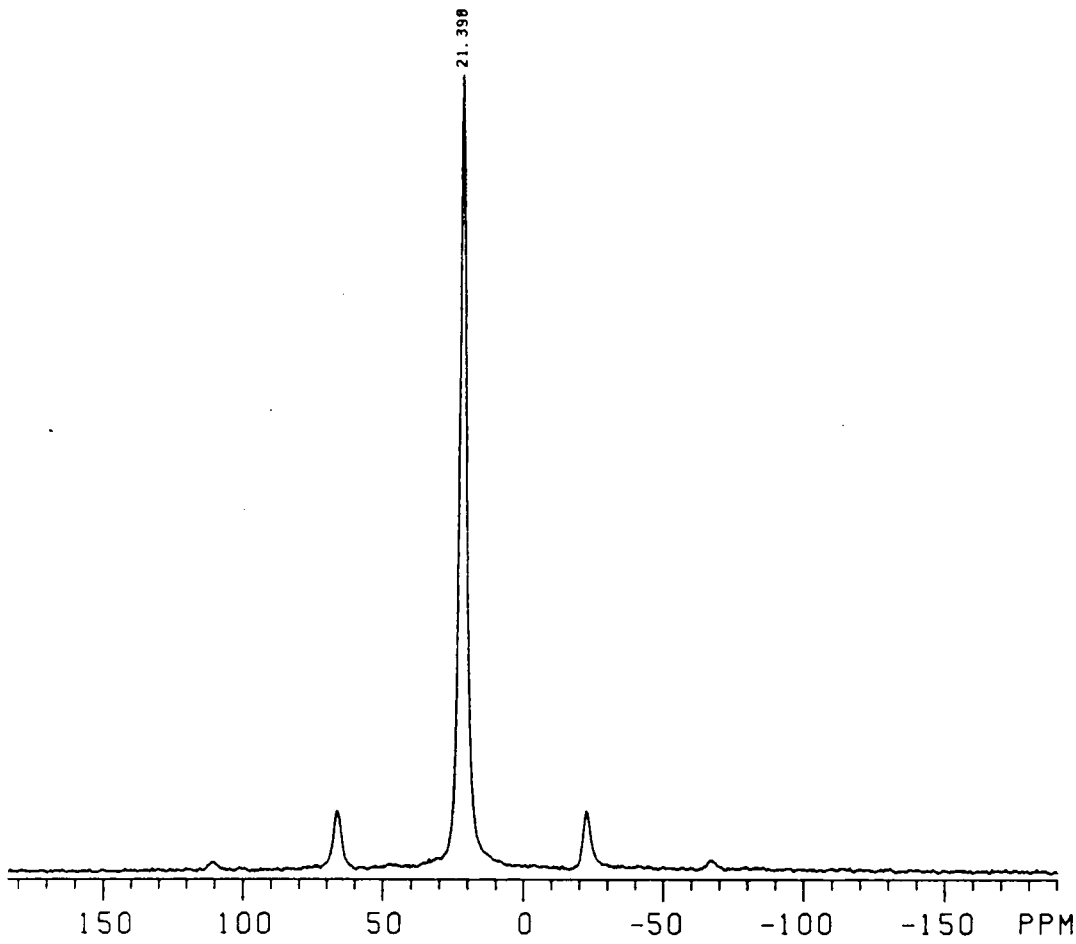


Figure 3.3. ^{31}P NMR Spectrum of Phosphonic Acid (STY)

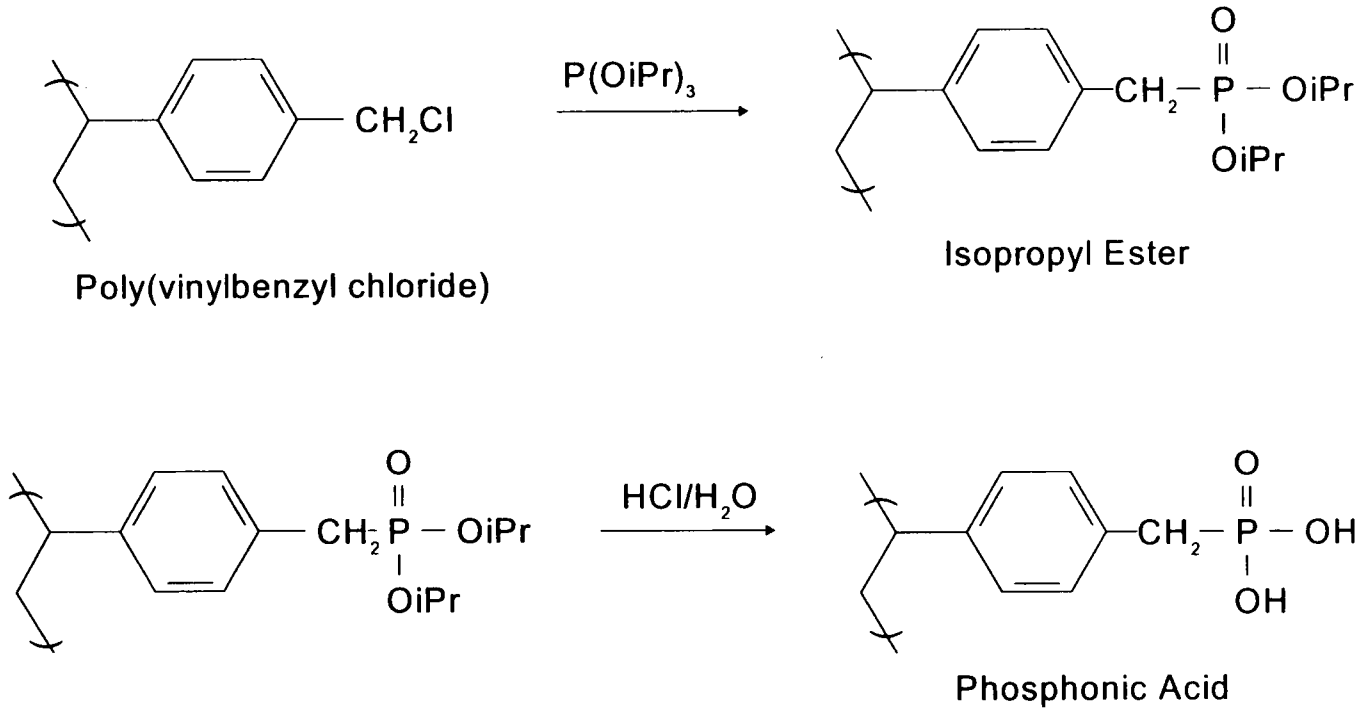


Figure 3.4. Synthesis of Isopropyl Ester and Phosphonic Acid Resins via the Arbuzov Reaction

with TMPTMA as well as those crosslinked with DVB. The solids level increased from 54.18% to 76.84% when the DVB crosslinking level was increased from 2% to 16%. The phosphonic acid resins crosslinked with TMPTMA exhibited solids levels of 59.72% and 64.48% for 5% and 12% crosslinking, respectively. The percent solids for the macroporous resins varied from 28.66% to 34.02% however, this increase does not correspond to an increase in crosslinking level. The solids level for the 2% DVB gel isopropyl ester resin was 81.13% and this high value was anticipated due to the hydrophobic nature of the ligand.

Phosphorus and acid capacities for resins crosslinked by DVB varied as anticipated i.e., decreasing with an increasing crosslinking level. Acid capacities were approximately twice that of the corresponding phosphorus capacities. The phosphorus capacities for the 2% DVB crosslinked gel and MR resins were 4.90 mequiv P/g and 4.73 mequiv P/g, respectively. The corresponding acid capacities were 9.62 mequiv/g and 9.48 mequiv/g, respectively. The phosphorus capacities for the 5% and 12% TMPTMA crosslinked phosphonic acid resins did decrease from 4.95 mequiv P/g to 4.56 mequiv P/g, respectively. However, the corresponding acid capacities were less than twice that of the phosphorus capacities, 8.70 mequiv/g and 7.37 mequiv/g, respectively. This may be due to a collapse of the polymer matrix during the analysis for the acid capacity.

The phosphonic acid (VBC) gel resins exhibited ^{31}P NMR chemical shifts

of 30.24 ppm, 30.57 ppm, and 30.66 ppm for the 2%, 5%, and 16% DVB crosslinking levels. In each spectrum only one peak is observed and the DVB crosslinking level does not affect the chemical shift. The ^{31}P NMR spectrum of phosphonic acid (VBC) is shown in Figure 3.5.

β-Ketophosphonic Acid

Microporous (gel) 2% DVB crosslinked poly(vinylbenzyl chloride) beads were reacted with bromoacetyl bromide and aluminum chloride in carbon disulfide. The resulting beads were then reacted with triisopropyl phosphite followed by hydrolysis in concentrated HCl (Figure 3.6). The resin was characterized by procedures described in the experimental chapter and the properties are summarized in Table 3.1.

The percent solids of the β-ketophosphonic acid was 53.82% and the phosphorus capacity was 3.70 mequiv P/g. The acid capacity was 7.52 mequiv/g, approximately twice the phosphorus capacity. The ^{31}P NMR chemical shift was 23.77 ppm.

Phosphoric Acid

Microporous (gel) 2% DVB crosslinked poly(vinylbenzyl chloride) beads were reacted with phenol and tin(IV) chloride in chloroform. The resulting phenol beads were then reacted with phosphorus oxychloride and pyridine in dioxane followed by hydrolysis (Figure 3.7). The resin was characterized by

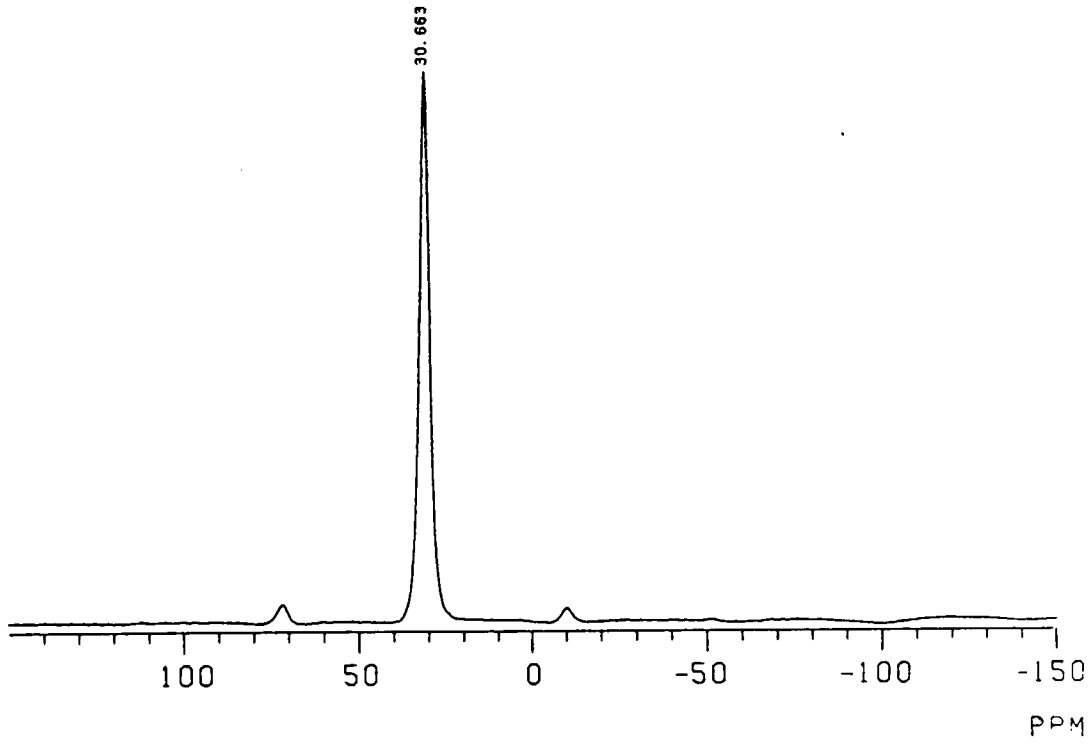


Figure 3.5. ^{31}P NMR Spectrum of Phosphonic Acid (VBC)

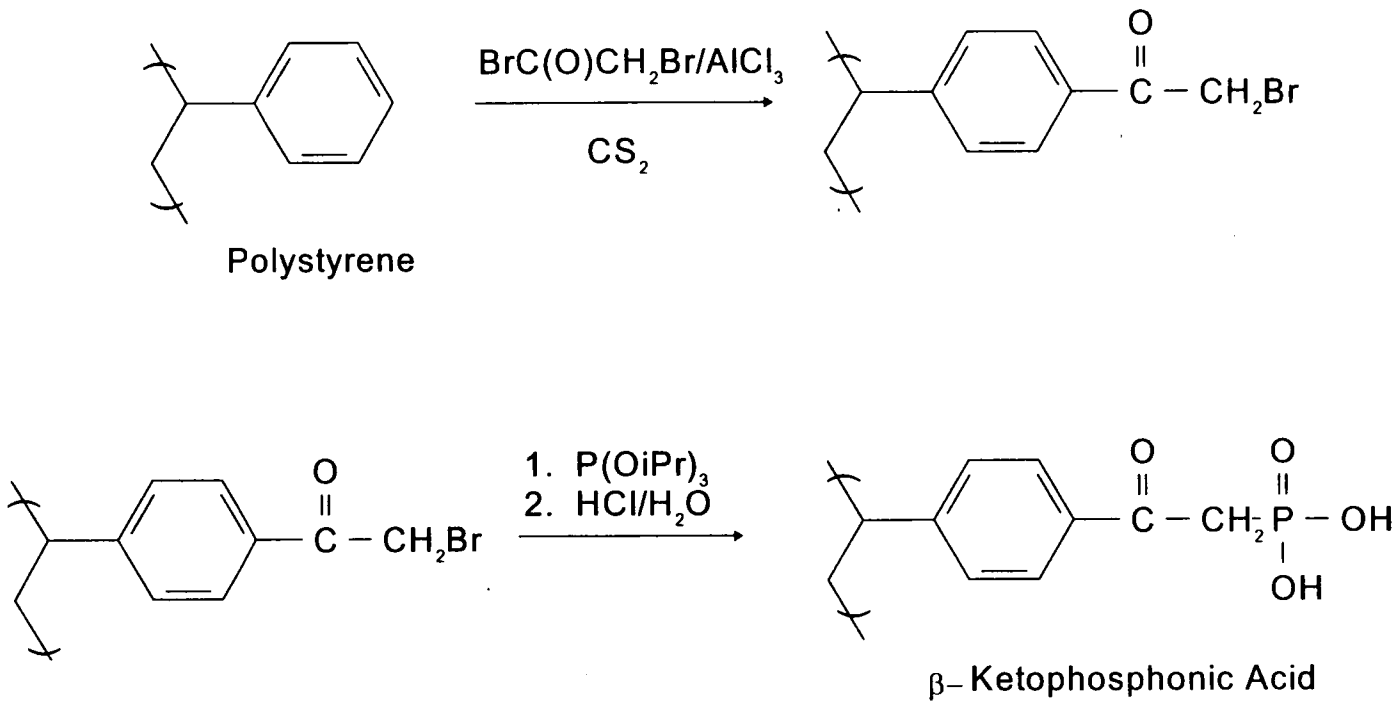


Figure 3.6. β-Ketophosphonic Acid Synthesis

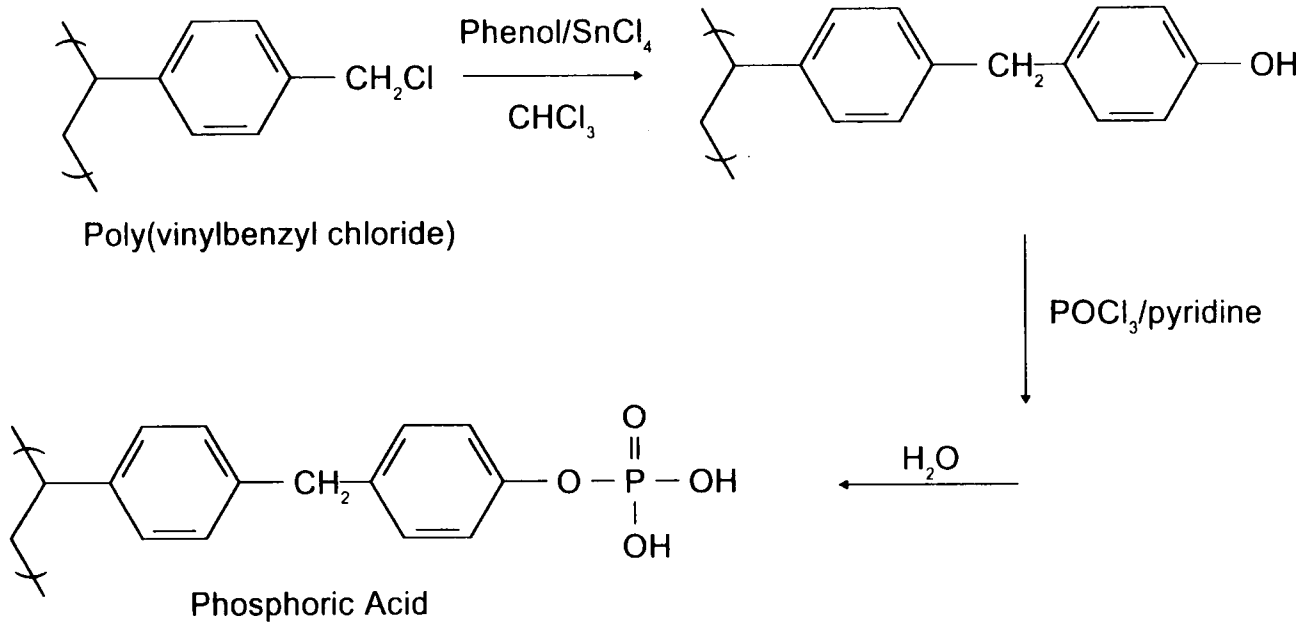


Figure 3.7. Phosphoric Acid Synthesis

procedures described in the experimental chapter and the properties are summarized in Table 3.1.

The percent solids of the phosphoric acid was 66.57% and the phosphorus capacity was 2.42 mequiv P/g. The acid capacity was 4.56 mequiv/g, approximately twice the phosphorus capacity. The ^{31}P NMR chemical shift was -1.02 ppm.

Bifunctional Phosphorus Acid/Ester Resins

The syntheses of the phosphonic acid/ethyleneimine and isopropyl ester/ethyleneimine resins have been described previously in Chapter 2. All resins were crosslinked with 2% DVB and had gel porosity. The resins were characterized by procedures described in the experimental chapter and the properties are summarized in Table 3.2.

The phosphonic acid/ethylenediamine (EDA) resin had a solids level of 54.98% and a phosphorus capacity of 2.30 mequiv P/g. The ^{31}P NMR chemical shift was 24.00 ppm. The phosphonic acid/diethylenetriamine (DETA) resin exhibited a solids level of 34.30% and a phosphorus capacity of 1.76 mequiv P/g. The ^{31}P NMR chemical shift was 23.44 ppm. The isopropyl ester/DETA resin had a solids level of 51.06% and a phosphorus capacity of 2.00 mequiv/g. The^{31}P NMR chemical shift was 30.28 ppm.

The remainder of the bifunctional resins were prepared by copolymerizing VBC with styrene (STY), methyl methacrylate (MMA), butyl

Table 3.2

Characterization of Bifunctional Phosphorus Acid/Ester Resins

Type	Crosslinking	%Solids (g_{dry}/g_{wet})100	Phosphorus Capacity (mequiv/g)	Acid Capacity (mequiv/g)	^{31}P NMR Chemical Shift (δ)
		Microporous (Gel)			
Phosphonic/STY	2% DVB	69.76	30.5	6.20	30.03
Phosphonic/MMA	2% DVB	67.84	3.18	7.63	29.92
Phosphonic/BuMA	2% DVB	73.82	2.59	5.92	29.80
Phosphonic/AA	2% DVB	65.04	3.38	10.10	30.26
Phosphonic/EDA	2% DVB	54.98	2.30	-	24.00
Phosphonic/DETA	2% DVB	34.30	1.76	-	23.44
Isopropyl Ester/DETA	2% DVB	51.06	2.00	-	30.28

methacrylate (BuMA) and ethyl acrylate (EA) each at 50 wt% and 2% DVB. The beads were then reacted with triisopropyl phosphite and hydrolyzed using concentrated HCl. Upon hydrolysis the ethyl acrylate was converted to acrylic acid (AA). The resins were characterized by procedures described in the experimental chapter and summarized in Table 3.2.

The solids levels of the STY, MMA, BuMA, and AA bifunctional resins were 69.76%, 67.84%, 73.82%, and 65.04%, and the phosphorus capacities were 3.05 mequiv P/g, 3.18 mequiv P/g, 2.59 mequiv P/g, and 3.38 mequiv P/g, respectively. The acid capacity for the phosphonic/STY resin was approximately twice the phosphorus capacity, 6.20 mequiv/g, and the acid capacities for the MMA and BuMA resins were slightly higher than twice the phosphorus, 7.63 mequiv/g and 5.92 mequiv/g, respectively. This is most likely due to partial hydrolysis of the MMA and BuMA. The acid capacity of the phosphonic acid/AA resin was much greater than twice the phosphorus capacity, 10.10 mequiv/g, this being due to complete hydrolysis of the ethyl acrylate groups. The ^{31}P NMR chemical shifts of the STY, MMA, BuMA, and AA bifunctional resins were 30.03 ppm, 29.92 ppm, 29.80 ppm, and 30.26 ppm, respectively. These chemical shifts indicate that STY, MMA BuMA and AA copolymerized at a level of 50% with VBC had a negligible effect on the environment of the phosphorus (the chemical shift of the 100% phosphonic acid (VBC) was 30.32 ppm for 2% DVB).

Metal Ion Studies

Complexing abilities of all phosphorus acid/ester resins were investigated using acid metal salt solutions of low concentration. Studies examined individual metal ions in which 10^{-4} N metal nitrate solutions in either 0.01 N, 0.1 N, 1 N, or 2 N HNO_3 were used. The results are reported as "percent M^{n+} complexed" and in terms of the distribution coefficient "*D*".

$$D = \frac{\textit{mequiv } M^{n+} \textit{ complexed / g dry polymer}}{\textit{mequiv } M^{n+} \textit{ free / mL solution}}$$

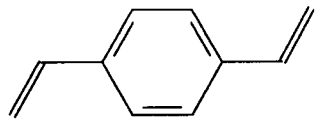
It should be noted that small differences in the percent M^{n+} complexed (exceeding 98%) can result in large differences in the corresponding distribution coefficients.

The complexing abilities of the resins with Eu^{3+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, and Fe^{3+} ions were determined as follows. An amount of polymer corresponding to one milliequivalent of ligand (based on the phosphorus capacity) was accurately weighed and the matrix equilibrated with the appropriate acid. The resin was then contacted with 10 mL of a metal ion solution for 30 min or 24 h. The systems were considered at equilibrium after 24 h. The metal ion concentrations in the resulting solutions were determined by atomic absorption spectrometry (Perkin-Elmer model 3100), from which the percent M^{2+} complexed values and distribution coefficients were calculated.

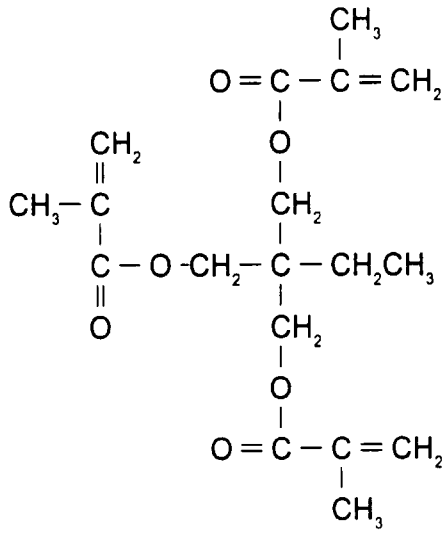
Matrix Rigidity Effects

Matrix rigidity can be affected by altering the crosslinking level and/or the crosslinking agent. Divinylbenzene (DVB) used as the crosslinking agent provides a more rigid polymer matrix than does the more flexible trimethylolpropane trimethacrylate (TMPTMA), (Figure 3.8). Increasing the level of DVB crosslinking increases the matrix rigidity.

Matrix rigidity influences on the uptake of Eu^{3+} from 10^{-4} N $Eu(NO_3)_3$ in 1 N HNO_3 by phosphonic acid resins from VBC were investigated and are summarized in Table 3.3. The MR resins contacted for 30 minutes showed a decrease in the distribution coefficient from 12.7 to 1.5 corresponding to an increase in DVB crosslinking level from 2% to 16%. Gel resins crosslinked with DVB and contacted for 24 h followed the same trend, with the distribution coefficient decreasing from 10.7 to 2.98 corresponding to an increase in crosslinking level from 2% to 16%. MR resins contacted for 24 h followed this trend after a crosslinking level of 8% DVB. Those resins crosslinked with 2%, 5% and 8% exhibited distribution coefficients of 16.8, 15.9 and 16.3, respectively. At 12% and 16% crosslinking the distribution coefficients dropped to 9.56 and 6.84, respectively. These trends are depicted in Figure 3.9. Resins crosslinked with the more flexible TMPTMA, contacted for 24 h, exhibited distribution coefficients of 4.83 and 11.4 for the 5% and 12% crosslinked resins, respectively. Comparing gel resins crosslinked at a level of 5%, a decrease in distribution coefficient, from 9.76 to 4.83, was observed when changing the



Divinylbenzene



Trimethylolpropane trimethacrylate

Figure 3.8. Crosslinking Agents

Table 3.3

Matrix Rigidity Effects on Eu(III) Uptake from 10^{-4} N $Eu(NO_3)_3$ in 1 N HNO_3 by 100% Phosphonic Acid Resins from VBC

Porosity	Type Crosslink	Crosslink Level				
		2%	5%	8%	12%	16%
		Kinetic Studies: 30 min Contact Time				
MR	DVB	12.7[a](21.2)[b]	11.4 (19.9)	9.24 (18.5)	3.51 (9.25)	1.50 (5.61)
		Equilibrium Studies: ≥24 h Contact Time				
MR	DVB	16.8 (26.3)	15.9 (25.7)	16.3 (28.7)	9.56 (21.8)	6.84 (21.4)
Gel	DVB	10.7 (17.7)	9.76 (17.3)	7.99 (15.5)	5.78 (12.6)	2.98 (8.22)
Gel	TMPTMA	-	4.83 (10.1)	-	11.4 (20.0)	-

[a]Distribution coefficient
[b]Percent Eu^{3+} complexed

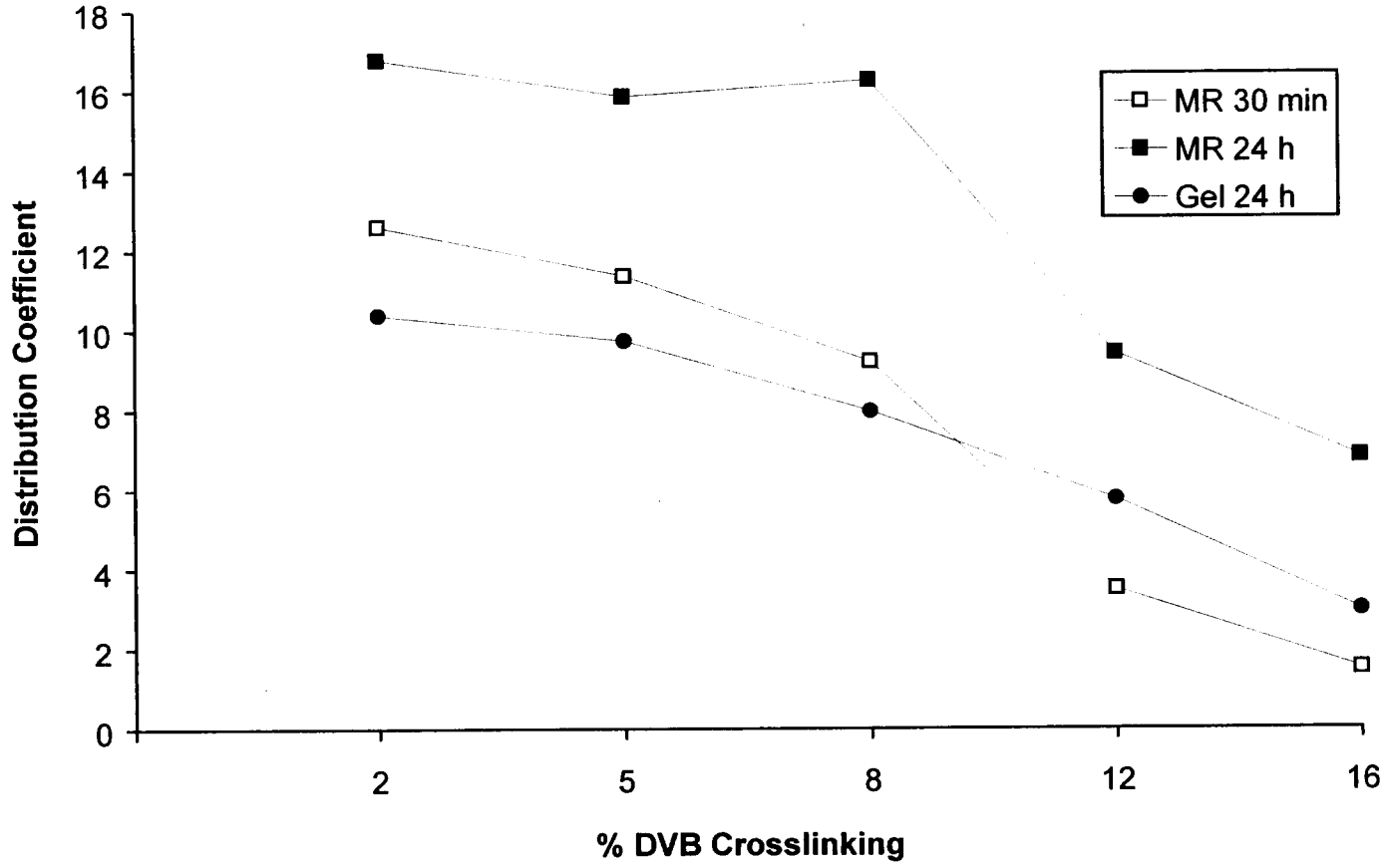


Figure 3.9. Matrix Rigidity Effects in Phosphonic Acid Resins

crosslinking agent from DVB to TMPTMA. This may be due to a collapse of the less rigid polymer matrix in highly ionic solutions.

Porosity Influence

Table 3.3 and Figure 3.9 also illustrate the influence porosity has on the resins' ability to complex Eu^{3+}. Distribution coefficients for the 2% to 8% crosslinked MR resins at a contact time of 30 minutes were greater than the corresponding values for the gel resins at 24 h. All distribution coefficients for the MR resins at 24 h were greater than the corresponding values for the gel resins at 24 h. Kinetic factors favor the MR resins, however, the uptake of Eu^{3+} is most likely controlled by thermodynamic factors since distribution coefficients for all the phosphonic acid resins are relatively low.

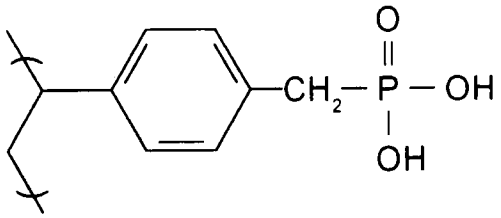
Polymer Support Effects

Chapters 4 and 5 have shown that the polymer support to which a particular ligand is bound is not simply a inert matrix but influences that ligands' ability to complex certain metal ions. Evidence supporting this theory was also observed in a series of 2% DVB phosphonic acid resins contacted with 10^{-4} N Fe^{3+} in 2 N HNO_3. Results of these contact studies are given in Table 3.4. The key variable in the monofunctional resins is the way in which the phosphonic acid ligand is attached to the polymer backbone. Figure 3.10 illustrates the attachment of the phosphonic acid ligand in the monofunctional resins.

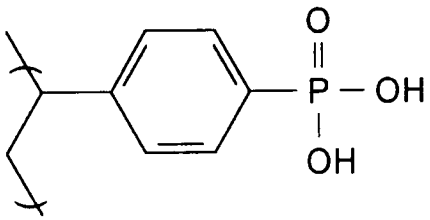
Table 3.4

Fe(III) Uptake from 10^{-4} N $Fe(NO_3)_3$ in 2 N HNO_3 by Phosphorus Acid/Ester Mono- and Bifunctional Resins

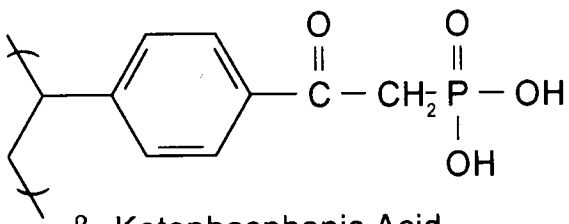
Resin	Type	% Fe^{3+} Complexed	Distribution Coefficient (D)
	Monofunctional		
CL3-063	Phosphonic (VBC)	91.6	506
CL3-218	Phosphonic (STY)	94.9	958
CL3-215	Phosphoric	90.0	213
CL2-218	β-Ketophosphonic	100	∞
CL3-062	Isopropyl Ester	0.00	0.00
	Bifunctional		
CL4-052	Phosphonic/STY	88.1	216
CL4-053	Phosphonic/MMA	84.0	165
CL4-056	Phosphonic/BuMA	47.27	22.4
CL4-057	Phosphonic/AA	92.2	397
CL4-123	Phosphonic/EDA	75.3	70.0
CL3-201	Phosphonic/DETA	60.4	29.5
CL4-133	Isopropyl Ester/DETA	2.26	0.404



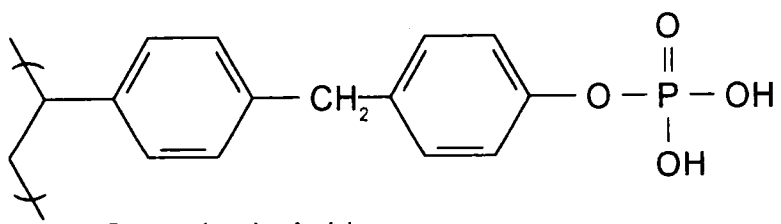
Phosphonic Acid (VBC)



Phosphonic Acid (STY)



β- Ketophosphonic Acid



Phosphoric Acid

Figure 3.10. Phosphorus Acid Resins

Although the complexing species in all resins was the $-P(O)(OH)_2$ ligand, the percent Fe^{3+} complexed values were 91.6, 94.9, 90.0, and 100 for the phosphonic (VBC), phosphonic (STY), phosphoric, and β-ketophosphonic, respectively. Later research by Dr. Latiff Hussain indicates that the carbonyl group in the β-ketophosphonic acid resin can, under certain conditions, cooperate with the phosphoryl group in complexing metal ions. The variation in distribution coefficients was even greater (i.e., 506, 958, 213, and ∞ for the above listed resins, respectively). Differences in the percent M^{n+} complexed are also observed in equilibrium studies using phosphoric, phosphonic (VBC), and phosphonic (STY) resins with Cd^{2+}, Cu^{2+}, Pb^{2+}, Eu^{3+} and Fe^{3+} in 0.01 N, 0.1 N, and 1 N HNO_3. Theses results are summarized in Table 3.5, and Figure 3.11 depicts the complexation in 0.1 N HNO_3. For each metal ion, the percent M^{n+} complexed was greatest for the phosphoric acid resin followed by the phosphonic acid (STY) then the phosphonic acid (VBC). The percent Eu^{3+} and Fe^{3+} complexed values were above 98% for all three resins. These results indicate that the polymer support plays a significant role in the uptake of Cd^{2+}, Cu^{2+}, and Pb^{2+} from 0.1 N HNO_3.

Another way the polymer support can have influence upon the binding ability of a particular ligand is through bifunctionality. Bifunctionality may be obtained by copolymerization of two different monomers, or by partial modification of a particular polymer support with two different ligands. The phosphonic/STY, phosphonic/MMA, phosphonic/BuMA, and phosphonic/AA

Table 3.5

Comparison of Metal Ion Uptake Using Phosphoric and Phosphonic Acid Resins

Type	Cd^{2+}	Cu^{2+}	Pb^{2+}	Eu^{3+}	Fe^{3+}
			0.01 N HNO_3		
Phosphoric	99.4[a](3580)[b]	99.8 (14,600)	98.0 (1130)	-	95.2 (462)
Phos[c](VBC)	98.7 (3350)	98.5 (3030)	98.0 (2230)	-	95.2 (895)
Phos (STY)	99.2 (6290)	99.8 (30,200)	98.0 (2440)	-	95.2 (953)
			0.1 N HNO_3		
Phosphoric	59.8 (35.0)	54.3 (28.0)	85.4 (138)	100.0 (∞)	98.3 (1370)
Phos (VBC)	37.9 (32.4)	25.2 (17.9)	59.0 (34.1)	99.3 (7320)	98.3 (3090)
Phos (STY)	53.0 (56.4)	48.0 (46.2)	67.8 (105)	99.5 (10600)	98.3 (2920)

Table 3.5 (continued)

Type	Cd^{2+}	Cu^{2+}	Pb^{2+}	Eu^{3+}	Fe^{3+}
			1 N HNO_3		
Phosphoric	-	-	-	43.1 (17.8)	100.0 (∞)
Phos (VBC)	-	-	-	12.5 (6.57)	100.0 (∞)
Phos (STY)	-	-	-	34.3 (26.2)	100.0 (∞)
			2 N HNO_3		
Phosphoric	-	-	-	-	90.0 (213)
Phos (VBC)	-	-	-	-	91.6 (506)
Phos (STY)	-	-	-	-	94.9 (958)

[a]Percent M^{n+} complexed
[b]Distribution coefficient
[c]Phos: Phosphonic acid

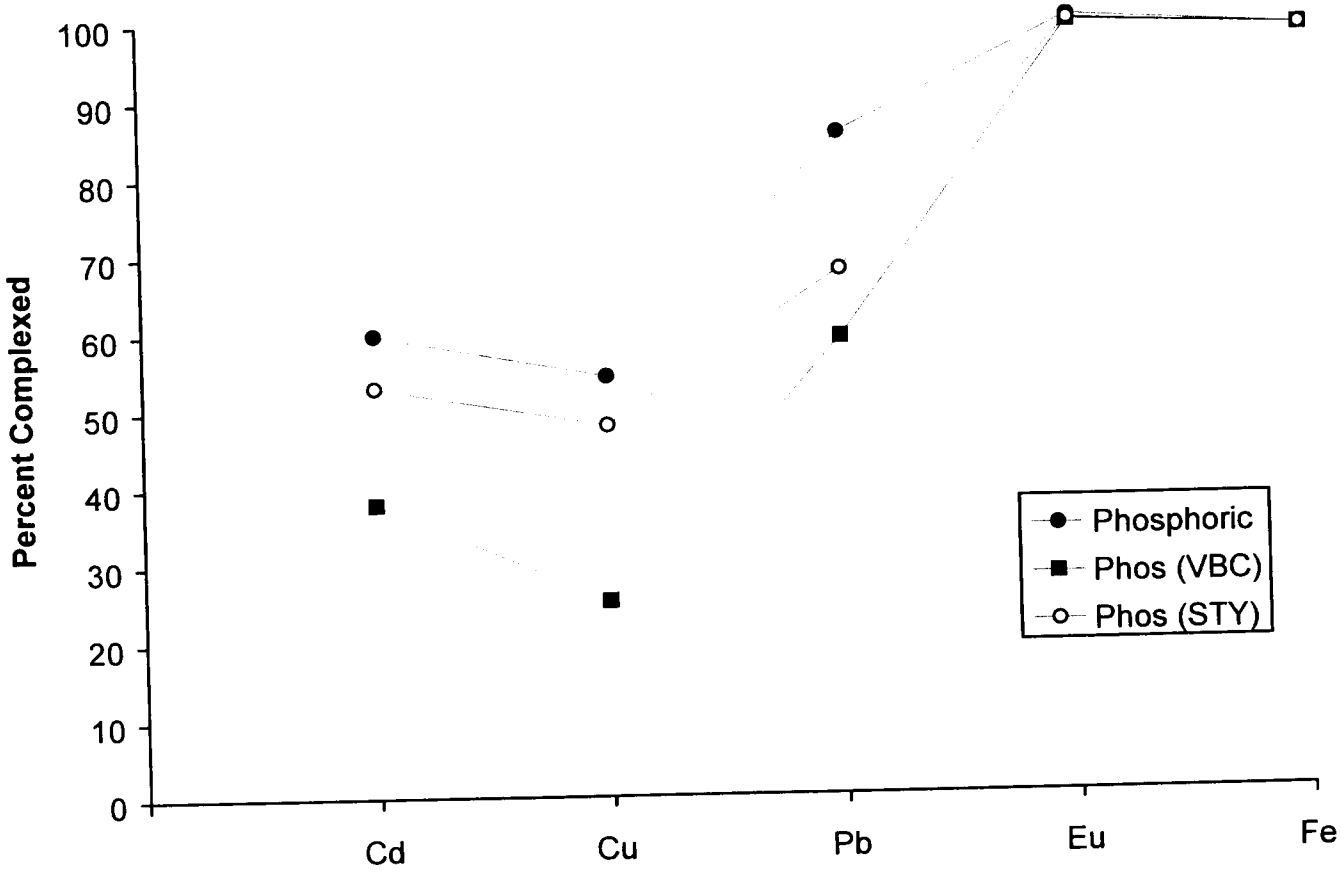


Figure 3.11. Metal Ion Uptake by Phosphorus Acid Resins in 0.1 N HNO_3

resins were prepared by the first method and the phosphonic/EDA, and phosphonic/DETA resins were prepared by the second. Although the complexing species is the $-P(O)(OH)_2$ ligand, the presence of the second functional group has an influence the ligands' ability to complex Fe^{3+} in 2 N HNO_3. The results of these studies are given in Table 3.4. The percent Fe^{3+} complexed values range from 47.3 for the phosphonic/BuMA resin to 92.2 for the phosphonic/AA resin.

Conclusions

A series of phosphorus acid/ester mono- and bifunctional resins have been prepared and their ability to complex Cd^{2+}, Cu^{2+}, Pb^{2+}, Eu^{3+}, and Fe^{3+} have been investigated. Several factors have been shown to influence the resin's ability to complex metal ions. These include (but certainly are not limited to) crosslinking level, crosslinking agent, porosity, bifunctionality, and the way in which a particular ligand is attached to the polymer backbone. In general, as the DVB crosslinking level increases Eu^{3+} uptake by phosphonic acid resins decreases. Increased accessibility was demonstrated by MR resins when compared to gel resins for the uptake of Eu^{3+} by phosphonic acid resins. The polymer supports to which the $-P(O)(OH)_2$ ligand was bound (mono- and bifunctional) were shown not to be inert matrices but exhibited a marked influence on the ligand's ability to bind Cd^{2+}, Cu^{2+}, Pb^{2+}, Eu^{3+}, and Fe^{3+} from dilute solutions. In 0.1 N HNO_3 solutions, resin binding ability increased in the

order: Phos (VBC) < Phos (STY) < Phosphoric. This influence may be using in the tailoring of phosphorus acid/ester resins for the removal of targeted metal ions from aqueous solutions.

CHAPTER 4

METAL ION SELECTIVITY INFLUENCES IN AMIDOXIME POLYMERS

Introduction

Oximes and oxime derivatives are well known in metal ion coordination chemistry. The ability of these compounds to ion exchange through the hydroxyl proton and/or coordinate through the nitrogen's lone pair allows them to function over a wide range of coordination conditions.[65] Probably the best known of these oxime coordination compounds is the red square planar complex bis(dimethylglyoximato)nickel(II).[66]

Amidoximes are a type of oxime in which the hydrogen on the carbon doubly bound to the nitrogen is replaced by $-NH_2$. The reaction of a nitrile with free hydroxylamine results in the formation of a hydroxyamidine (Figure 4.1a), which is readily stabilized as the amidoxime tautomer (Figure 4.1b).[67] The resulting amidoximes are amphoteric, with the ionizable hydrogen being of low acidity (pK_a's from 3 - 5).[68]

Amidoximes have been used in the spectrophotometric determinations of first row transition metals which form highly colored complexes with these organic reagents.[69-71] Uranium(VI) (which exists as the uranyl ion, UO_2^{2+}, in aqueous solutions) also forms colored complexes with amidoximes, and

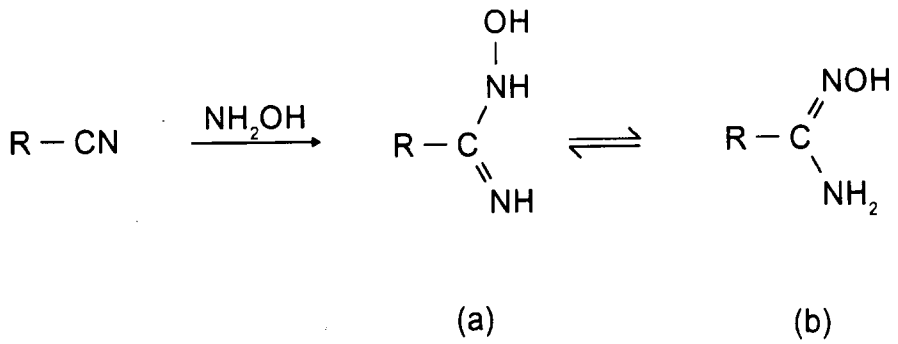


Figure 4.1. Reaction of a Nitrile Functional Group with Free Hydroxylamine

spectrophotometric analyses of these systems have been performed as well.[72] Long chain amidoximes and amidoxime esters, which exhibit enhanced solubility in hydrocarbon solvents, have been successfully utilized in the solvent extraction of uranyl and other metal ions from aqueous solutions.[73] Coordination (or ion exchange) through the oxime oxygen and amine nitrogen results in the formation of a stable five-membered ring,[39] and coordination with more than one ligand leads to further stabilization by a multiple ring system.[40]

The concern over the anticipated depletion of terrestrial uranium and other metals has led researchers to develop recovery methods for the almost endless supply of these species contained in the seas.[73-75] The recovery of uranium is especially important to Japan as it has no ore resources yet an ever growing demand for energy. Although the concentration of uranium in the oceans is only 3.3 μg/L, this represents a total uranium content of 4.5×10^9 tons. For economic as well as environmental reasons certain criteria for the recovery must be met. The "collector" must be insoluble in seawater and must be able to be recovered easily and completely. It must also be able to function with the existing conditions of seawater without alteration. The "collector" must be of high physical and chemical stability, and be able to selectively remove uranium at a fast rate. Ion-exchange resins possessing the appropriate ligand(s) meet these criteria and are a possible solution to the uranium recovery problem.[74,75]

Extensive investigation has been done into the use of polymers with

pendant amidoxime ligands for the separation and recovery of uranium from seawater.[73-79] The binding abilities of polymer-supported amidoximes with UO_2^{2+}, Cu^{2+}, Mg^{2+}, Ca^{2+}, Hg^{2+}, Ag^{+}, Fe^{3+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, in seawater and other aqueous solutions, have also been studied.[7,15,19,80-88] Commonly studied influences on the binding ability of a polymer-supported ligand include: porosity and surface area;[73,76,81] the level and type of crosslinking, e.g., divinylbenzene (DVB) or tetraethylene glycol dimethacrylate (TEGDM);[73,75,76] and the pH of the aqueous solution.[83,86] A somewhat less studied influence on the complexing ability of the selected ligand is the polymer support to which it is bound. The polymer support for the amidoxime ligand may be 100% acrylonitrile (AN), a copolymer of AN and another monomer such as styrene (STY), glycidyl methacrylate (GMA), or any other polymer which contains, or can be altered to contain, a nitrile functional group.[73,77]

The polymer support to which a ligand or reagent is bound has been shown to influence ligand- (reagent-) substrate interactions in organic syntheses,[19,89] metal ion complexation,[90] and molecular recognition studies.[91] These influences of neighboring groups on ligand- (reagent-) substrate interactions brought about by changes in polarity, hydrophilicity, etc., are termed the "microenvironmental effect."[15]

This work examines the complexing abilities of a series of polymer-supported amidoxime resins with metal ions from dilute solutions. The role of polymer support is investigated and it's influence on complexing ability reported.

Synthesis and Characterization

Brief descriptions of all syntheses follow. Details of these syntheses are found in the experimental chapter.

Polymer Supports

Acrylonitrile (AN), acrylonitrile-*co*-styrene (AN/STY), vinylbenzyl chloride (VBC), and glycidyl methacrylate (GMA) polymer supports were prepared by suspension polymerization with divinylbenzene (DVB) as the crosslinking agent. All microporous (i.e., gel) beads were prepared with a crosslinking level of 2 wt% DVB while the macroreticular (MR) beads were prepared with crosslinking levels of 5, 7.5, and 10 wt% DVB. The AN/STY beads were synthesized using monomer ratios of 25/75, 50/50, and 75/25 wt%. Due to the high aqueous solubility of the monomer AN, the polymerizations of 100% AN were carried out using aqueous phases with different stabilizers and ionic concentrations in an attempt to obtain uniform, usable beads. Tables 4.1 and 4.2 summarize the polymerizations of 100% AN gel and MR resins, respectively.

Nitrile resins were obtained from the VBC and GMA beads by reaction with KCN, Figure 4.2. Reaction conditions (KCN reaction) and characterizations of all nitrile resins are given in Table 4.3. The reactions were carried out at reflux unless otherwise indicated, after which the solutions were removed and the resins washed four times with H_2O and dried. No further modification of the

Table 4.1

Copolymerization of 100% Acrylonitrile, 2% DVB, Gel Resins

Resin	Aqueous Phase	Reaction Conditions	Comments
CL2-062	PVA (0.19%)[a], NaCl (2%)	Standard; 230 rpm	Clumps
CL2-063	PVA (0.56%), NaCl (2%)	1 h @ 50 °C & 60 °C, 2 h @ 70 °C, 6 h @ 85 °C; 200 rpm	Clumps
CL2-135	PVA (0.60%), $CaCl_2$ (9.6%)	1 h @ 50° C, 60 °C, 70 °C, 10 h @ 80 °C; 210 rpm	Very small beads clumped together
CL2-136	PVA (1.0%), $CaCl_2$ (9.6%)	1 h @ 50 °C, 60 °C, 70 °C, 10 h @ 80 °C; 178 rpm	Clumps
CL2-139	PVA (1.0%), $CaCl_2$ (14%)	1 h @ 50 °C, 60 °C, 70 °C, 10 h @ 80 °C; 160 rpm	Opaque and translucent beads
CL2-148	PADMAC/Pharmagel 50% satd. NaCl	1 h @ 50 °C, 60 °C, 70 °C, 10 h @ 80 °C; 210 rpm	Opaque and translucent beads

[a]Wt % of total aqueous phase

Table 4.2

Copolymerization of 100% Acrylonitrile MR Resins

Resin	Aqueous Phase	Reaction Conditions	Comments
CL2-158	PVA (1.0%)[a], $CaCl_2$ (14%)	1 h @ 50 °C, 60 °C, 70 °C, 10 h @ 80 °C; 210 rpm	Very small beads, chaff
CL2-160	PADMAC/Pharmagel 50% satd. NaCl	1 h @ 50 °C, 60 °C, 70 °C, 10 h @ 80 °C; 170 rpm	Clumps
CL2-164	PADMAC[b]/Pharmagel 50% satd. NaCl	1 h @ 50 °C, 60 °C, 70 °C, 10 h @ 80 °C; 170 rpm	No form, very friable
CL2-166	PVA (1.3%), NaCl (8.1%)	1 h @ 50 °C, 60 °C, 70°C, 10 h @ 80 °C; 150 rpm	Beads, very friable
CL2-176[c]	PVA (1.0%), $CaCl_2$ (14%)	1 h @ 50 °C, 60 °C, 70 °C, 10 h @ 80 °C; 145 rpm	Beads, very friable
CL2-177[d]	PVA (1.0%), $CaCl_2$ (14%)	1 h @ 50 °C, 60 °C, 70 °C, 10 h @ 80 °C; 145 rpm	Beads, slightly friable

[a]Wt % of total aqueous phase
[b]50% additional PADMAC
[c]7.5% DVB
[d]10% DVB

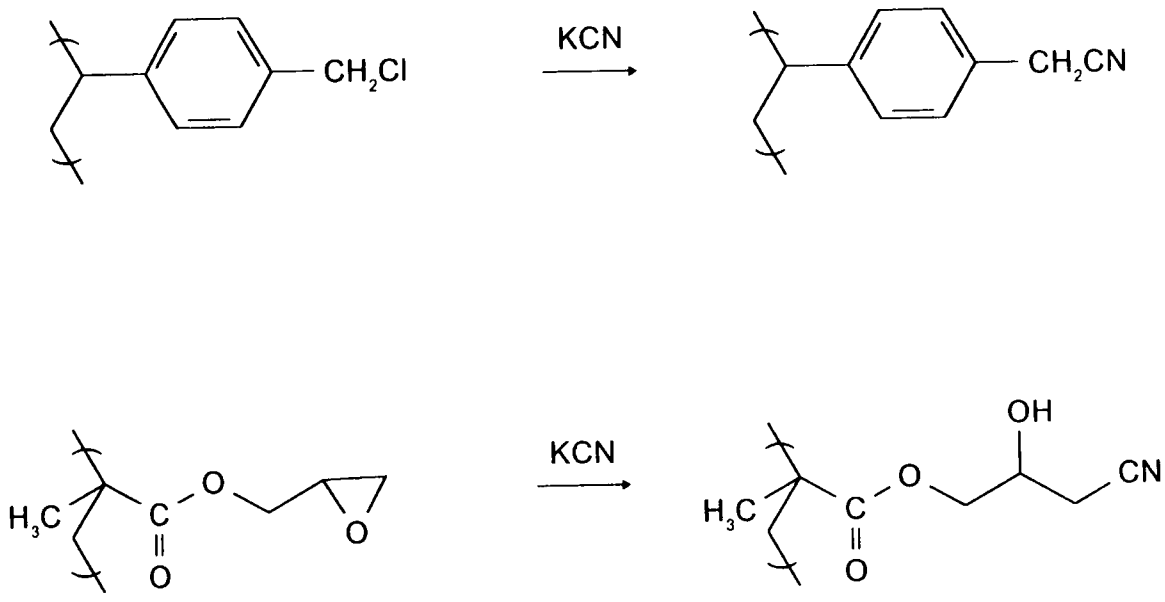


Figure 4.2. Syntheses of Polymer-Supported Nitriles

Table 4.3

Reaction Conditions and Characterization of Nitrile Resins

Resin	Copolymer	Solvent, KCN Ratio[a] Reaction Time	IR Peak @ ~ 2250 cm^{-1}	Nitrogen Capacity (mequiv/g)
CL2-063	AN	-	yes	16.2[b](18.2)[c]
CL2-148	AN	-	yes	16.9 (18.2)
CL2-158[d]	AN	-	-	15.8 (17.1)
CL2-177[e]	AN	-	-	14.0 (15.4)
CL2-065	VBC	Acetonitrile, 1.5:1, 24 h	yes	2.75 (6.73)
CL2-068	VBC	Acetonitrile, 3.7:1, 72 h	yes	5.24 (6.73)
CL2-069	VBC	Acetonitrile, 3.7:1, 72 h	yes	6.48 (6.73)
CL2-079	VBC	Acetonitrile, 5:1, 72 h	yes	4.19 (6.73)
CL2-092	VBC	Acetonitrile, 5:1, 72 h	yes	4.57 (6.73)
CL2-072	GMA	EtOH / H_2O, 3.8:1, 24 h[f]	yes	2.33 (5.70)
CL2-073	GMA	EtOH / H_2O, 3.8:1, 72 h[f]	yes	1.83 (5.70)
CL2-074	GMA	Acetonitrile, 3.8:1, 72 h	no	-
CL2-078	GMA	EtOH / H_2O, 3.8:1, 18 h[f]	yes	2.03 (5.70)

Table 4.3 (continued)

Resin	Copolymer	Solvent, KCN Ratio[a] Reaction Time	IR Peak @ ~ 2250 cm^{-1}	Nitrogen Capacity (mequiv/g)
CL2-140	AN/STY (25/75)[g]	-	-	4.25 (4.57)
CL2-147	AN/STY (25/75)	-	-	4.04 (4.54)
CL2-087	AN/STY (50/50)	-	yes	7.85 (9.08)
CL2-134	AN/STY (75/25)	-	-	12.9 (13.9)
CL2-159[d]	AN/STY (75/25)	-	-	11.7 (12.9)
CL2-161[d]	AN/STY (75/25)	-	-	12.0 (12.9)

[a]Mole ratio of KCN to copolymer
[b]Experimental
[c]Theoretical calculated based on complete functionalization or polymerization
[d]MR, 5% DVB
[e]MR, 10% DVB
[f]@ 50°C
[g]Wt%

AN and AN/STY resins was needed. Characterizations are described in detail in the experimental chapter.

Experimental nitrogen capacities of the AN and AN/STY resins were very close to the calculated theoretical capacities and intense peaks ~2250 cm^{-1}, characteristic of nitrile stretching,[92] were observed in the infrared (IR) spectra (Figures 4.3 and 4.4). Peaks ~2250 cm^{-1} were also observed in the IR spectra of the nitriles from VBC, "Benzonitrile" (Figure 4.5). The experimental nitrogen capacities of the benzonitriles vary with reaction conditions and indicate a KCN to copolymer mole ratio of 3.7:1, and reflux in acetonitrile for 72 h to be optimum conditions. In the IR spectra for the nitriles from GMA, peaks ~2250 cm^{-1} were observed when the reaction was carried out in a mixture of ethanol and H_2O (50/50 vol%) but were not observed with acetonitrile as the solvent (Figures 4.6 and 4.7). The ethanol/water reactions were carried out at 50°C with a KCN to copolymer mole ratio of 3.8:1. Although all experimental nitrogen capacities for the GMA nitriles were quite close, 1.83 to 2.33 mequiv/g, the optimum reaction time seems to be 24 h. The highest capacity for this resin, 2.33 mequiv/g, is considerably lower than the theoretical value of 5.70 mequiv/g suggesting incomplete conversion.

Amidoxime Resins

All amidoxime resins were prepared without deviation from the general procedure. Beads possessing nitrile moieties were reacted with a 4-fold excess

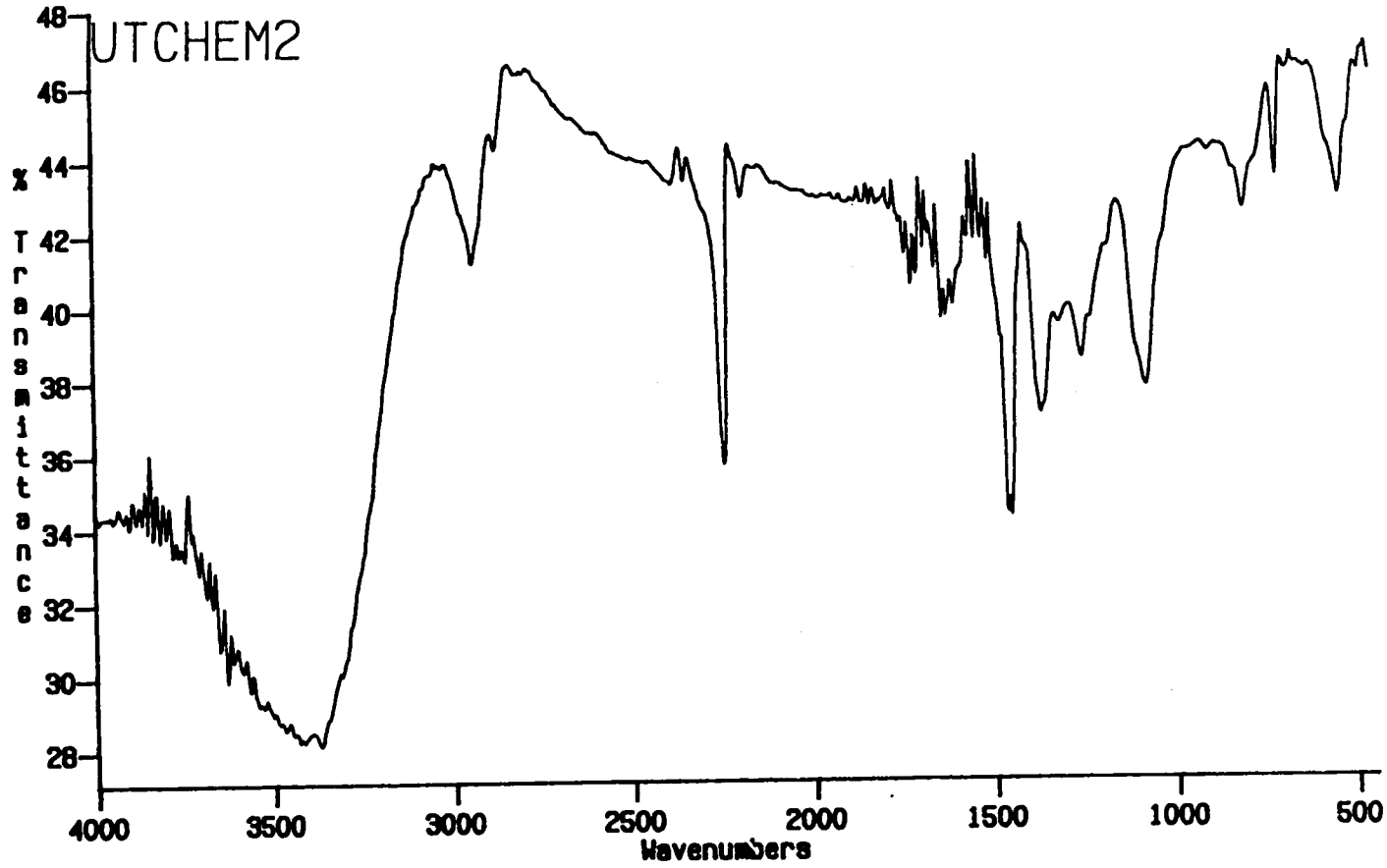


Figure 4.3. IR Spectrum of Poly(Acrylonitrile), 2% DVB, CL2-063

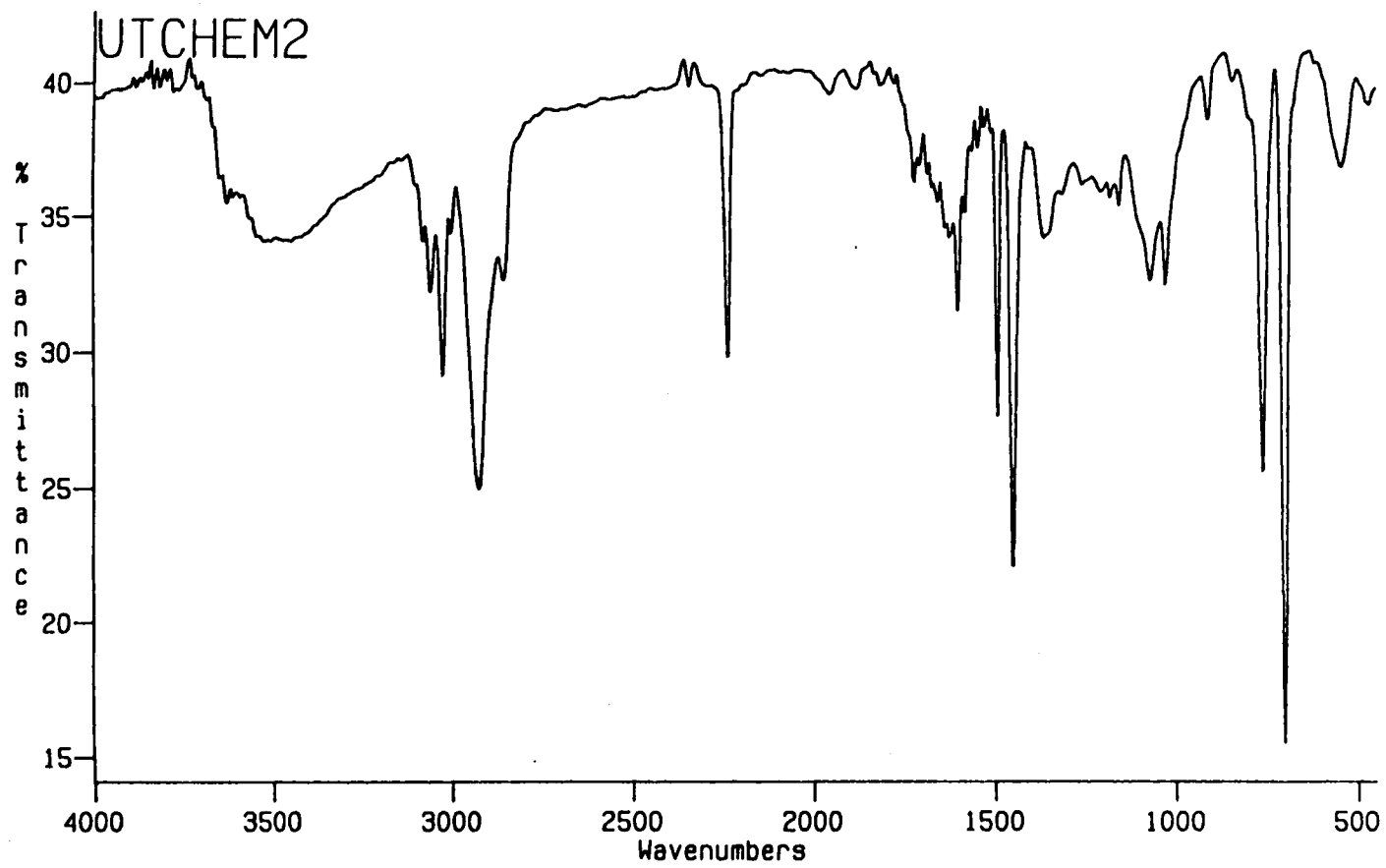


Figure 4.4. IR Spectrum of Poly(Acrylonitrile-co-Styrene) 50/50, 2% DVB, CL2-087

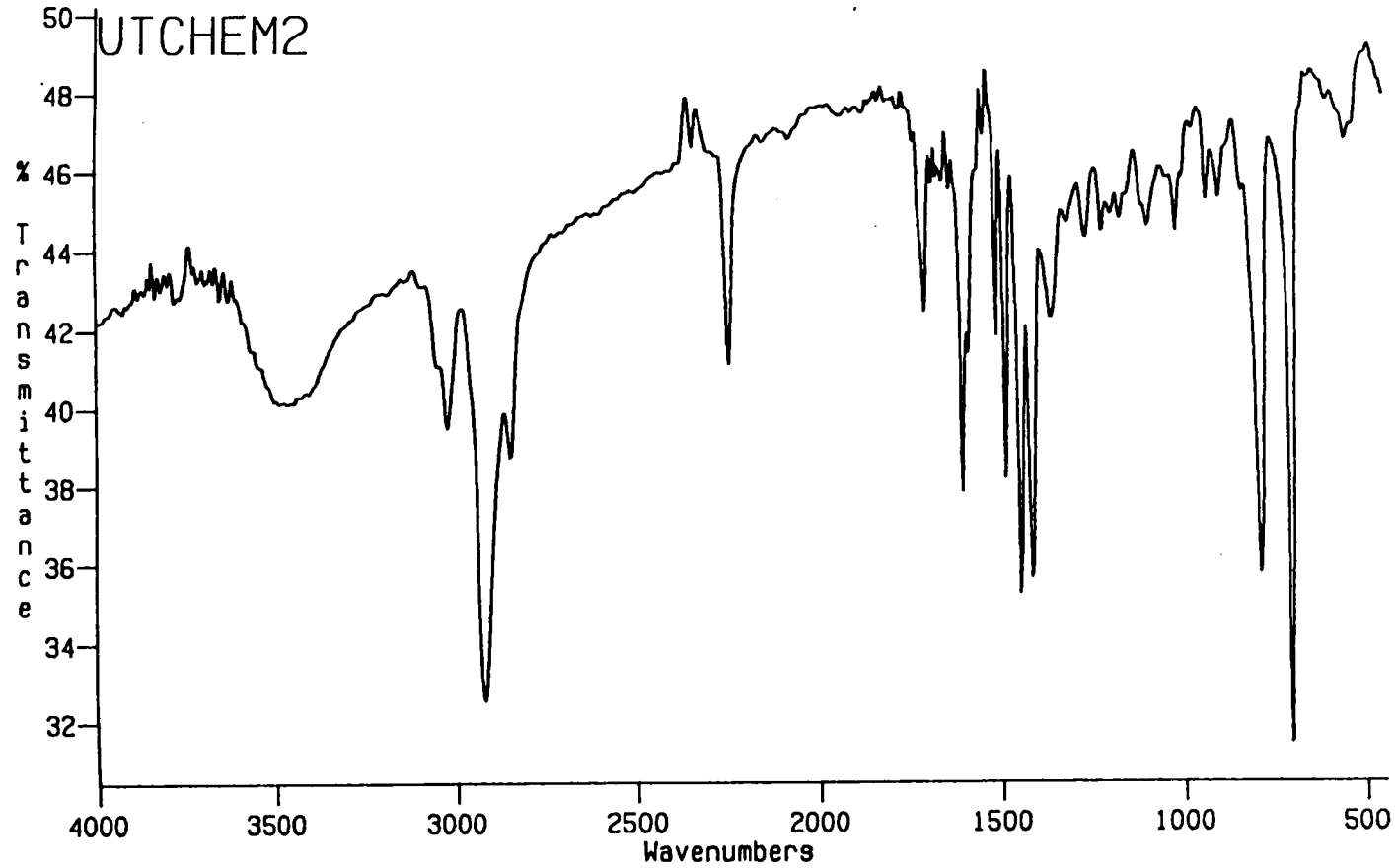


Figure 4.5. IR Spectrum of Poly(Benzonitrile) from VBC, 2% DVB, CL2-079

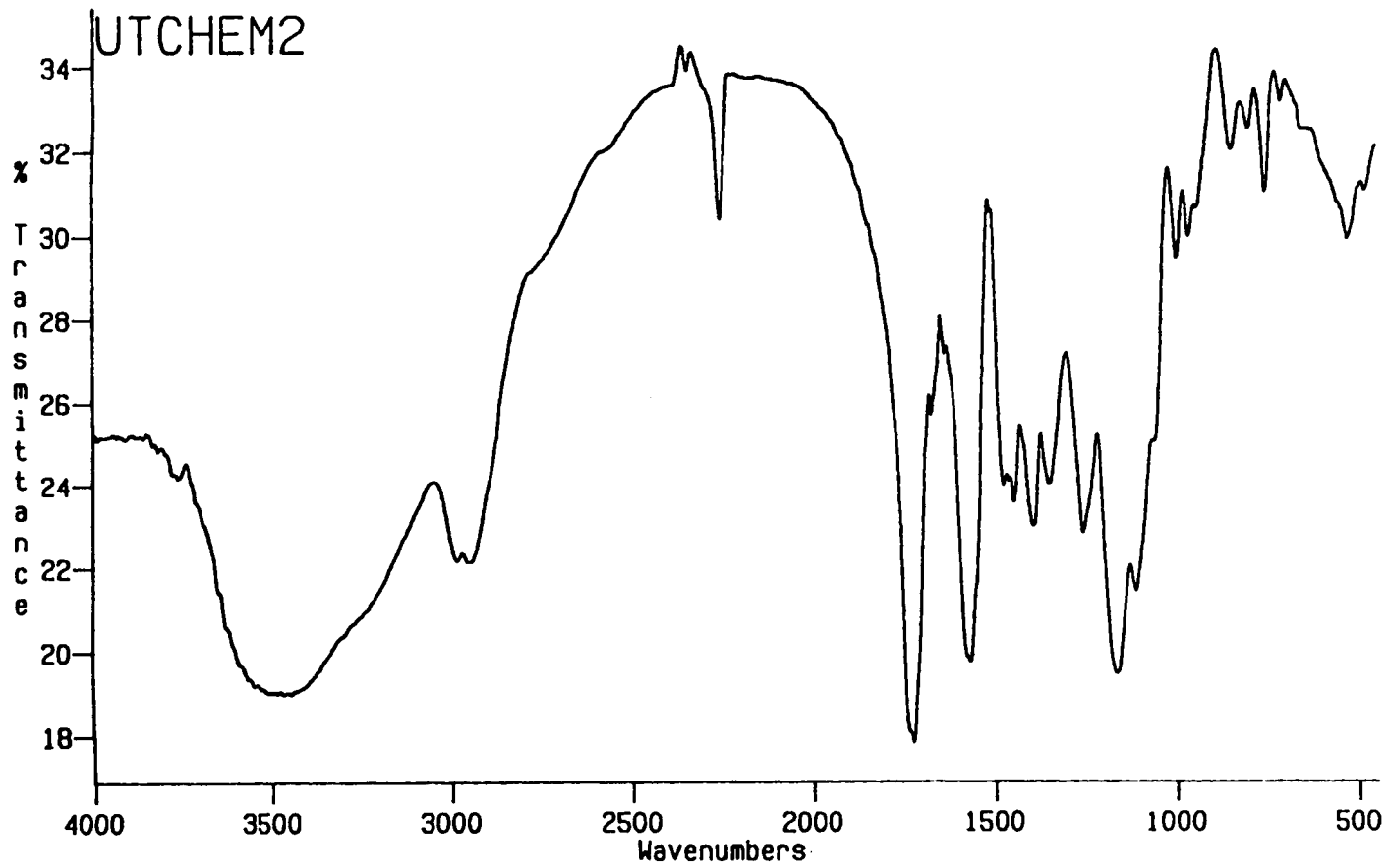


Figure 4.6. IR Spectrum of Poly(3-Cyano-2-Hydroxypropyl Methacrylate), from GMA, 2% DVB, CL2-072

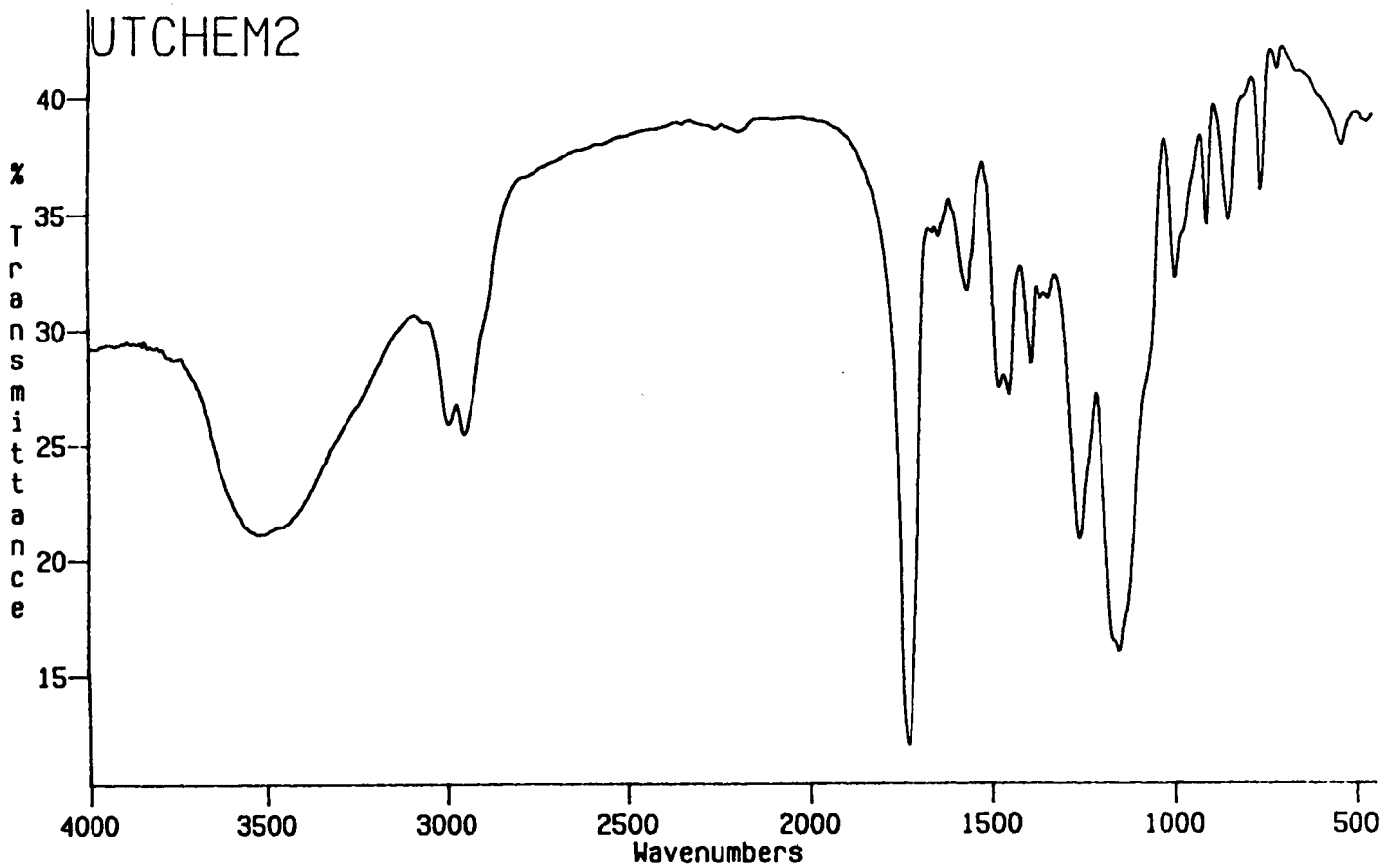


Figure 4.7. IR Spectrum of Poly(3-Cyano-2-Hydroxypropyl Methacrylate), from GMA, 2% DVB, CL2-074

of free hydroxylamine in anhydrous methanol. Reaction of the hydroxylamine hydrochloride salt and sodium methoxide in methanol yielded the soluble free hydroxylamine and sodium chloride which was filtered from the solution. All reactions were carried out at reflux for the times indicated in Table 4.4. The beads were washed with water and eluted in the sequences also indicated in Table 4.4. Samples of the amidoxime resins CL2-111 and CL2-109, from AN/STY (50/50) and VBC nitriles respectively, were further modified to contain sulfonic acid functionalities (CL2-117 and CL2-118 respectively). The water was removed from the amidoxime resins by azeotropic distillation with heptane, and the beads were then reacted with chlorosulfonic acid in ethylene dichloride. No further characterizations were performed on the beads containing the sulfonic acid functionalities.

Experimental nitrogen capacities of the resins from 100% AN are considerably lower than those of the theoretical capacities (based on copolymer nitrogen capacities). For example, resin CL2-080 had experimental and theoretical nitrogen capacities of 15.63 and 21.61 mequiv/g, respectively. The possibility of two explanations exists. First, accessibility into the resin may be limited, leaving unreacted nitrile groups, in which case the experimental nitrogen capacity would be lower than anticipated. However, the IR spectrum of resin CL2-080 (Figure 4.8) is compared to that of the copolymer CL2-063 (Figure 4.3), it shows the disappearance of the nitrile peak ~2250 cm^{-1}, and the appearance of peaks at ~3400, 3325, and 1650 cm^{-1}, which are indicative of the

Table 4.4

Reaction Conditions and Characterization of Amidoxime Resins

Resin	Nitrile Type	% Solids (g_{dry}/g_{wet})	Rxn.Time/ (Elution)[a]	Capacities (mequiv/g)			Total Cap. (mmol/g)
				Acid	Base	Nitrogen	
CL2-070	AN	38.11	10 h / (3)	3.50	5.81	17.10 (21.61)[b]	4.66
CL2-070	AN	37.82	10 h / (4)	5.39	2.92	15.46 (21.61)	4.16
CL2-080	AN	20.10	48 h / (2)	5.64	5.33	15.63 (21.61)	5.49
CL2-080[c]	AN	34.41	48 h / (2)	5.24	5.16	16.21 (21.61)	5.20
CL2-095	AN	53.23	10 h / (1)	2.76	6.09	19.85 (21.61)	4.43
CL2-095e	AN	18.20	10 h / (2)	7.06	2.75	15.78 (21.61)	4.91
CL2-151	AN	72.48	24 h / (3)	2.65	1.15	15.52 (21.90)	1.90
CL2-138	AN/STY (75/25)[d]	61.28	24 h / (4)	4.99	1.82	11.83 (18.41)	3.41
CL2-093	AN/STY (50/50)	73.11	10 h / (1)	0.651	3.78	10.43 (12.63)	2.22
CL2-093e	AN/STY (50/50)	57.34	10 h / (2)	2.95	1.32	-	2.14
CL2-093e	AN/STY (50/50)	60.19	10 h / (5)	3.56	0.000	-	1.78

Table 4.4 (continued)

Resin	Nitrile Type	% Solids (g_{dry}/g_{wet})	Rxn.Time/ (Elution)[a]	Capacities (mequiv/g)			Total Cap. (mmol/g)
				Acid	Base	Nitrogen	
CL2-093e	AN/STY (50/50)	61.27	10 h / (6)	0.855	3.11	-	1.98
CL2-111	AN/STY (50/50)	54.46	10 h / (5)	3.96	0.103	9.29 (12.63)	2.03
CL2-112	AN/STY (50/50)	48.44	72 h / (5)	4.55	0.090	8.76 (12.63)	2.32
CL2-113	AN/STY (50/50)	66.89	2 h / (2)	3.16	0.000	8.29 (12.63)	1.58
CL2-132	AN/STY (50/50)	58.00	24 h / (1)	2.88	1.02	8.93 (12.63)	1.95
CL2-143	AN/STY (25/75)	75.53	24 h / (4)	0.45	0.73	5.35 (7.51)	-
CL2-150	AN/STY (25/75)	72.26	24 h / (4)	0.30	0.17	4.86 (7.18)	0.24

Table 4.4 (continued)

Resin	Nitrile Type	% Solids (g_{dry}/g_{wet})	Rxn.Time/ (Elution)[a]	Capacities (mequiv/g)			Total Cap. (mmol/g)
				Acid	Base	Nitrogen	
CL2-083	Benzo[e]	43.27	21 h / (2)	2.24	2.98	7.67 (7.36)	2.61
CL2-083[c]	Benzo	48.80	21 h / (2)	2.27	3.01	7.65 (7.36)	2.64
CL2-109	Benzo	36.72	10 h / (5)	4.41	0.000	7.63 (7.94)	2.21

[a]Elution/equilibration sequence:

(1) None
(2) 1 L each: H_2O, 0.1 N NaOH, H_2O, 0.1 N HCl, H_2O (standard sequence)
(3) 1 L each: H_2O, 0.1 N HCl, H_2O, 0.1 N NaOH, H_2O (reverse sequence)
(4) Reverse sequence (3) followed by 1 L each: 0.1 N HCl, H_2O
(5) Standard sequence (2) followed by equilibration with 0.1 N HCl
(6) Standard sequence (2) followed by equilibration with 0.1 N NaOH

[b]Theoretical values calulated based on copolymer nitrogen capacity
[c]Recharacterization
[d]Wt%
[e]Nitriles from VBC

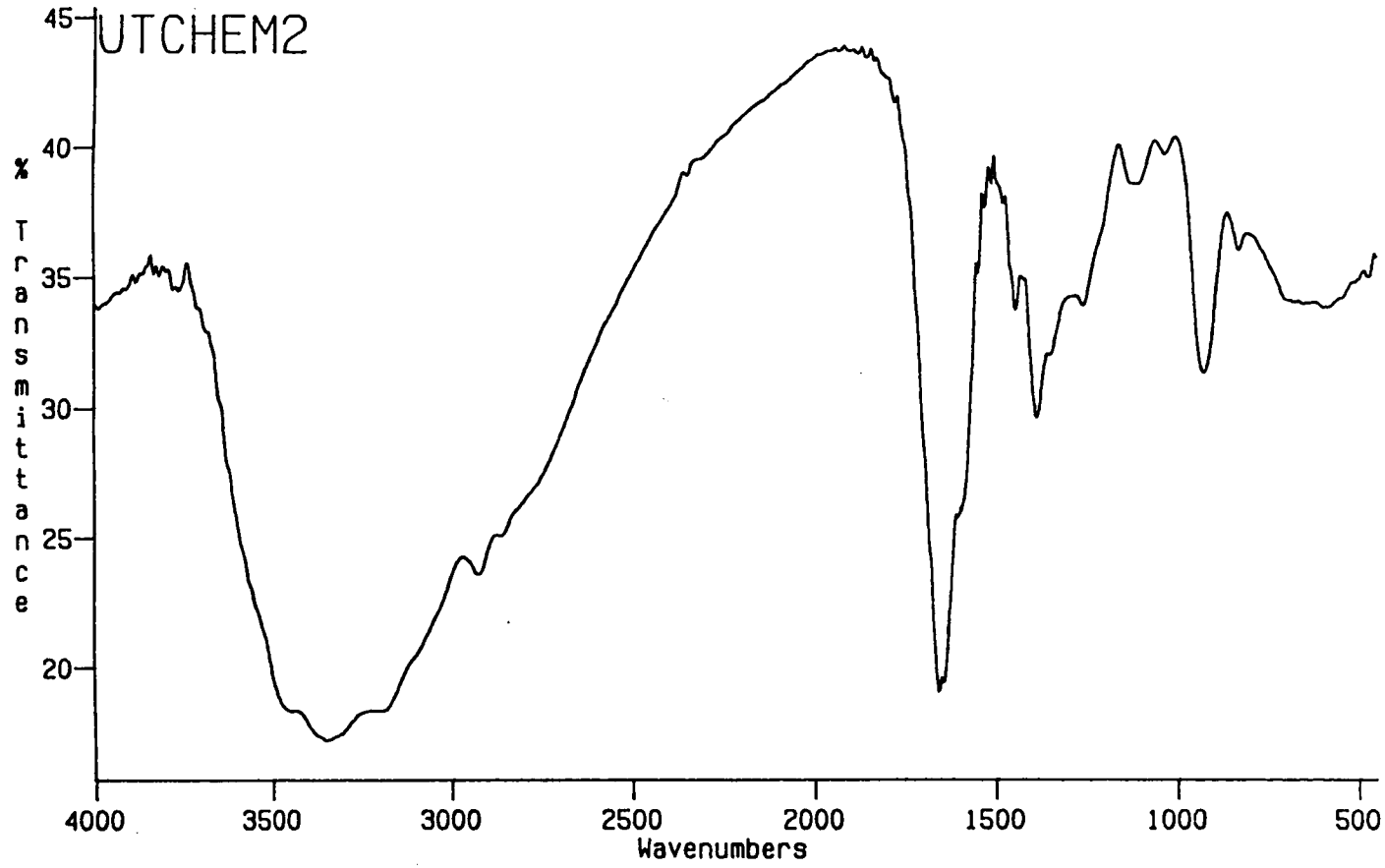


Figure 4.8. IR Spectrum of CL2-080, Amidoxime Resin from 100% AN

amidoxime -NH_2, -OH, and -C=N stretchings.[88] A more probable explanation is the formation of cyclic ladder structures during the reaction of AN with hydroxylamine shown in Figure 4.9,[74] also leading to a lower experimental nitrogen capacity than expected. It is thought that these cyclic structures are also formed by amidoximes in acidic solutions, and that the cyclic imide dioxime may be responsible for the enhanced selectivity and capacity towards the uranyl ion.[79]

Experimental nitrogen capacities for the amidoxime resins from AN/STY copolymers were also lower than the corresponding theoretical capacities. However, this is attributed, at least in part, to an accessibility problem due to increased hydrophobicity brought about by the inclusion of styrene. The IR spectrum of CL2-093, an amidoxime from AN/STY (50/50) (Figure 4.10), shows a distinct peak ~2250 cm^{-1} indicating the presence of unreacted nitrile moieties. Also, the inclusion of styrene decreases the probability of cyclic structure formation due to the distance between nitrile and/or amidoxime groups.

Experimental nitrogen capacities for the amidoxime resins from the benzonitriles (VBC nitriles) are extremely close to the corresponding theoretical values. The IR spectrum of CL2-083 (Figure 4.11) shows no peak ~2250 cm^{-1} indicating no unreacted nitrile groups. As with the AN/STY amidoximes, the formation of cyclic structures is not favored.

The solids levels of the amidoxime resins from AN and AN/STY varied as expected, with an increase in the solids level with increasing styrene content.

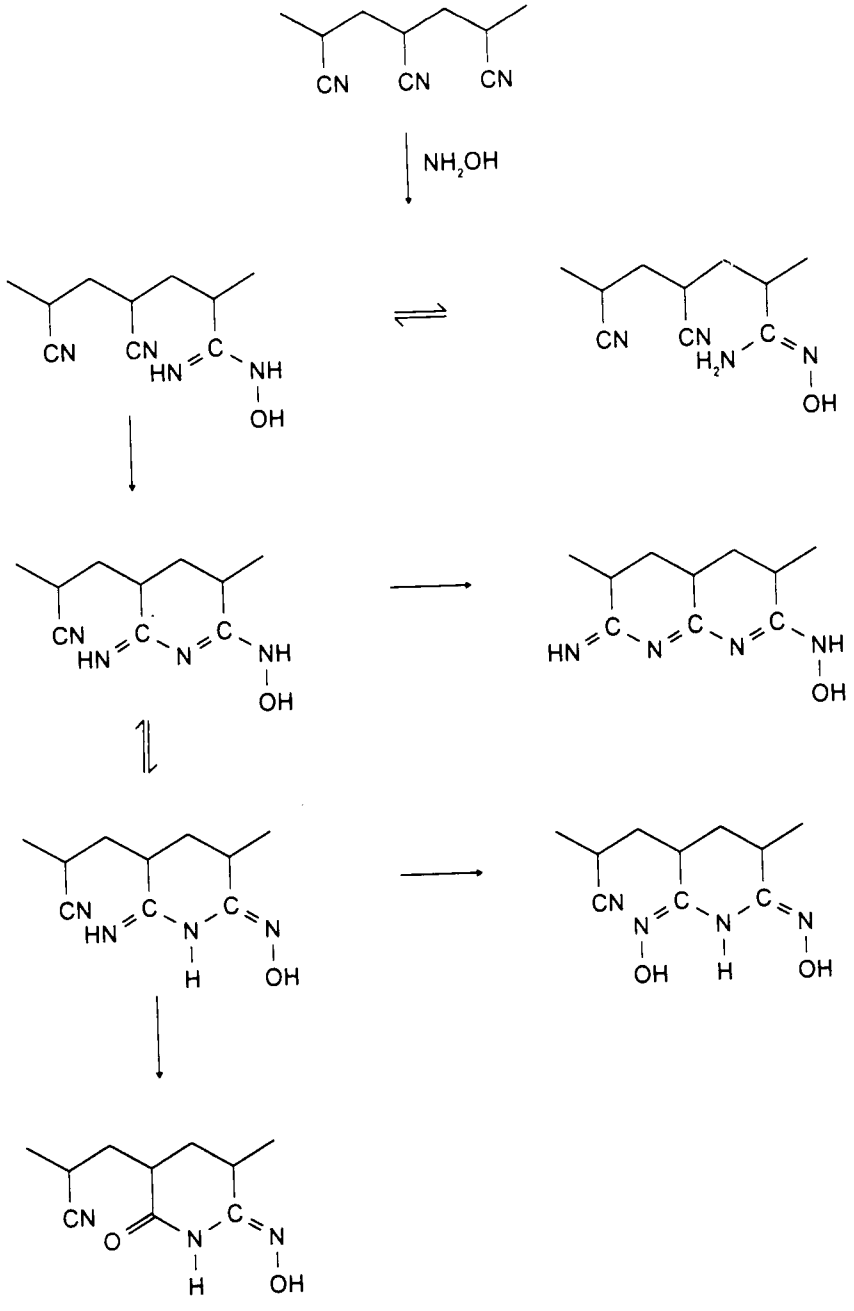


Figure 4.9. Possible Reactions of Poly(acrylonitrile) with Hydroxylamine

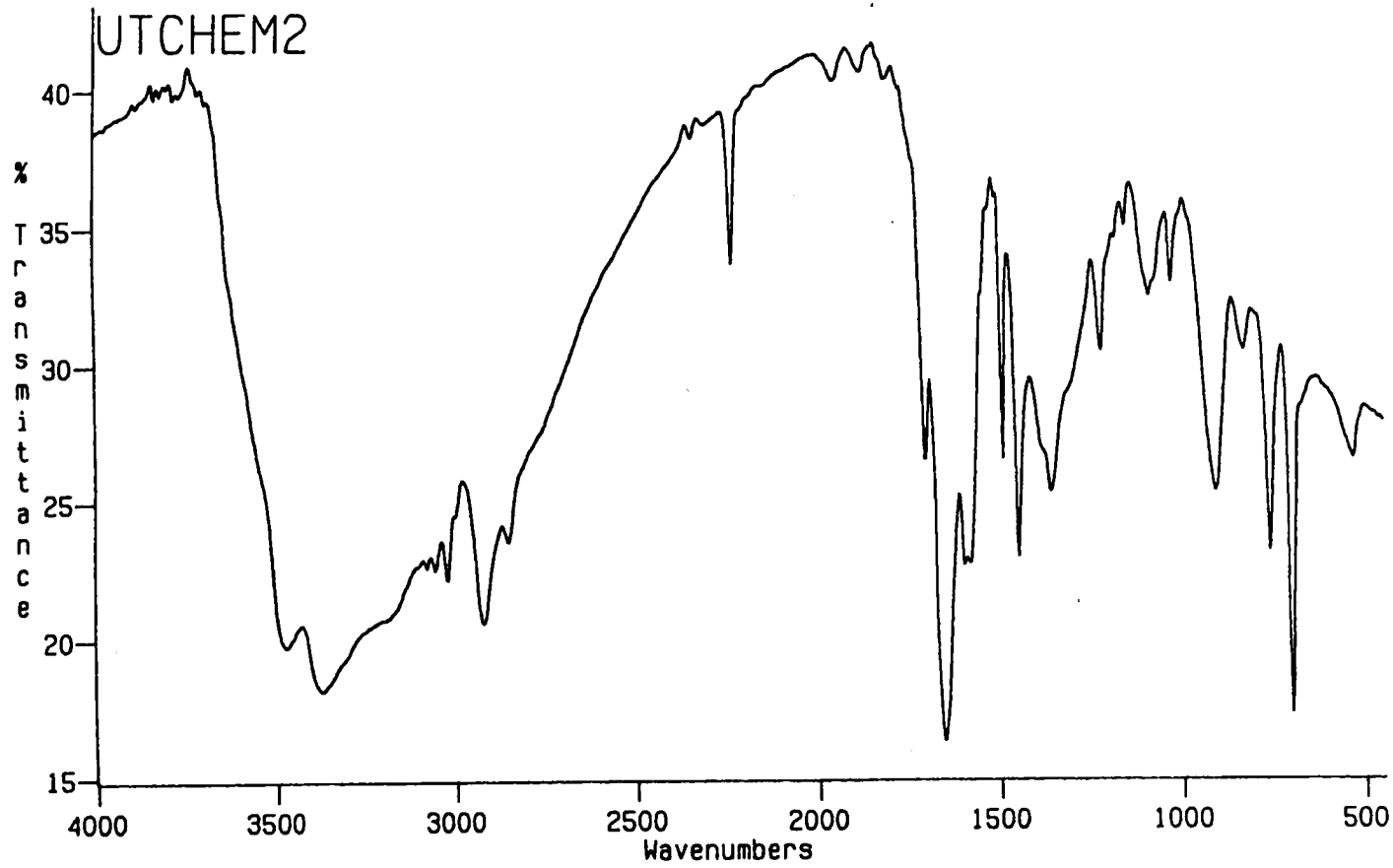


Figure 4.10. IR Spectrum of CL2-093, Amidoxime Resin from AN/STY (50/50)

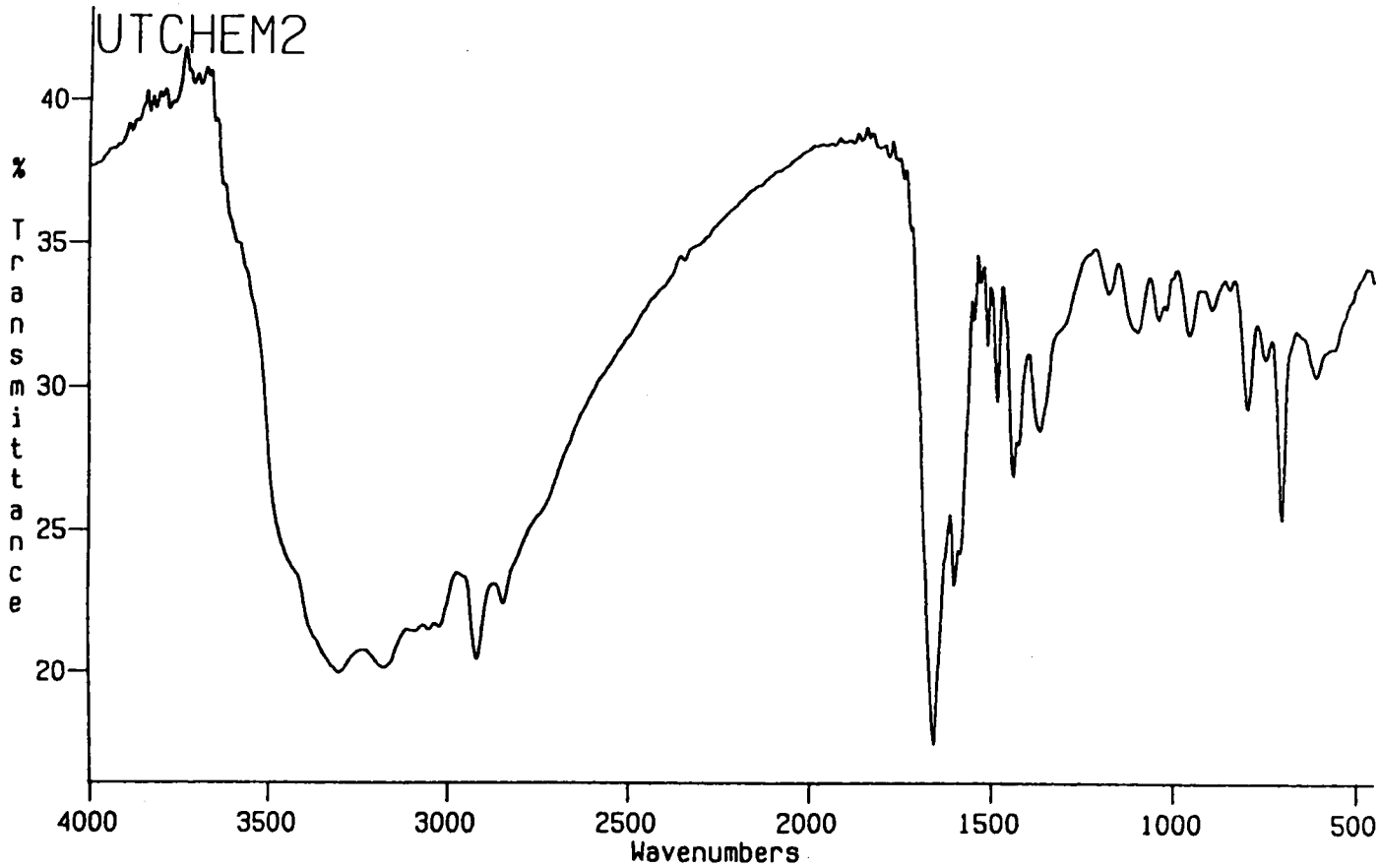


Figure 4.11. IR Spectrum of CL2-083, Amidoxime Resin from 100% Benzonitrile (VBC)

For example, resins CL2-070 (AN), CL2-138 (AN/STY, 75/25), and CL2-143 (AN/STY, 25/75), had solids levels of 37.82, 61.28, and 75.53%, respectively. Again, this is due to the hydrophobicity of styrene.

Due to the possible presence of unreacted nitrile groups and cyclic structures the amidoxime capacity of a resin is determined by its apparent acid and base capacities. Depending on the elution sequence, an amidoxime resin may exist as neutral, protonated, deprotonated, or a combination. The total capacity of an amidoxime resin in mmol/g is simply the average of the acid and base capacities (which are expressed as mequiv/g). For example, CL2-080 most likely exists with some neutral and some protonated amidoxime sites since HCl was at the end of the elution sequence. The base capacity represents the unprotonated amine sites in mequiv/g and is also the capacity of the neutral amidoxime sites in mmol/g. The acid capacity in mequiv/g represents protons from the hydroxyl group on the neutral amidoxime sites as well as those from the hydroxyl and amine groups on the protonated amidoxime sites.
The capacity in mmol/g of protonated amidoxime sites is the (acid capacity - base capacity) / 2 (since there are two acid protons per protonated amidoxime site). The total capacity in mmol/g is the neutral amidoxime capacity plus the protonated amidoxime capacity, or more simply the average of the acid and base capacities.

Metal Ion Studies

Complexing abilities of the amine resins were investigated using acidic metal salt solutions of low concentration. In the studies examining a single metal ion, 10^{-4} N metal nitrate salt solutions in 0.01 N HNO_3 were used. In the studies involving ion competition, a solution which was 10^{-1} N $Fe(NO_3)_3$ and 10^{-4} N $Cu(NO_3)_2$ in 0.01 N HNO_3 was used. The results are reported as "percent M^{n+} complexed" and in terms of the distribution coefficient "*D*".

$$D = \frac{\textit{mequiv } M^{n+} \textit{ complexed / g dry polymer}}{\textit{mequiv } M^{n+} \textit{ free / mL solution}}$$

It should be noted that small differences in the percent M^{n+} complexed can result in large differences in the corresponding distribution coefficients.

The complexing abilities of the resins with Cu^{2+} and Fe^{3+} ions were determined as follows. An amount of polymer corresponding to one milliequivalent of ligand (based on the total amidoxime capacity) was accurately weighed and the matrix equilibrated with 0.01 N HNO_3. The resin was then contacted with 10 mL of a metal ion solution for 30 min, 1 h, or 24 h, as indicated. The systems were considered at equilibrium after 24 h, as no additional metal ion uptake was observed for longer contact times. The concentrations of metal ions in the resulting solutions were determined by atomic absorption/emission spectrometry (Perkin-Elmer model 3100), from

which the percent M^{n+} complexed values and distribution coefficients were calculated.

Results of the complexation studies using amidoximes from 100% AN, AN/STY (75/25), AN/STY (50/50), AN/STY (25/75) , and 100% Benzonitrile (from VBC) are listed in Tables 4.5 - 4.8. A summary of the equilibrium studies is given in Table 4.9.

The results in Table 4.5 indicate the for the amidoxime resins from 100% AN there is a tendency for preferential complexation of Cu^{2+} over Fe^{3+} ions. This preference is most pronounced in the direct competition studies, where in solutions with a 1000:1 excess of Fe^{3+} to Cu^{2+}, the percent Cu^{2+} complexed was 67.3 and the percent Fe^{3+} was 38.9. (Resin CL2-151 is not used in comparisons due to the low total amidoxime capacity.) In the individual ion studies a percent Cu^{2+} complexed of 100.0 and a percent Fe^{3+} complexed of 89.9 was observed. The kinetics studies of resin CL2-095e indicate that after a 1 h contact time equilibrium is almost established.

The amidoxime resin from AN/STY (75/25) shows no affinity for Cu^{2+} or Fe^{3+} (Table 4.6). The percent Fe^{3+} complexed in the individual ion and competition studies was 4.85, and the percent Cu^{2+} complexed values in the individual and competition studies were 0.00 and 0.29, respectively.

No affinity for Cu^{2+} or Fe^{3+} was observed for the unsulfonated resins from AN/STY (50/50) (Table 4.7). The average values for percent Cu^{2+} and Fe^{3+} complexed in the individual ion studies were 3.24 and 3.78, respectively.

Table 4.5

Metal Ion Uptake from $Cu(NO_3)_2$ and/or $Fe(NO_3)_3$ in 0.01 N HNO_3 by Amidoxime Resins from 100% Acrylonitrile

Resin	Cu^{2+}	Fe^{3+}	Ion Competition 1000:1	
			Fe^{3+}	Cu^{2+}
Kinetic Studies: 30 min Contact Time				
CL2-151	5.20[a](1.04)[b]	15.5 (3.49)	6.84 (0.529)	6.84 (1.39)
Kinetics Studies: 1 h Contact Time				
CL2-095e	96.2 (1210)	79.6 (189)	40.0 (32.3)	64.7 (88.8)
Equilibrium Studies: ≥24 h Contact Time				
CL2-095e	100.0 (∞)	89.9 (413)	38.9 (29.7)	67.3 (95.9)
CL2-151	60.0 (28.5)	47.6 (17.3)	26.2 (6.75)	69.8 (44.0)

[a]Percent M^{n+} complexed
[b]Distribution coefficient

Table 4.6

Metal Ion Uptake from $Cu(NO_3)_2$ and/or $Fe(NO_3)_3$ in 0.01 N HNO_3 by Amidoxime Resins from 75% Acrylonitrile / 25%Styrene

Resin	Cu^{2+}	Fe^{3+}	Ion Competition 1000:1	
			Fe^{3+}	Cu^{2+}
	Kinetic Studies: 30 min Contact Time			
CL2-138	0.00[a](0.00)[b]	0.00 (0.00)	2.71 (0.950)	0.00 (0.00)
	Equilibrium Studies: ≥24 h Contact Time			
CL2-138	0.00 (0.00)	4.85 (1.74)	4.85 (1.74)	0.29 (0.0991)

[a]Percent M^{n+} complexed
[b]Distribution coefficient

Table 4.7

Metal Ion Uptake from $Cu(NO_3)_2$ and/or $Fe(NO_3)_3$ in 0.01 N HNO_3 by Amidoxime Resins from 50% Acrylonitrile / 50% Styrene

Resin	Cu^{2+}	Fe^{3+}	Ion Competition 1000:1	
			Fe^{3+}	Cu^{2+}
Kinetic Studies: 30 min Contact Time				
CL2-132	0.00[a](0.00)[b]	0.00 (0.00)	2.71 (0.543)	0.00 (0.00)
Kinetics Studies: 1 h Contact Time				
CL2-111	0.500 (.0078)	0.700 (0.101)	3.56 (0.572)	2.29 (0.365)
Equilibrium Studies: ≥24 h Contact Time				
CL2-111	5.79 (1.25)	0.00 (0.00)	0.00 (0.00)	3.33 (0.698)
CL2-112	2.81 (0.490)	6.49 (1.18)	11.1 (2.12)	6.47 (1.17)
CL2-132	1.11 (0.218)	4.85 (0.994)	2.71 (0.540)	1.93 (0.383)
CL2-117[c]	100.0 (∞)	100.0 (∞)	51.2 (29.6)	0.00 (0.00)
CL2-117[c]	100.0 (∞)	100.0 (∞)	57.4 (28.9)	0.00 (0.00)

[a]Percent M^{n+} complexed
[b]Distribution coefficient
[c]Sulfonated

Table 4.8

Metal Ion Uptake from $Cu(NO_3)_2$ and/or $Fe(NO_3)_3$ in 0.01 N HNO_3 by Amidoxime Resins from 100% Benzonitrile

Resin	Cu^{2+}	Fe^{3+}	Ion Competition 1000:1	
			Fe^{3+}	Cu^{2+}
Kinetics Studies: 1 h Contact Time				
CL2-109	0.00 (0.00)	0.00 (0.00)	17.8 (3.35)	5.87 (0.966)
Equilibrium Studies: ≥24 h Contact Time				
CL2-109	16.9 (4.51)	20.1 (5.58)	29.5 (9.22)	0.250 (0.551)
CL2-118[c]	96.2 (486)	100.0 (∞)	12.4 (2.68)	-

[a]Percent M^{n+} complexed
[b]Distribution coefficient
[c]Sulfonated

Table 4.9

Summary of Metal Ion Uptake from $Cu(NO_3)_2$ and/or $Fe(NO_3)_3$ in 0.01 N HNO_3 by Amidoxime Resins

Support Type	Cu^{2+}	Fe^{3+}	Ion Competition 1000:1	
			Fe^{3+}	Cu^{2+}
	Equilibrium Studies: ≥24 h Contact Time			
AN	100.0[a](∞)[b]	89.9 (413)	38.9 (29.7)	67.3 (95.9)
AN/STY (75/25)	0.00 (0.00)	4.85 (1.74)	4.85 (1.74)	0.29 (0.0991)
AN/STY (50/50)	*3.24 (0.653)	*3.78 (0.724)	*4.60 (0.887)	*3.91 (0.750)
AN/STY (50/50)[c]	*100.0 (∞)	*100.0 ∞)	*54.3 (29.3)	*0.00 (0.00)
Benzo	16.9 (4.51)	20.1 (5.58)	29.5 (9.22)	0.250 (0.551)
Benzo[c]	96.2 (486)	100.0 (∞)	12.4 (2.68)	-

[a]Percent M^{n+} complexed, *Indicates average values
[b]Distribution coefficient
[c]Sulfonated

The competition studies followed the same trend with an average percent Cu^{2+} complexed of 3.91 and an average percent Fe^{3+} of 4.60. A dramatic increase in percent Cu^{2+} complexed and percent Fe^{3+} complexed values in the individual ion studies was observed when sulfonic acid moieties were introduced to these resins. No selectivity between Cu^{2+} and Fe^{3+} was detected as both percent complexed values were 100. In the competition studies the average percent Fe^{3+} complexed was 54.3 while no Cu^{2+} uptake was observed. Further investigation is needed to determine which ligand, the amidoxime or sulfonic acid, is responsible for complexation.

The same trend in complexation was followed by the amidoxime resins from benzonitrile (VBC) upon sulfonation (Table 4.8). While the percent Cu^{2+} and Fe^{3+} complexed values were low in the individual ion studies for the unsulfonated resin, 16.9 and 20.1, respectively, these values increased dramatically to 96.2 and 100.0 upon sulfonation. The competition study values for percent $Cu^{2=}$ complexed and percent Fe^{3+} complexed were 0.250 and 29.5 for the unsulfonated resin, and the percent Fe^{3+} complexed was 12.4 for the sulfonated resin, (experimental error forced the exclusion of the percent Cu^{2+} complexed value).

Conclusions

A series of resins has been prepared in which amidoxime ligands were covalently bound to different polymer supports. These polymer supports were

shown not to be inert matrices, but exhibited a marked influence on the ligand's ability to bind Cu^{2+} and Fe^{3+} from dilute solutions. In the single metal ion studies binding ability of the unsulfonated resins in 0.01 N HNO_3 followed the order: AN > Benzo > AN/STY (50/50) ≈ AN/STY (75/25). A preferential complexation of Cu^{2+} over Fe^{3+} was observed with the AN resins which became more pronounced during competition studies. Sulfonation of the Benzo and AN/STY (50/50) resins increased complexation of both Cu^{2+} and Fe^{3+}, in the single metal ion studies, to approximately 100%. A preferential complexation of Fe^{3+} over Cu^{2+} was observed in the competition studies with the sulfonated Benzo. Such influences of the polymer support may be used in the tailoring of amidoxime resins for the selective removal of targeted metal ions from aqueous solutions.

CHAPTER 5

METAL ION SELECTIVITY INFLUENCES IN INTERPENETRATING POLYMER NETWORKS

Introduction

Interpenetrating polymer networks (IPNs) make up a novel class of resins wherein two different polymer networks are held together by physical entanglement rather than covalent bonds. Four types of IPNs exist and are named for their synthetic preparation. First, IPNs which are prepared by reacting a mixture of two monomer solutions, and their crosslinking agents are called simultaneous IPNs (SINs). Second, IPNs in which a monomer and crosslinking agent are reacted with a crosslinked polymer are known as sequential IPNs (SIPNs). Semi-IPNs are sequential IPNs in which one of the polymers is not crosslinked and pseudo-IPNs are simultaneous IPNs in which one of the polymers is not crosslinked.[93]

Early work in the area of ion exchange IPNs involved the synthesis of a polymer containing both anion and cation exchange sites. This IPN was prepared with poly(vinyl benzylchloride) as one network and polystyrene as the second. The sequential IPN support was then modified by reactions with trimethylamine and concentrated sulfuric acid yielding an aminated VBC network as well as a sulfonated styrene network.[94] Other applications of IPNs

include adhesives, coatings, impact resistant plastics, and thermoplastic elastomers.[95]

It has been shown (Chapters 2 - 4) that the polymer support is not an inert matrix, but can exhibit a marked influence on a ligands ability to bind metal ions. Varying either network of an IPN may lead to changes in the microenvironment of a given ligand, and thus changes in ligand-metal ion interactions.[96,97]

This work examines the complexing abilities of a series of vinyl imidazole (VIm), ethyl acrylate (EA), and hydrolyzed ethyl acrylate or acrylic acid (AA) IPNs with Cu^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}. The role of polymer support is investigated and its influence on binding constants and saturation capacities reported.

Synthesis and Characterization

Brief descriptions of all syntheses follow. Details of these syntheses are found in the experimental chapter.

Network I of all IPNs consisted of polystyrene xerogel (2% crosslinked, 40% toluene) beads which were prepared by suspension polymerization without deviation from the general procedure. All network I copolymers had a particle size of 250 μm - 425 μm. Incorporation of network II is as follows.

Network I was allowed to swell in the monomer solution which contained the indicated (Table 5.1) monomer(s), 10% (mol%) divinyl benzene (DVB), and initiator. The excess monomer solution was filtered from the beads and the

Table 5.1

Characterization of IPN Resins

Resin	Network II	% Solids (g_{dry}/g_{wet})	Capacities (mequiv/g)			Total Cap. (mmol/g)
			Acid	Base	TAEC	
CL1-002	Vlm	55.69	1.65	2.95	1.49	4.60[a](5.10)[b]
CL1-034	VP	68.30	0.405	5.87	0.537	6.27 (5.67)
CL1-046a	Vlm/EA (70/30)[c]	65.40	1.05	2.02	1.36	3.07 (3.63)
CL1-046b	Vlm/EA (30/70)	72.19	1.17	1.24	0.538	2.41 (1.73)
CL1-065a	Vlm/AA[d] (70/30)	63.43	1.76	2.66	0.827	4.42 (5.19)
CL1-065b	Vlm/AA (30/70)	58.88	4.10	1.89	0.182	5.99 (5.76)

Table 5.1 (continued)

Resin	Network II	% Solids (g_{dry}/g_{wet})	Capacities (mequiv/g)			Total Cap. (mmol/g)
			Acid	Base	TAEC	
CL1-076	VIm/EA (70/30)	62.60	1.57	2.28	1.28	3.85 (3.57)
CL1-082a	VIm/EA (50/50)	63.83	0.821	1.38	0.576	1.96 (2.65)
CL1-088	AA	61.25	5.40	-	-	5.40 (5.18)
CL1-089	VIm/AA (50/50)	56.96	1.79	2.83	0.946	5.62 (5.24)
CL1-090	VIm/AA (70/30)	57.12	2.87	2.75	0.390	4.62 (5.10)

[a]Experimental
[b]Theoretical, calculated based on residual monomer solution
[c]Mole %
[d]Acrylic acid from hydrolyzed ethyl acrylate

volume measured. The swollen beads were then polymerized via suspension polymerization resulting in the formation of the IPN. The beads were washed with water, extracted with methanol, and eluted with 1 L each: H_2O, 4 wt% NaOH, H_2O, 4 wt% HCl, and H_2O until a neutral drip was obtained. The poly(4-vinylpyridine) (VP), VIm, and VIm/EA resins were characterized and used without further modification. Results of the characterizations are given in Table 5.1.

It is important to note that after elution the VIm and VP exist in two forms, a protonated and unprotonated form. Thus, an acid and base capacity are required to find the total capacity of the IPN. The total capacity of the IPN is dependent upon inclusion of network II into network I, thus the theoretical total capacity is calculated from the residual monomer solution filtered from the beads after swelling. A total anion exchange capacity (TAEC) is also performed to determine the number protonated nitrogens. In the case of VP, VIm , and VIm/EA the value for the acid capacity should equal that of the TAEC, since the only acid sites are those of the protonated nitrogens.

As expected with the VIm/EA IPNs, the solids level increases with an increasing amount of EA. The solids levels for 100% VIm, VIm/EA (70/30), and VIm/EA (30/70) are 55.69, 65.40, and 72.19% respectively. In addition the VIm capacity, or total capacity, decreases with increasing EA content with values of 4.60, 3.07, and 2.41 mmol/g.

The acrylic acid IPNs are obtained by hydrolysis of the EA or VIm/EA resins. Hydrolysis of the VIm/EA (70/30) was carried out in concentrated HCl while all other hydrolyses were performed using a 2 N KOH solution which was 90% dioxane. The resins were the eluted with 1 L each: H_2O, 4 wt% NaOH, H_2O, 4 wt% HCl, and H_2O until a neutral drip was obtained.

Capacities of the IPNs containing AA are carried out as above with the exception of 100% AA in which no base capacity is required. For the VIm/AA resins, the total capacity is equal to the sum of the acid and base capacities, wherein the VIm capacity is equal to the base capacity plus the TAEC, and the AA capacity is equal to the acid capacity less the TAEC. For example, resin CL1-065a, VIm/AA (70/30), has acid, base and total anion exchange capacities of 1.76, 2.66, and 0.827 mequiv/g, respectively. The VIm capacity is then 2.66 + 0.827 or 3.49 mequiv/g and the AA capacity is 1.76 - 0.827 or 0.93 mequiv/g.

Metal Ion Studies

Complexing abilities of the IPNs were investigated using metal nitrate salt solutions of varying concentrations in pH 5, 0.6 N acetate buffer. Examination of ligand-metal ion interactions over a range of contact solution concentrations allows for the determination of an equilibrium (binding) constant, *K*, as opposed to a distribution coefficient, D, as reported in Chapters 2 - 4.

Initial analyses were done based on simple adsorption isotherms, developed by Langmuir[98], in which all binding sites were thought to behave

identically. The amount of metal ion complexed and the amount of metal ion free in solution are determined and reported in terms of r and c where r is the amount of metal ion complexed per gram of dry resin (mequiv/g) and c is the amount of free metal ion remaining in solution (mequiv/mL). A plot of r vs. c yields the binding isotherm which follows the equation

$$r = \frac{ac}{b + c}$$

where r and c are described above, a is the saturation capacity (maximum value of r), and b is the inverse of the binding constant or $1/K_{11}$, the subscript indicating formation of a 1:1 complex.

The binding constant K_{11} may also be described by the equilibrium expression

$$K_{11} = \frac{[LS]}{[L][S]}$$

where [LS] is the concentration of the ligand-metal ion complex, [L] is the concentration of free ligand, and [S] is concentration of free metal ion. Realizing

$$r = [LS]$$

and

$$c = [S]$$

Mathematical manipulation leads to the equation

$$\frac{c}{r} = \frac{1}{S_t}c + \frac{1}{K_{11}S_t}$$

where S_t is the saturation capacity and is defined as

$$S_t = [LS] + [L]$$

The binding constant and saturation capacity may be obtained from a plot of c/r vs. c, or y-reciprocal plot,[99] where

$$S_t = \frac{1}{slope}$$

and

$$K_{11} = \frac{slope}{intercept}$$

Studies by other group members[100,101] indicate that in the case of polymer-supported ligands all binding sites are not identical. In most cases at least two types of binding sites exist. Thus the r vs. c curve is best described as a double hyperbolic function where

$$r = \frac{ax}{b + x} + \frac{cx}{d + x}$$

Use of this equation yields two saturation capacities a and c, and two corresponding dissociation constants ($1/K_{11}$) b and d.

In all studies an amount of polymer corresponding to one milliequivalent of ligand (based on the total capacity) was accurately weighed and the matrix

equilibrated with 0.6 N acetate buffer at pH 5. The resin was then contacted with 10 mL of metal ion solution for seven days. For the single metal ion studies, R_i (milliequivalents of metal ion contacted) values ranged from 0.050 - 2.5 for Cu^{2+}, 0.050 - 2.5 for Zn^{2+}, 0.050 - 3.0 for Co^{2+}, and 0.10 - 3.5 for Ni^{2+}. For the competition studies, R_i values ranged from 0.050 - 3.0 where each metal provided half of the R_i. Unless indicated, the metal ion solutions for the competition studies were not mixed prior to contact with the Co^{2+} solution added first. The concentrations of metal ions in the resulting solutions were determined by atomic absorption/emission spectrometry (Perkin-Elmer model 3100), from which r and c values were calculated.

Results of initial binding constant studies are listed in Table 5.2 and were calculated base upon a single hyperbolic function. The binding isotherm and y-reciprocal plots for the 100% AA IPN contacted with Zn^{2+} and Co^{2+} are given in Figures 5.1 and 5.2 respectively. Binding isotherms and y-reciprocal plots for the VIm/AA (70/30) IPN with Cu^{2+} and the VIm/AA (50/50) IPN with Ni^{2+} are shown in Figures 5.3 and 5.4 respectively.

The results of the binding constant studies of VIm, VIm/EA (50/50), VIm/AA (50/50) and AA IPNs with Cu^{2+} are listed in Table 5.3. These values were calculated using double hyperbolic functions and therefore two binding constants and two saturation capacities are given. A total saturation capacity (the sum of the individual saturation capacities) is also listed. The binding

Table 5.2

Binding Constants and Saturation Capacities of IPN's[a]

Network II	Cu(II)		Zn(II)		Co(II)		Ni(II)	
	K_{11}[b]	S_t[c]	K_{11}	S_t	K_{11}	S_t	K_{11}	S_t
AA	-	-	32.0	4.0	68.2	2.4	-	-
Vlm/AA (70/30)[d]	3080	2.2	-	-	-	-	-	-
Vlm/AA (50/50)	-	-	-	-	-	-	326	2.3

[a]Cory Grady resins: CG3-122a, CL2-230, and CG3-114a respectively
[b]Binding constant (N^{-1})
[c]Saturation capacity (mequiv/g)
[d]Mole %

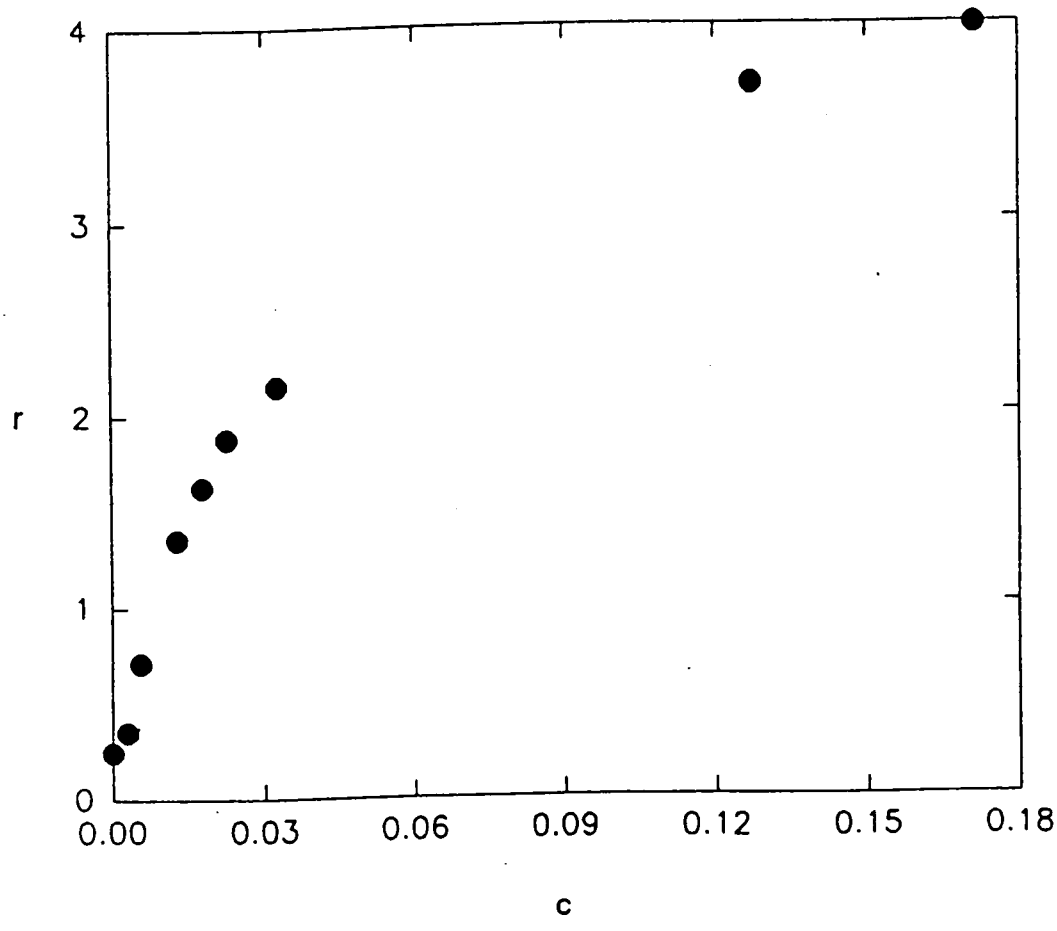
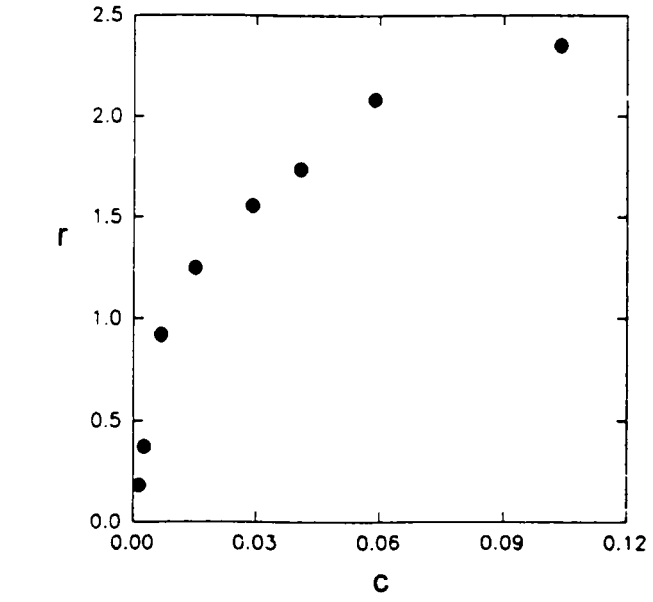


Figure 5.1. Binding Isotherm Plot of 100% AA with Zn(II)



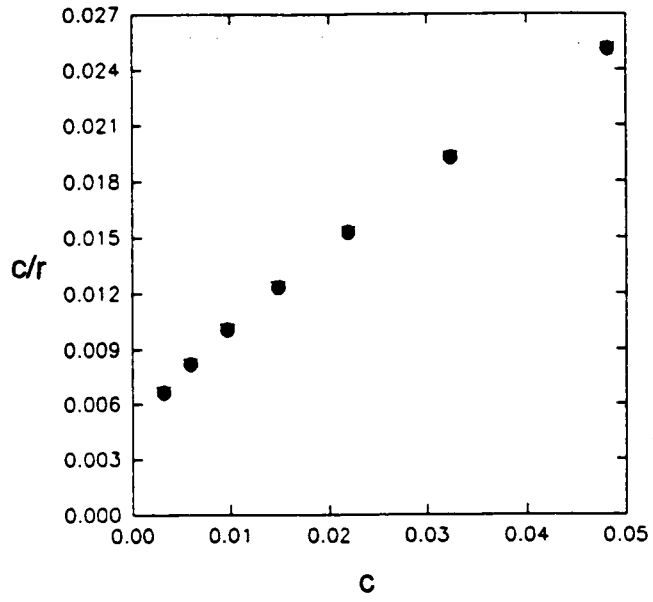


Figure 5.2. Binding Isotherm and y-Reciprocal Plots of 100% AA with Co(II)

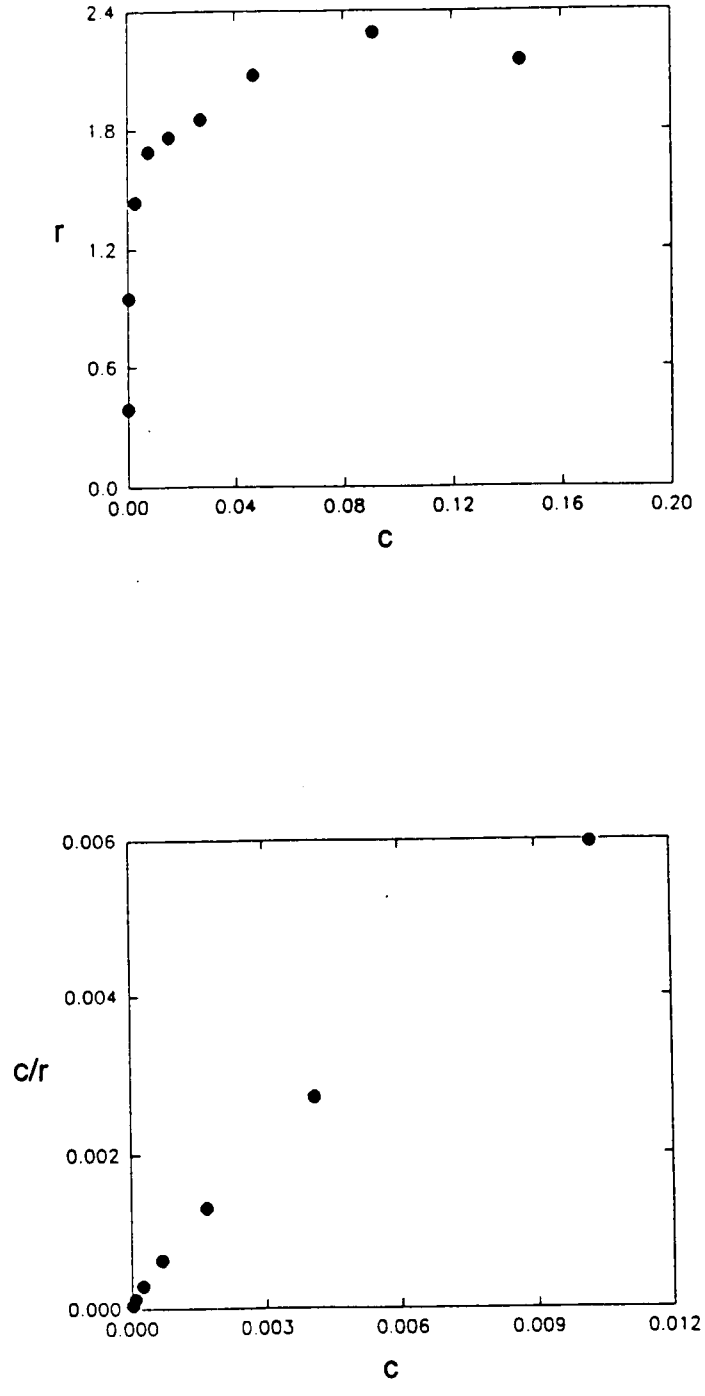


Figure 5.3. Binding Isotherm and y-Reciprocal Plots of Vlm/AA (70/30) with Cu(II)

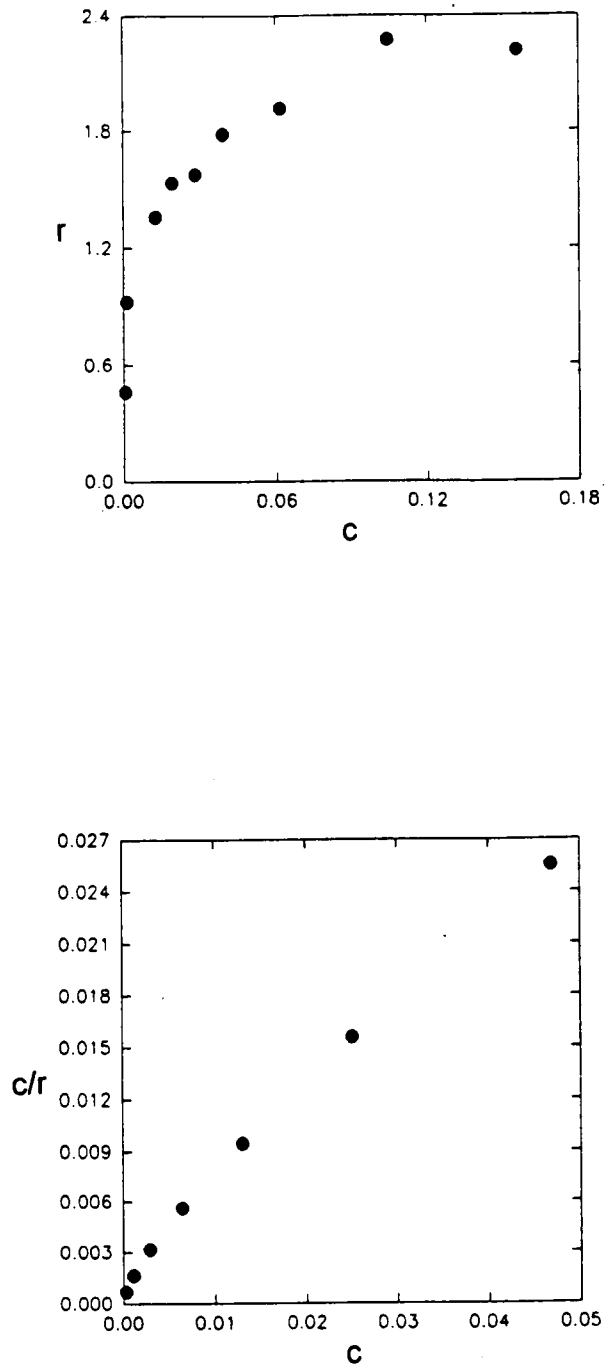


Figure 5.4. Binding Isotherm and y-Reciprocal Plots of Vlm/AA (50/50) with Ni(II)

Table 5.3

Binding Constants and Saturation Capacities of Cu(II) with IPN's[a] using Double Langmuir Isotherms

Network II	Binding Type 1		Binding Type 2		Total S_t
	K_{11}[b]	S_t[c]	K_{11}	S_t	
VIm	15,900	2.0	381	1.5	3.5
VIm/EA (50/50)[d]	200,000	0.36	328	0.45	0.81
VIm/AA (50/50)	32,800	1.3	336	1.6	2.9
AA	284	2.0	40.4	1.5	3.5

[a]Resins CL1-002, CL1-082a, CL1-089, and CL1-088 respectively
[b]Binding constant (N^{-1})
[c]Saturation capacity (mequiv/g)
[d]Mole %

isotherms and y-reciprocal plots for these studies are shown in Figures 5.5 - 5.8. The results indicate that binding strength increases in the order AA < Vlm < Vlm/AA (50/50) < Vlm/EA (50/50) for type 1 binding sites. The total saturation capacities increase in the order Vlm/EA (50/50) < Vlm/AA (50/50) < Vlm = AA. Although the Vlm/EA (50/50) IPN exhibits the largest K_{11} value for type 1 binding sites (200,000 N^{-1}), it has the lowest total S_t (0.81 mequiv/g). The K_{11} values for type 2 binding sites are approximately equal for Vlm, Vlm/EA, and Vlm/AA (~350 N^{-1}) with that of AA being considerably less (40.4 N^{-1}).

Competition study results of the Vlm, Vlm/EA (50/50), Vlm/AA (50/50) and AA with simultaneous contact of Cu^{2+} and Co^{2+} are given in Table 5.4. The binding isotherms for these studies are shown in Figures 5.9 - 5.12 with a separate isotherm given for each metal. The isotherms for Cu^{2+} in the competition studies were almost identical to those in the single metal ion studies. However, binding constants and saturation capacities for the IPNs with Co^{2+} could not be determined as the experimental values of r and c did not fit the double Langmuir isotherm. The results indicate that binding strength increases in the order AA < Vlm/AA (50/50) < Vlm < Vlm/EA (50/50) for type 1 binding sites. The total saturation capacities increase in the order Vlm/EA < AA < Vlm/AA (50/50) < Vlm. As with the single metal ion studies, the Vlm/EA (50/50) exhibits the largest K_{11} (1,400,000 N^{-1}) and the smallest total S_t (0.73 mequiv/g). It should be noted that when the metal ion solutions were

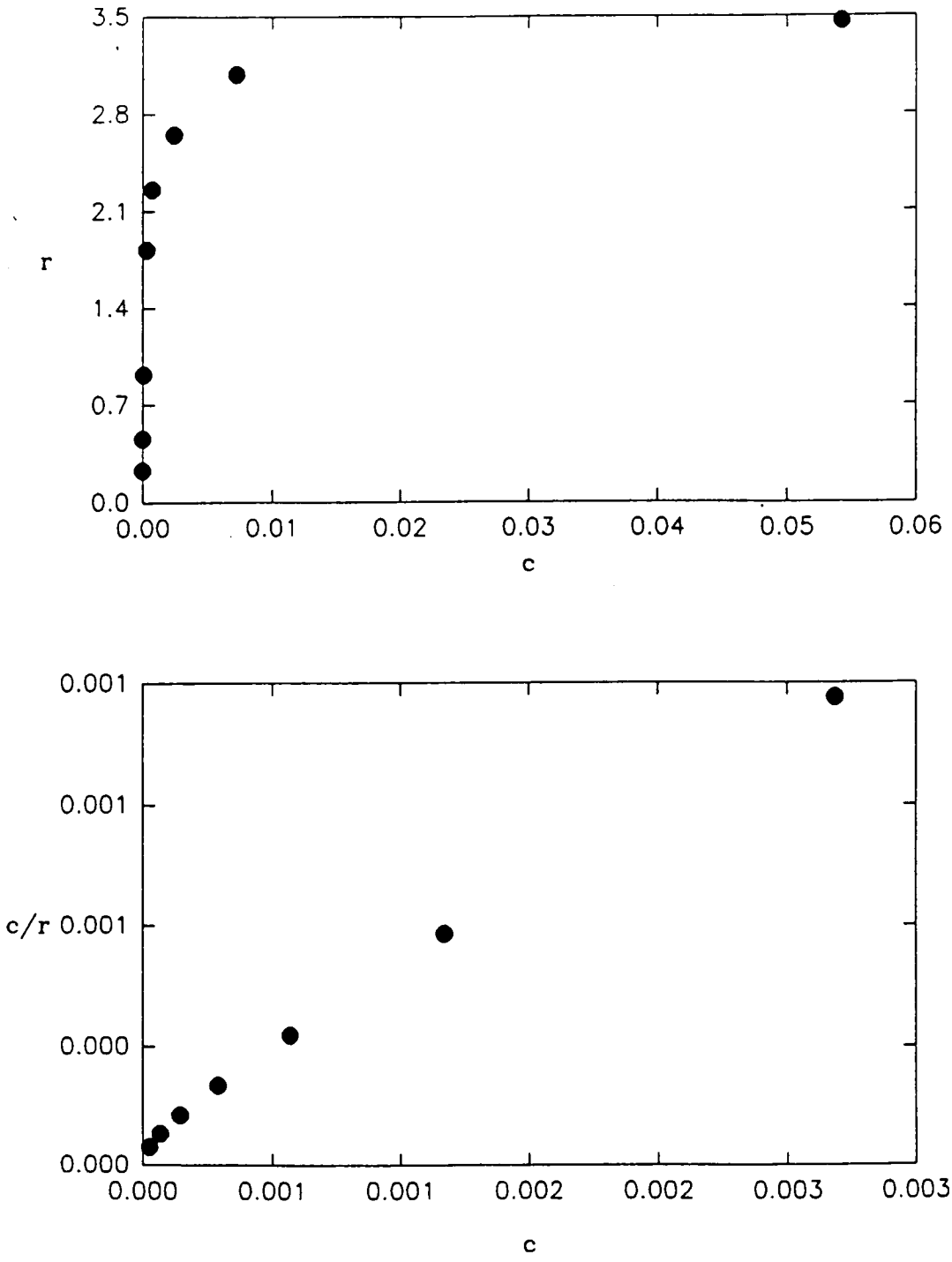


Figure 5.5. Binding Isotherm and y-Reciprocal Plots of 100% Vim with Cu(II)

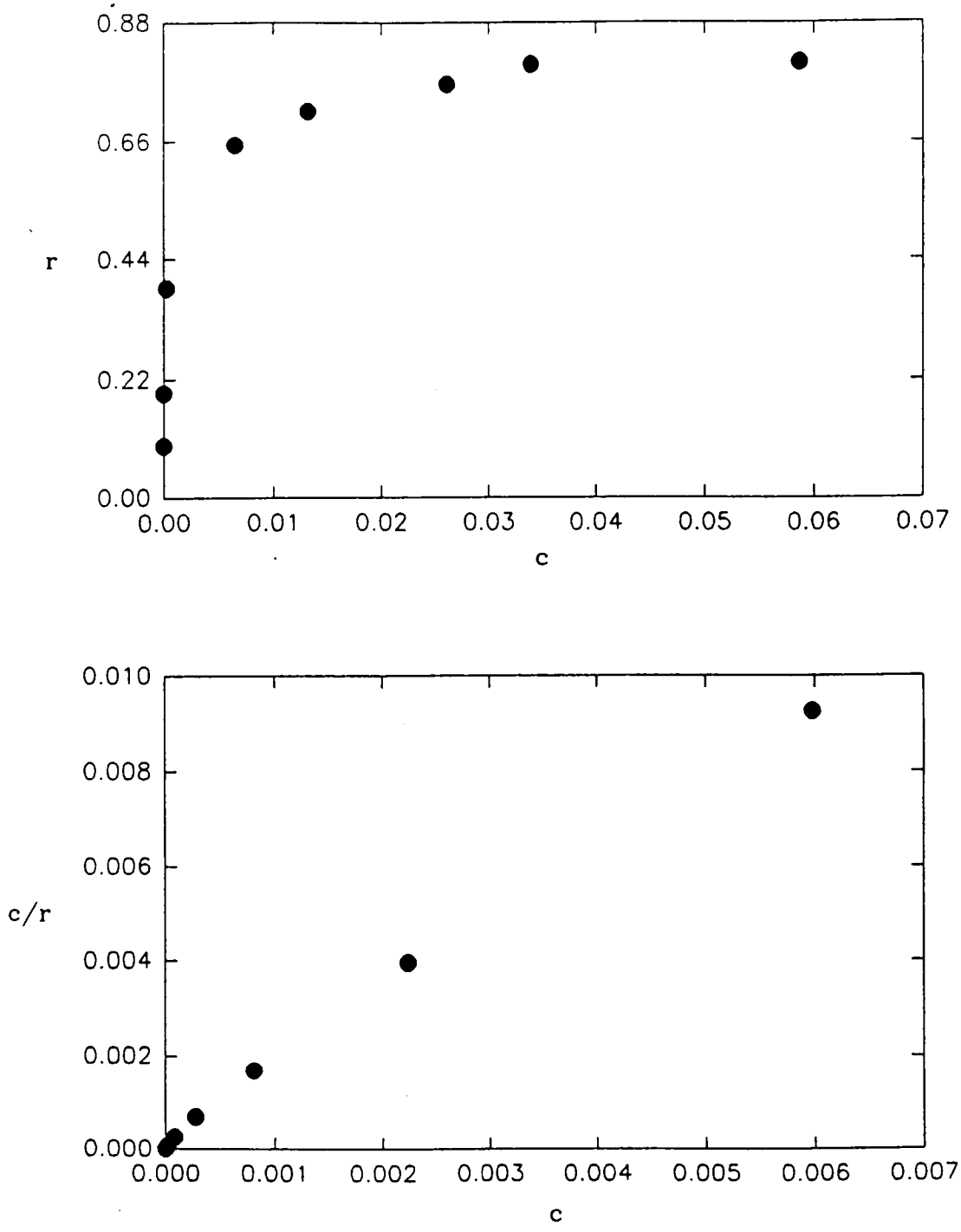


Figure 5.6. Binding Isotherm and y-Reciprocal Plots of VIm/EA (50/50) with Cu(II)

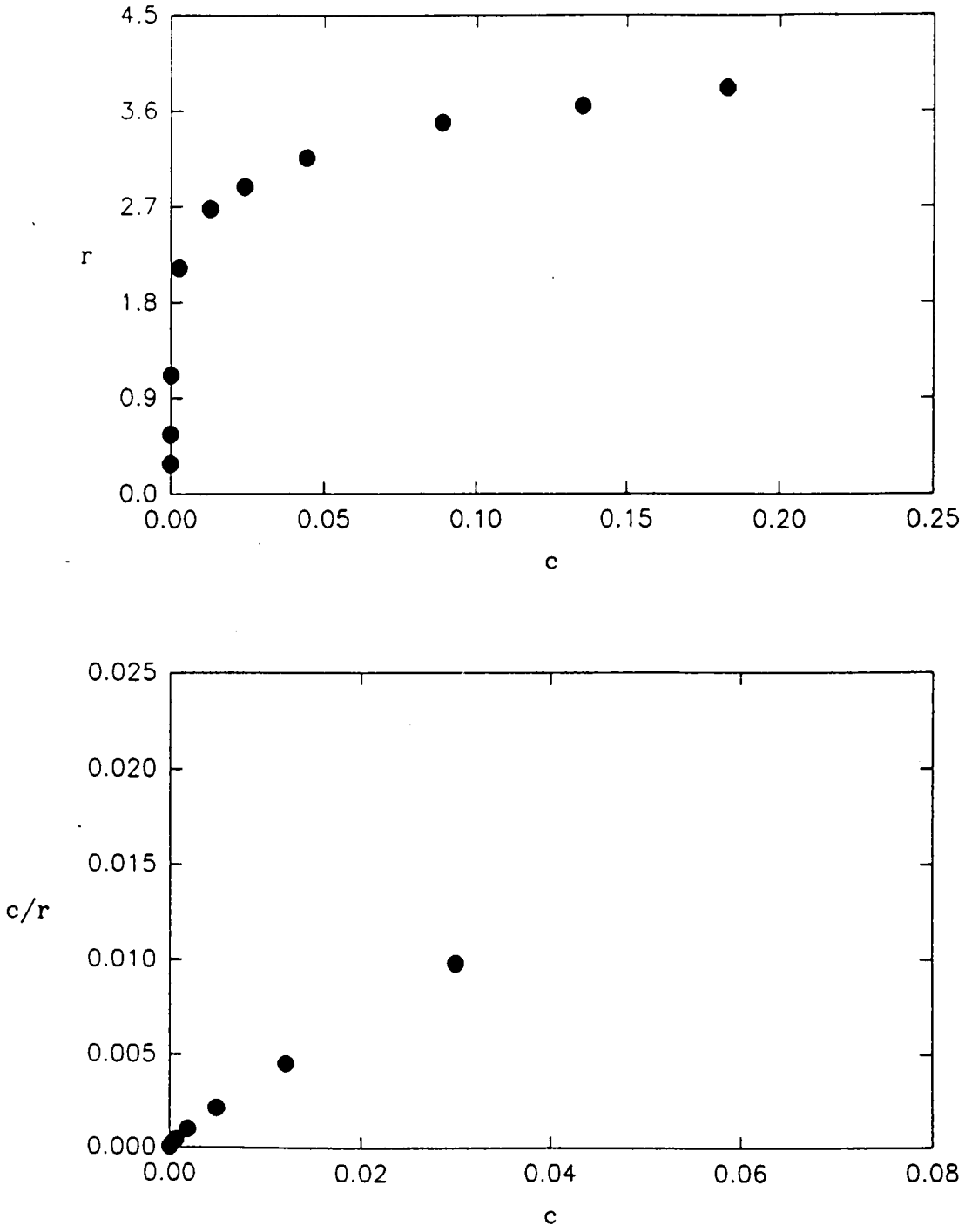


Figure 5.7. Binding Isotherm and y-Reciprocal Plots of Vlm/AA (50/50) with Cu(II)

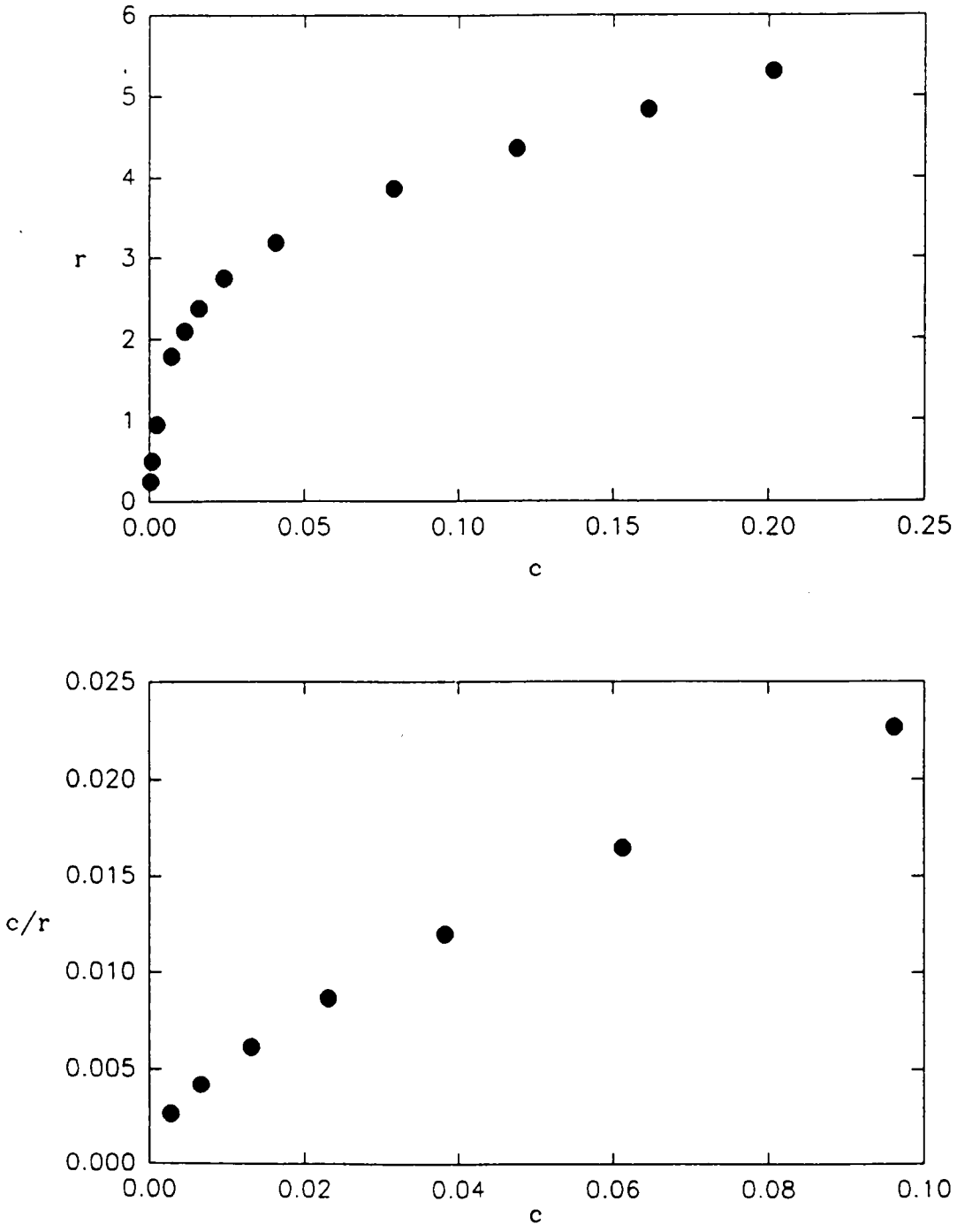


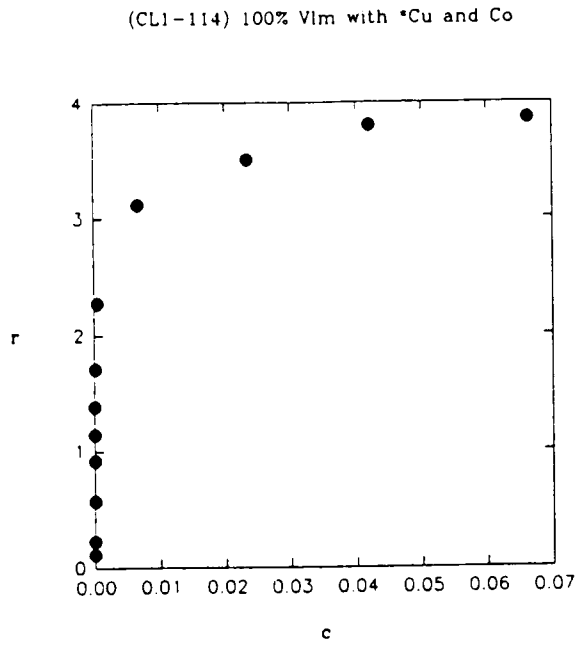
Figure 5.8. Binding Isotherm and y-Reciprocal Plots of 100% AA with Cu(II)

Table 5.4

Binding Constants and Saturation Capacities of Cu(II) with IPN's[a]
Competition Studies with Co(II)

Network II	Binding Type 1		Binding Type 2		Total S_t
	K_{11}[b]	S_t[c]	K_{11}	S_t	
VIm	26,100	2.2	258	1.4	3.6
VIm[d]	72,600	1.1	1830	2.1	3.2
VIm/EA (50/50)[e]	1,400,000	0.23	1310	0.50	0.73
VIm/AA (50/50)	19,000	1.4	395	1.5	2.9
AA	207	2.4	2.74×10^{11}	0.020	2.4

[a]Resins CL1-002, CL1-082a, CL1-089, and CL1-088 respectively
[b]Binding constant (N^{-1})
[c]Saturation capacity (mequiv/g)
[d]Metal ions mixed prior to contact
[e]Mole %



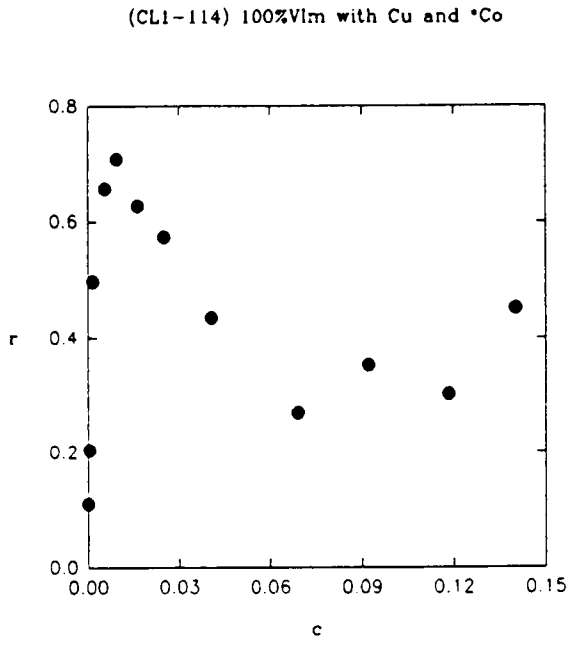
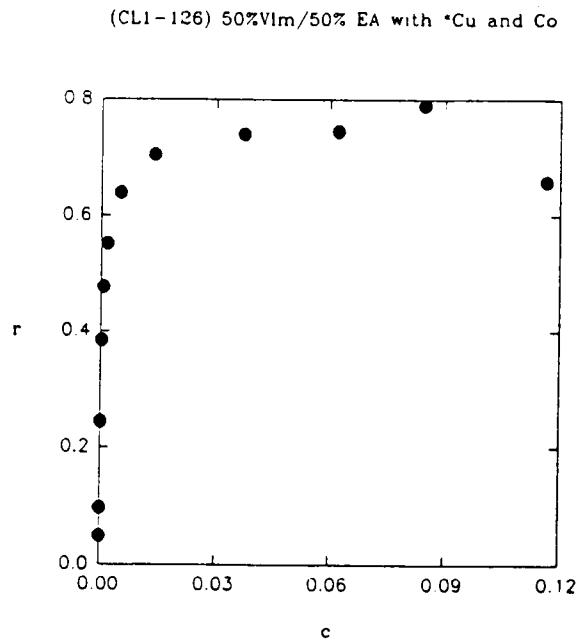


Figure 5.9. Binding Isotherms of Vim with Cu(II) and Co(II)



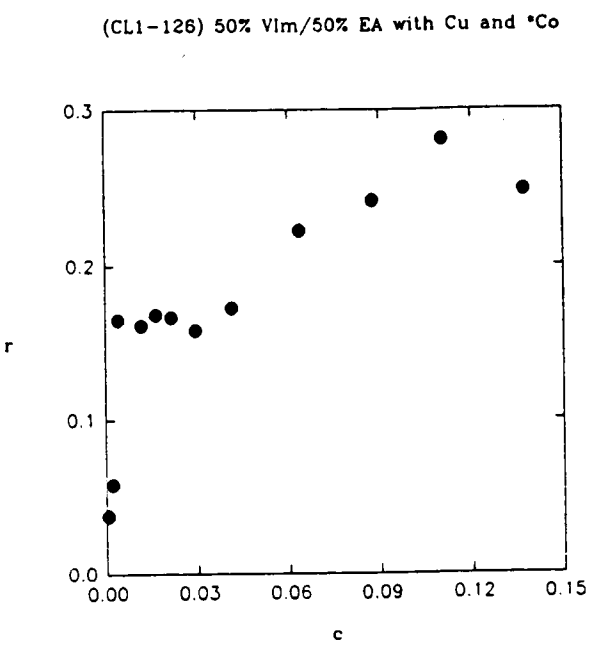
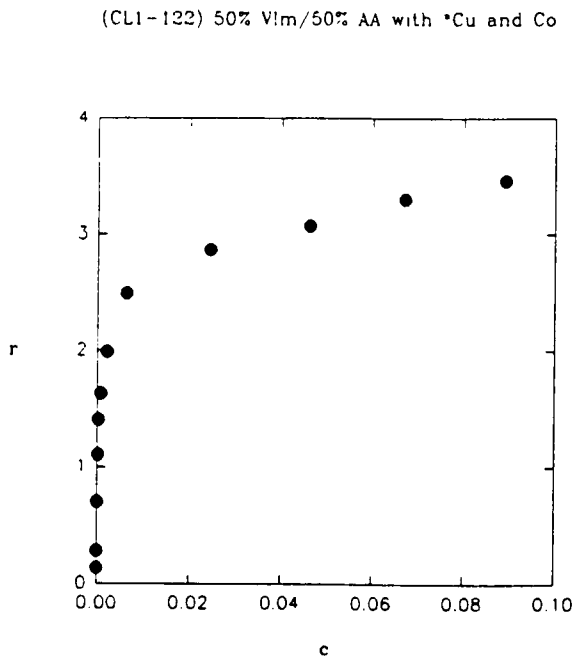


Figure 5.10. Binding Isotherms of Vlm/EA (50/50) with Cu(II) and Co(II)



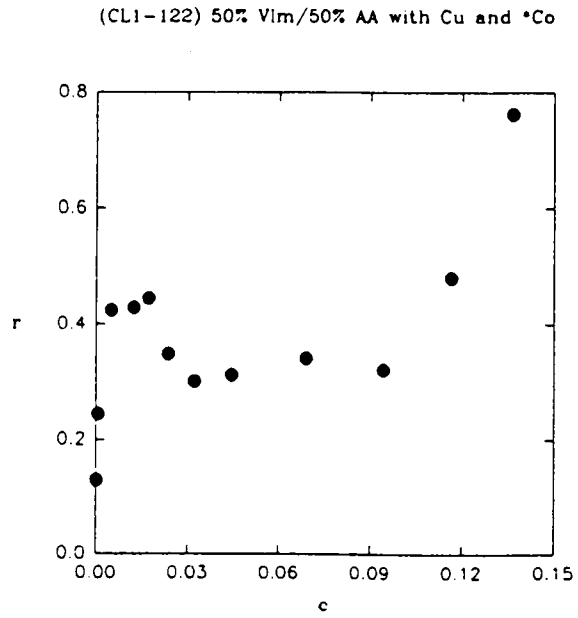
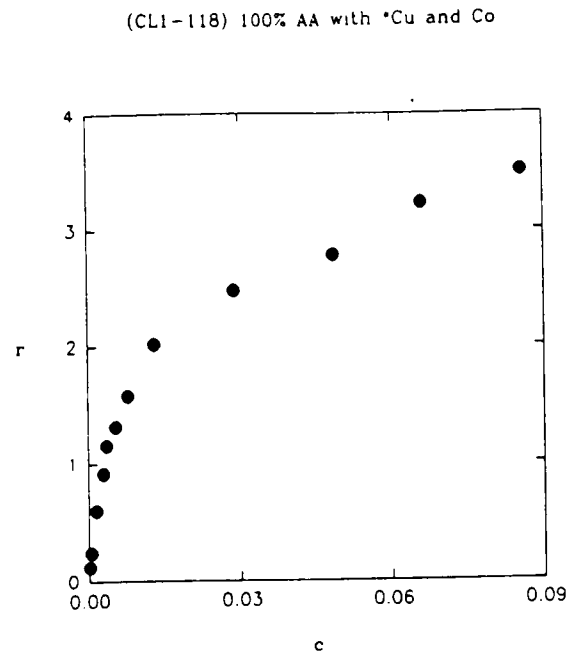


Figure 5.11. Binding Isotherms of Vim/AA (50/50) with Cu(II) and Co(II)



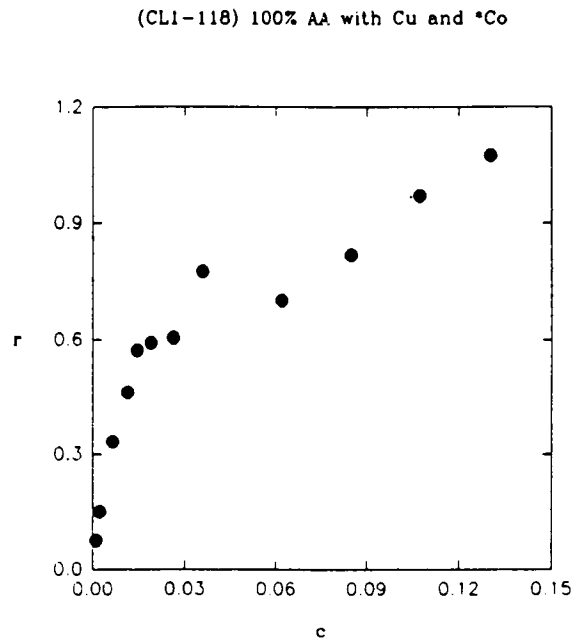


Figure 5.12. Binding Isotherms of 100% AA with Cu(II) and Co(II)

mixed prior to contact, the VIm type 1 binding site K_{11} value increased from 26,100 N^{-1} (for the unmixed solutions) to 72,600 N^{-1}.

Conclusions

A series of interpenetrating polymer networks has been prepared in which the microenvironment around the VIm ligand has been altered. The polymer support was shown not to be an inert matrices, but exhibited a marked influence on the ligand's ability to bind Cu^{2+}. In single metal ion studies K_{11} values increased in the order: AA < VIm < VIm/AA (50/50) < VIm/EA (50/50) with corresponding values of 284, 15,900, 32,800, and 200,000, respectively. When Cu^{2+} ions were put in competition with Co^{2+} ions the K_{11} values (for Cu^{2+} complexation) followed the order: AA < VIm/AA (50/50) < VIm < VIm/EA (50/50) with corresponding values of 207, 19,000, 72,600, and 1,400,000, respectively. Such microenvironmental effects may be used in the tailoring of IPNs for the selective removal of targeted metal ions from aqueous solutions.

CHAPTER 6

EVALUATION OF THE IRVING-WILLIAMS SERIES OF STABILITY USING POLYMER-SUPPORTED LIGANDS

Introduction

As mentioned in Chapter 2 of this work, development of metal ion extractants has relied upon experimental evidence as well as inorganic principles such as valence bond theory, Pearson's hard and soft acid and base theory, chelate or macrocyclic effects, and the Irving-Williams series of stability.[10] Although these principles most often describe interactions between small molecule coordinators and metal ions, they also serve as a useful starting point in the development of polymer-supported coordinating reagents.[34]

The Irving-Williams series was one of the earliest correlations of trends in metal complex stability.[102] H. Irving and R.J.P. Williams found that formation constants of dipositive metal ion complexes follow the order: $Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$.[102,103] This series of stability is insensitive to the particular ligand involved and reflects electrostatic as well as ligand field effects.[103] Figure 6.1 illustrates the Irving-Williams series of stability with four different ligands.

Pearson's hard and soft acid and base principles are often considered in conjunction with the Irving-Williams series in the development of metal ion

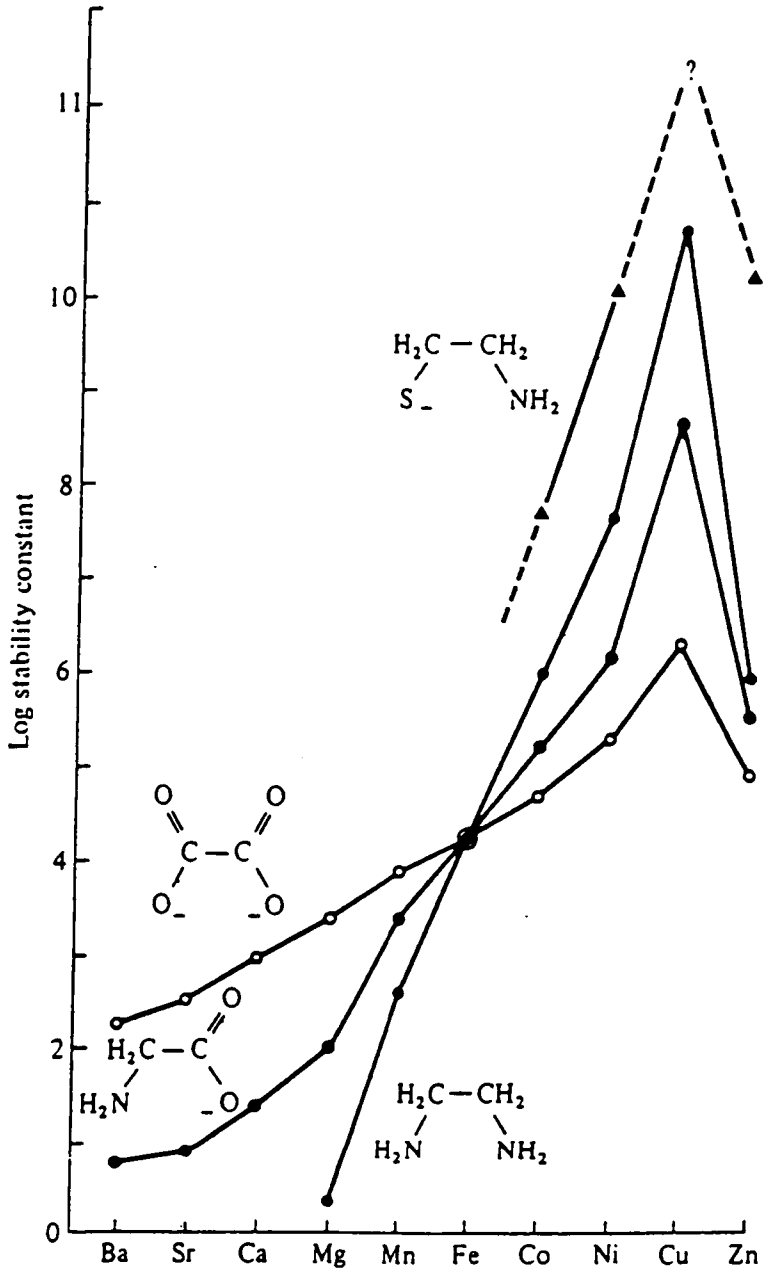


Figure 6.1.[106] The Irving-Williams Series of Stability

extractants. These principles state that harder acids (metal ions with few or no *d* electrons) preferentially bind with harder bases (O > N > S), and softer acids preferentially bind with softer bases (S > N > O).[104] This idea is also illustrated in Figure 6.1, where acid softness increases across the series.[105]

Although these principles serve as a useful starting point in the development of ion selective polymer-supported extractants, limitations due to the polymer itself cannot be overlooked. Accessibility into the polymer matrix may be limited due to hydrophobicity of the polymer support.[42] More importantly, steric restrictions upon chelate formation may arise due to limited mobility of the ligand bound to the polymer support.[34] Results consistent with the Irving-Williams series of stability have been reported using polymer-supported reagents to extract Ni - Zn,[30] and Co - Zn.[34,85,86] However, when more complete metal ion series were examined (i.e., Fe - Zn), results inconsistent with the Irving-Williams series of stability were obtained.[10,107]

This work examines the binding ability of five polymer-supported extractants with dipositive metal ions of the Irving-Williams series (Mn - Zn).

Synthesis

Brief descriptions of all syntheses are found in Chapters 2 and 3 of this work. Characterizations of the resins used are also found in these chapters. Details of these syntheses are found in the experimental chapter.

All copolymer beads were microporous (i.e., gel) with a crosslinking level of 2 wt% divinylbenzene (DVB). The vinylbenzyl chloride-*co*-methyl methacrylate (VBC/MMA) beads were prepared with a monomer ratio of 50/50 mol%. Structures of the functionalized resins used in this study are shown in Figure 6.2.

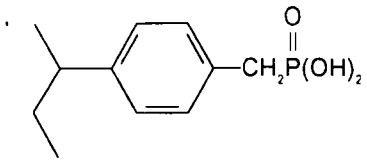
Metal Ion Studies

Complexing abilities of the five resins were investigated using acidic metal salt solutions of low concentration. Studies examined individual metal ions in which 10^{-4} N metal chloride solutions in either 0.01 N or 0.1 N HCl were used. The results are reported as "percent M^{2+} complexed" and in terms of the distribution coefficient "*D*".

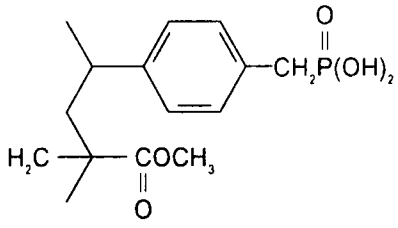
$$D = \frac{\textit{mequiv } M^{n+} \textit{ complexed / g dry polymer}}{\textit{mequiv } M^{n+} \textit{ free / mL solution}}$$

It should be noted that small differences in the percent M^{2+} complexed (exceeding 98%) can result in large differences in the corresponding distribution coefficients.

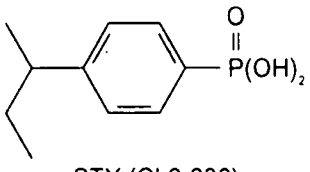
The complexing abilities of the resins with Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions were determined as follows. An amount of polymer corresponding to one milliequivalent of ligand (based on the phosphorus



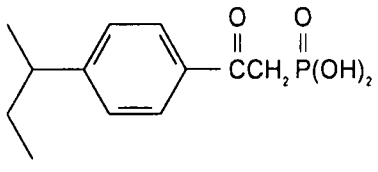
VBC (CL2-237)



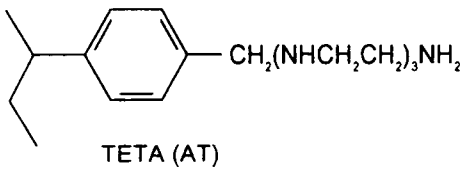
VBC/MMA (CL2-225)



STY (CL2-236)



Acetyl (CL2-218)



TETA (AT)

Figure 6.2. Resins Used in Irving-Williams Study

capacity, with the exception of TETA which was based on the total nitrogen capacity divided by the number of nitrogens in the ligand) was accurately weighed and the matrix equilibrated with the appropriate acid. The resin was then contacted with 10 mL of a metal ion solution for 24 h. The systems were considered at equilibrium after 24 h. The metal ion concentrations in the resulting solutions were determined by atomic absorption spectrometry (Perkin-Elmer model 3100), from which the percent M^{2+} complexed values and distribution coefficients were calculated.

Results of the complexation studies using phosphonic acid resins with Irving-Williams series metal ions in 0.1 N HCl are listed in Table 6.1. These results are depicted graphically in Figure 6.3. Clearly, the metal ion uptake under these conditions does not follow that of the Irving-Williams series of stability. Each resin exhibited it's highest percent M^{2+} complexed values of the series with Fe^{2+}, which is inconsistent with the Irving-Williams series of stability, where Cu^{2+} is preferentially bound. One possible explanation is the oxidation of Fe^{2+} to Fe^{3+} during the studies. However, all Fe^{2+} solutions were sparged with nitrogen and checked with NaSCN. No red color was observed upon addition of NaSCN indicating minimal (if any) oxidation to Fe^{3+}. Observed percent Mn^{2+} complexed values were also much higher than expected, given that the Irving-Williams stability series indicates these values should be the lowest of the metal ions studied. With the exception of the STY phosphonic acid resin, essentially identical percent M^{2+} complexed values were observed for Co^{2+} and Ni^{2+} for a

Table 6.1

Metal Ion Uptake from MCl_2 in 0.1 N HCl by Phosphonic Acid Resins

Copolymer	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Acetyl	72.3[a] (98.4)[b]	95.8 (860)	52.2 (41.9)	52.0 (40.0)	66.0 (74.4)	50.9 (39.1)
VBC/MMA	15.0 (7.10)	41.2 (28.2)	10.6 (4.07)	10.5 (4.03)	17.2 (7.11)	12.3 (5.67)
VBC	49.2 (50.6)	94.6 (912)	36.3 (30.9)	36.7 (31.4)	44.9 (44.1)	35.6 (28.8)
STY	31.6 (22.4)	87.3 (334)	19.2 (11.4)	17.7 (10.3)	27.1 (17.2)	20.8 (12.7)

[a]Percent M^{2+} complexed
[b]Distribution coefficient

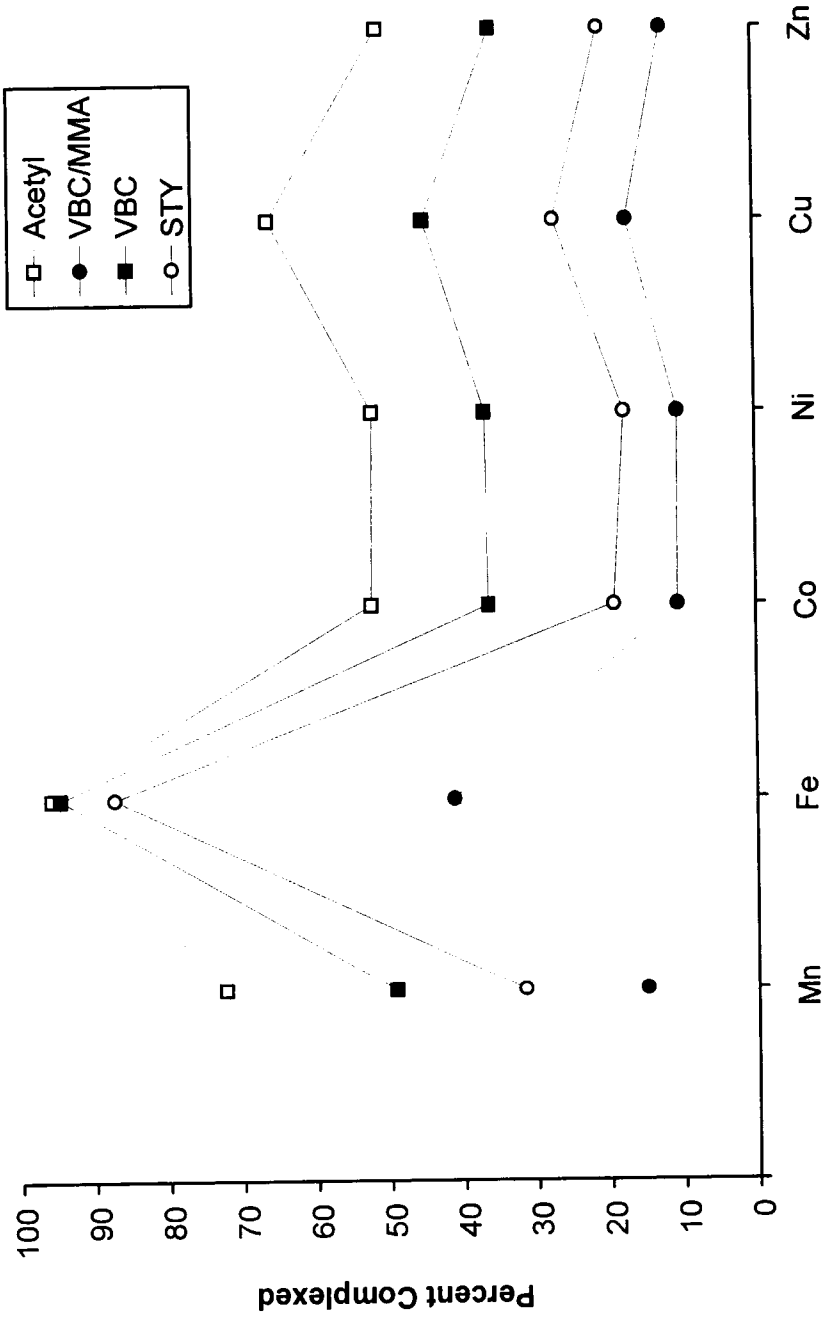


Figure 6.3. Percent M^{2+} Complexed by Phosphonic Acid Resins

given resin. This trend has also been observed with polymer-supported oximes.[10]

Superimposed in these results is the fact that the polymer support to which the phosphonic acid ligand is bound influences that ligand's ability to bind the indicated metal ion. For each metal ion studied the percent M^{2+} complexed values increase with resins in the order: VBC/MMA < STY < VBC < Acetyl.

Results of the complexation studies using the phosphonic acid and TETA (triethylenetetramine) resins with Irving-Williams series metal ions in 0.01 N HCl are given in Table 6.2. Each phosphonic acid resin exhibited percent M^{2+} complexed values of 100.0 for all metal ions studied, with the exception of VBC/MMA and STY which had percent Zn^{2+} complexed values of 94.6 and 98.4 respectively. The TETA resin was consistent with the Irving-Williams series of stability in that Mn^{2+} exhibited the lowest percent complexed value (0.00), Cu^{2+} the highest value (90.7), and a Zn^{2+} value less than Cu^{2+} (21.3). However, the percent M^{2+} complexed values for Fe^{2+}, Co^{2+} and Ni^{2+} (20.1, 17.4, and 6.12 respectively) did not follow the Irving-Williams series of stability.

Conclusions

Basic inorganic principles such as the Irving-Williams series of stability serve as useful starting point in the development of ion selective polymer-supported extractants. However, other factors such as the nature of polymer itself must be considered when developing polymer-supported reagents using

Table 6.2

Metal Ion Uptake from MCl_2 in 0.01 N HCl by Phosphonic Acid and TETA Resins

Resin	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Acetyl[a]	100.0[b] (∞)[c]	100.0 (∞)	100.0 (∞)	100.0 (∞)	100.0 (∞)	100.0 (∞)
VBC/MMA[a]	100.0 (∞)	100.0 (∞)	100.0 (∞)	100.0 (∞)	100.0 (∞)	94.6 (590)
VBC[a]	100.0 (∞)	100.0 (∞)	100.0 (∞)	100.0 (∞)	100.0 (∞)	100.0 (∞)
STY[a]	100.0 (∞)	100.0 (∞)	100.0 (∞)	100.0 (∞)	100.0 (∞)	98.4 (2930)
TETA[d]	0.00 (0.00)	20.1 (4.44)	17.4 (3.73)	6.12 (1.15)	90.7 (172)	21.3 (4.78)

[a]Copolymer for phosphonic acid
[b]Percent M^{2+} complexed
[c]Distribution coefficient
[d]AT resin

small molecule principles. It has been shown that the polymer support itself is not simply an inert matrix to which a particular ligand is bound, but exhibits an influence on that ligands ability to complex metal ions. Although the ligand in each resin was phosphonic acid, the percent M^{2+} complexed values increased in the order: VBC/MMA < STY < VBC < Acetyl. The Irving-Williams series of stability for small molecule ligands follows the order: Mn < Fe < Co < Ni < Cu > Zn for metal ions in the 2+ oxidation state. However, for all polymer-supported ligands used a maximum percent complexed was observed with Fe^{2+}. Percent Mn^{2+} complexed values were not at a minimum with the polymer-supported ligands which also contradicts the Irving-Williams series.

CHAPTER 7

EXPERIMENTAL PROCEDURES

Copolymer Syntheses

All copolymer beads were prepared by suspension polymerization. Chemical reagents were used without modification unless otherwise indicated.

Microporous (Gel) Copolymers

Poly(vinylbenzyl chloride) (VBC)

The preparation of 300 grams of gel (microporous) beads, crosslinked with 5 wt% DVB (divinylbenzene) is described as follows. The organic phase was prepared by thoroughly mixing 269.93 g VBC, 27.08 g technical grade DVB (55.4% DVB, 44.6% ethylvinylbenzene (EVB)), and 3.00 g benzoyl peroxide (BPO). This solution was sparged slowly with nitrogen for five minutes to remove any dissolved oxygen. The aqueous phase was prepared by dissolving 1.44 g gelatin in 159.25 mL distilled water (heating was required for dissolution, but a temperature of 50 °C was not exceeded to avoid denaturazation). Once dissolved, a solution of containing 9.50 g boric acid and 17.85 g poly(diallyl-dimethylammonium chloride) (PADMAC) in 316.50 mL distilled water was added and the resulting solution mixed thoroughly. The pH was adjusted to 10.3 using

50% NaOH and the solution sparged slowly with nitrogen for 10 minutes. The aqueous phase was transferred to a 1000 mL round bottom flask which was fitted with a condenser, nitrogen inlet, thermometer with Therm-O-Watch temperature control, and overhead stir apparatus consisting of motor, shaft, bearing and Teflon blade. The organic phase was slowly added and the blade adjusted so the top edge was just above the bottom layer. The stir motor was set at a stir speed of 375 rpm to give beads with standard sieve sizing between 40 and 60 mesh. Sieve sizes are listed in Table 7.1. The stir motor is then turned on for two minutes. During this time the bead size was visually inspected and the stir speed was adjusted accordingly. The motor was then turned off for one minute to insure that no separation of the aqueous and organic phase was occurring. This "on/off" cycle was repeated to additional times. The reaction was heated to 80 °C (using a heat lamp) over a period of two hours corresponding to an increase of 7 °C every 15 minutes. The reaction was held at 80 °C for 10 hours after which time heating and stirring were terminated. To "finish-off" the polymerization, approximately 100 mL distilled water was added and the mixture was allowed to reflux with stirring for two hours. Once cooled, the solution was removed using a gas dispersion tube and water aspiration. The beads were washed with 10^{-4} N HCl while stirring for 15 minutes. The acid solution was removed as above and the beads washed three additional times with water. The beads were Büchner dried and extracted

Table 7.1

Standard Sieve Sizes

Sieve Number	Diameter of Opening (mm)
16	1.19
20	0.84
40	0.42
60	0.25
100	0.149
200	0.074
325	0.044

with toluene for 17 hours using a Soxhlet apparatus. The beads were then placed in a drying dish and allowed to air dry.

Polystyrene (STY)

Polystyrene gel beads were prepared in a manner identical to that above with the following exceptions. In the organic phase, the vinylbenzyl chloride was replaced by an equal weight of styrene. Also, the amount of boric acid was decreased by one tenth (i.e., 0.950 g) and the pH of the aqueous phase was adjusted to 10.0 with 50% NaOH.

Poly(glycidyl methacrylate) (GMA)

GMA beads were prepared in a manner identical to that of the VBC beads with the following exceptions. A poly(vinyl alcohol) (PVA) aqueous phase was used consisting of 1.41 g PVA (1.5 wt% total organic phase), 22.56 g $CaCl_2 \bullet 2H_2O$, and 210.09 g distilled water. Just prior to extraction with toluene the beads were washed with acetone and Büchner dried.

Polyacrylonitrile (AN)

AN beads were prepared in a manner identical to that of the VBC beads with the following exceptions. Due to the solubility of acrylonitrile in water, a 50% saturated NaCl solution was used in lieu of water in the aqueous phase

and the pH was adjusted to 11.0. The heating period was altered to one hour each at 50°C, 60°C, and 70°C, followed by 10 hours at 80°C.

Bifunctional Copolymers

All bifunctional copolymers were prepared in a manner identical to that of the VBC beads with the VBC being replaced by monomer ratios indicated in the preceding chapters. Exceptions are the acrylonitrile/styrene copolymers which were prepared using an aqueous phase consisting of 0.6 wt% PVA, and 9.6 wt% $CaCl_2 \bullet 2H_2O$, both based upon the total aqueous phase. The AN/STY copolymers were not washed and extracted as above but were washed five times with hot water and allowed to air dry.

Other Porosity Copolymers

Macroreticular (MR) Resins

MR resins were prepared in a manner similar to that of gel resins. However, to induce porosity a portion of the organic phase was replaced with a porogen or diluent. Unless otherwise indicated, 4-methyl-2-pentanol (4M2P) was used as the diluent at 50% by weight of the organic phase. The "finish-off" period for the MR beads consisted of a six hour steam distillation at which time the diluent was removed from the beads. The round bottom flask was fitted with a Dean Stark trap which was periodically drained of the diluent and water.

Water was added back to the reaction vessel to replace that which was removed.

Xerogel Resins

Xerogel resins were prepared in a manner similar to that of the VBC gel resins. However, porosity was induced by replacing 40% of the organic phase with toluene. After the "finish-off" period the beads were washed with methanol and allowed to air dry.

Copolymer Functionalizations

Ethyleneimine Resins

EDA, DETA, TETA, and PEHA Resins from VBC and/or VBC/STY

All ethyleneimine resins were prepared identically with the exception of the tetraethylenepentamine (TEPA) resins. A four fold stoichiometric excess of the appropriate amine relative to vinylbenzyl chloride (VBC) was used in each synthesis. Using the synthesis of diethylenetriamine (DETA) as an example: 10.0 g (0.063 mol) VBC 2% DVB crosslinked gel beads were weighed into a three neck round bottom flask fitted with an overhead stirrer, Friedrich's condenser, and stopper. A solution of 28 mL (0.25 mol) diethylenetriamine and 100 mL dioxane were added to the round bottom flask and the mixture was heated to reflux. The mixture was held at reflux 17 h. After cooling to room

temperature the solution was removed using a gas dispersion tube and the beads were washed two times with very dilute HCl (~0.001 N). The beads were then conditioned as indicated in Chapter 2, extracted with water for 17 h using a Soxhlet apparatus, and reconditioned by the same method. The resin was characterized by percent solids, and nitrogen capacity.

TEPA Resins

The TEPA resins were prepared in a similar manner however, the amine used was isolated from the hydrochloride salt. This was done due to the low purity level of the liquid TEPA (60%). The TEPA• 5HCl was dissolved in aqueous NaOH and extracted into dioxane. From this point the synthesis and characterization was identical to that described above.

Sulfonated TETA Resins

VBC/STY beads (75/25 wt%, 2% DVB) were functionalized with TETA as described above. The second HCl wash solution was removed using a gas dispersion tube and the remaining water was removed from the beads by azeotropic distillation with heptane. The heptane removed using a gas dispersion tube and the beads were allowed to swell in 100 mL ethylene dichloride (EDC) for one hour. A mixture of 10 mL chlorosulfonic acid in 20 mL EDC was added by addition funnel while the reaction vessel was cooled in an ice/water bath. The reaction was brought to room temperature and held there

24 h. The solution was removed and the beads were quenched with dioxane/water washes, starting from 100% dioxane and gradually increasing the amount of water in the washes. The beads were then conditioned as indicated in Chapter 2, extracted with water, and reconditioned.

Phosphinic, Phosphonic, and Phosphoric Acid/Ester Resins

Phosphinic Acid

All functionalizations of polystyrene to phosphinic acid resins followed the same general procedure. The functionalization of macroporous (20 wt% 4-methyl-2-pentanol (4M2P)) polystyrene crosslinked by 12% DVB is described. 10 g dry polystyrene beads (0.10 mol) were weighed into a 3-neck round bottom flask fitted with a thermometer, overhead stirrer, and Friedrich's condenser with $CaCl_2$ drying tube. 130 mL PCl_3 (1.49 mol) was added and the mixture was allowed to swell with gentle stirring for 1 h. Since the PCl_3 was in excess the amount used was not changed with a change in crosslinking level or type. 16 g $AlCl_3$ (0.12 mol) was added and the mixture was brought to reflux over one hour. The amount of $AlCl_3$ was based on 1.2 mol $AlCl_3$ to 1 mol styrene functional groups. The mixture was allowed to reflux 4 h. After cooling to room temperature the reaction was quenched (hydrolyzed) by slowly pouring the reaction mixture into a ice/water/NaCl slurry with vigorous stirring. The water was then decanted and the beads washed six times with distilled water. The beads were transferred to a glass fritted column and conditioned by elution

with 1 L each (at a rate of 1 L/hour): H_2O, 4 wt% NaOH, H_2O, 4 wt% HCl, and H_2O until a neutral drip was obtained. The beads were then extracted with water 17 h in a Soxhlet apparatus and reconditioned as above.

Phosphonic Acid from Polystyrene

The phosphonic acid functional group on polystyrene was obtained through oxidation of supported phosphinic acid. Phosphinic acid resin was Büchner dried and placed in a 3-neck round bottom flask fitted with a thermometer, overhead stirrer, and Friedrich's condenser. (It is not necessary that the phosphinic acid beads be extracted and reconditioned.) Excess concentrated HNO_3 was added and the mixture was brought to 60°C. The reaction was held at that temperature 17 h. The HNO_3 was removed by a gas dispersion tube and aspiration and the beads were washed four times with distilled water. The beads were transferred to a glass fritted column and conditioned by elution with 1 L each (at a rate of 1 L/hour): H_2O, 4 wt% NaOH, H_2O, 4 wt% HCl, and H_2O until a neutral drip was obtained. The beads were then extracted with water 17 h in a Soxhlet apparatus and reconditioned as above.

Phosphonic Acid from Poly(vinylbenzyl chloride)

Two methods were used to functionalize poly(vinylbenzyl chloride) with the phosphonic acid ligand. The second method is preferred for safety reasons

and for the elimination of cracked beads.

Method 1: The functionalization of microporous (gel) poly(vinylbenzyl chloride) crosslinked by 12% DVB is described. 10 g dry VBC beads (0.10 mol) were weighed into a 3-neck round bottom flask fitted with a thermometer, overhead stirrer, and Friedrichs condenser with $CaCl_2$ drying tube. 130 mL PCl_3 (1.49 mol) was added and the mixture was allowed to swell with gentle stirring for 1 h. Since the PCl_3 was in excess the amount used was not changed with a change in crosslinking level or type. 16 g $AlCl_3$ (0.12 mol) was added and the mixture was brought to reflux over one hour. The amount of $AlCl_3$ was based on 1.2 mol $AlCl_3$ to 1 mol styrene functional groups. The mixture was allowed to reflux 4 h. After cooling to room temperature the reaction was quenched (hydrolyzed) by slowly pouring the reaction mixture into a ice/water/NaCl slurry with vigorous stirring. The water was then decanted and the beads washed six times with distilled water. The beads were transferred to a glass fritted column and conditioned by elution with 1 L each (at a rate of 1 L/hour): H_2O, 4 wt% NaOH, H_2O, 4 wt% HCl, and H_2O until a neutral drip was obtained. The beads were then extracted with water 17 h in a Soxhlet apparatus and reconditioned as above. Upon examination under a microscope some beads appeared cracked. This may be due to the exothermicity of the hydrolysis reaction.

Method 2: This method employs the Arbuzsov reaction to the phosphonate ester followed by hydrolysis to the phosphonic acid. The functionalization of 2%

DVB crosslinked, gel poly(vinylbenzyl chloride) is described. 20 g dry VBC resin is weighed into a 500 mL 3-neck round bottom flask fitted with a stopper, overhead stirrer, and Friedrich's condenser. Approximately 300 mL triisopropyl phosphite was added and the mixture was brought to reflux. Since the phosphite was in excess the amount used was not changed with a change in crosslinking level or type or when multifunctional resins were used. The mixture was held at reflux 17 h. The phosphite was removed with a gas dispersion tube and aspiration and the resin was washed three times with dilute HCl. The last wash was removed and 300 mL concentrated HCl was added. The mixture was brought to reflux and held 17 h. The HCl was removed by a gas dispersion tube and aspiration and the beads were washed three times with distilled water. The beads were transferred to a glass fritted column and conditioned by elution with 1 L each (at a rate of 1 L/hour): H_2O, 4 wt% NaOH, H_2O, 4 wt% HCl, and H_2O until a neutral drip was obtained. The beads were then extracted with water 17 h in a Soxhlet apparatus and reconditioned as above.

Phosphonate Ester from Poly(vinylbenzyl chloride)

The synthesis of the triisopropyl phosphonate ester resin followed that of Method 2 of the phosphonic acid from VBC synthesis. However, the concentrated HCl hydrolysis was eliminated.

Bifunctional Phosphonic Acid/Ethyleneimine

VBC beads were partially functionalized via the Arbuzsov reaction using toluene as the solvent. The synthetic method in which 2% DVB crosslinked microporous (gel) VBC beads were 50% functionalized with phosphonic acid groups is described. 20 g dry VBC beads were weighed into a 500 mL 3-neck round bottom flask fitted with a stopper, overhead stirrer, and Friedrich's condenser. 100 mL triisopropyl phosphite and 200 mL toluene were added. The mixture was brought to reflux and held there 24 h. After cooling the phosphite was removed and the resin was washed three times with dilute HCl. 300 mL concentrated HCl was added, the mixture brought to reflux and held there 17 h. The HCl was removed and the resin was washed three times with water. The beads were transferred to a glass fritted column and conditioned by elution with 1 L each (at a rate of 1 L/hour): H_2O, 4 wt% NaOH, H_2O, 4 wt% HCl, and H_2O until a neutral drip was obtained. The beads were then Büchner dried and reacted with the indicated amine following the procedure described above in the ethyleneimine section.

Phosphoric Acid

The preparation of benzophenol beads from 2% DVB crosslinked microporous (gel) VBC beads and further functionalization to the phosphoric acid resin is described. 15 g dry VBC beads (0.095 mol) were weighed into a 500 mL 3-neck round bottom flask fitted with a condenser, overhead stirrer, and

nitrogen inlet/outlet. 375 mL chloroform and 43.29 g phenol (0.46 mol) were added and the stirring started. 5.28 mL $SnCl_4$ (0.045 mol) was withdrawn via a syringe and added to the flask. The mixture was brought to reflux and held 17 h. The solution was removed by a gas dispersion tube and aspiration. The resin was washed in the following order, 15 minutes each: $CHCl_3$, toluene (3 times), MeOH, H_2O, concentrated HCl, 1 N NaOH, concentrated HCl, and H_2O. The beads were transferred to a glass fritted column and conditioned by elution with 1 L each (at a rate of 1 L/hour): H_2O, 4 wt% NaOH, H_2O, 4 wt% HCl, and H_2O until a neutral drip was obtained. The beads were then extracted with water 17 h in a Soxhlet apparatus and reconditioned as above. The beads were Büchner dried then dried in a vacuum oven 24 h at 60°C. 10 g oven dried phenol beads (0.032 mol, theoretical based upon complete functionalization) were weighed into a 500 mL 3-neck round bottom flask fitted with a stopper, overhead stirrer, and condenser with a $CaCl_2$ drying tube. 200 mL dry dioxane was added and the beads were allowed to swell 24 h with gentle stirring. The dioxane was removed and 100 mL dry dioxane and 100 mL dry toluene were added. 75 mL dry pyridine (0.93 mol) was added and the stopper was replaced by an addition funnel. The mixture was cooled in an ice/salt bath and 40 mL $POCl_3$ was added slowly via the addition funnel. The mixture was allowed to come to room temperature the heated to reflux over one hour. The mixture was held at reflux 17 h. The solution was removed and the beads were washed with dioxane. The beads were hydrolyzed with 300 mL water which was

immediately withdrawn to remove the liberated HCl. The beads were washed three times with water. During the last wash five drops 1 N HCl were added to remove the remaining pyridine smell. The beads were transferred to a glass fritted column and eluted with water until a neutral drip was obtained.

β-Ketophosphonic Acid

The functionalization of 2% DVB crosslinked microporous (gel) polystyrene beads is described. 30 g polystyrene beads (0.28 mol) were weighed into a 500 mL 3-neck round bottom flask fitted with an overhead stirrer and two stoppers. 300 mL CS_2 was added and the beads were allowed to swell overnight with gentle stirring. 120 g $AlCl_3$ (0.90 mol) was added then 32.63 mL $BrCH_2COBr$ was slowly added and the mixture was allowed to stir at room temperature for 72 h. The mixture was quenched using a methanol/ice mixture. After removing the solution the beads were washed two times with methanol, then once each with water, dilute acetic acid, and methanol. The beads were Büchner dried then dried in a vacuum oven for 17 h at 75°C. The beads were then functionalized further via the Arbuzsov reaction and hydrolyzed with concentrated HCl as described above.

Nitrile Functionalized and Amidoxime Resins

Polybenzonitrile from Poly(vinylbenzyl chloride)

The nitrile functionalization of 2% DVB crosslinked microporous (gel)

poly(vinylbenzyl chloride) is described. 2.0 g dry VBC beads (0.013 mol) were weighed into a 250 mL 3-neck round bottom flask fitted with an overhead stirrer, condenser and stopper. 150 mL acetonitrile and 3.09 g KCN (0.047 mol) were added and the reaction was brought to reflux. The mixture was held at reflux 72 h. The solution was removed and the beads were washed four times with water. The beads were Büchner dried and placed in a drying dish and allowed to air dry.

Poly(3-cyano-2-hydroxypropyl methacrylate) from Poly(glycidyl methacrylate)

The nitrile ring opening functionalization of 2% DVB crosslinked microporous (gel) poly(glycidyl methacrylate) is described. 2.5 g dry GMA beads (0.017 mol) were weighed into a 300 mL 3-neck round bottom flask fitted with an overhead stirrer, condenser, and thermometer. 200 mL ethanol/water (1:1) and 4.18 g KCN (0.064 mol) were added and the mixture was brought to reflux. The mixture was held at reflux 18 h. The solution was then removed and the resin washed with water three times with water and one time with acetone. The beads were Büchner dried then placed in a drying dish and allowed to air dry.

Amidoxime Resins

All amidoxime syntheses followed the same general procedure of reacting nitrile functional groups with a three fold molar excess of free hydroxyl

amine. The functionalization of 2% DVB crosslinked microporous (gel) polyacrylonitrile is described. 10 g AN beads were weighed into a 500 mL 3-neck round bottom flask fitted with a stopper, overhead stirrer, and Friedrich's condenser. In a beaker 38.89 g NH_4OH• HCl was dissolved in 200 mL anhydrous methanol. In a separate beaker 31.50 g $NaOCH_3$ was dissolved in 200 mL anhydrous methanol. The solutions were then combined and the NaCl was vacuum filtered from the solution. The free hydroxylamine solution was added to the round bottom flask and the mixture was brought to reflux. The mixture was held at reflux 24 h. The solution was removed and the beads were washed three times with hot water. The beads were transferred to a glass fritted column and conditioned by elution with 1 L each (at a rate of 1 L/hour): H_2O, 0.1 N HCl, H_2O, 0.1 N NaOH, H_2O, 0.1 N HCl, and H_2O until a neutral drip was obtained.

Interpenetrating Polymer Networks (IPN's)

All IPN's were synthesized using xerogel (2% DVB crosslinked, 40% toluene) polystyrene as network I. The synthesis of an IPN using 10% DVB crosslinked poly(vinylimidazole) (Vim) as network II is described. 60 mL of an organic phase which was 4.25 M in functional groups was prepared by weighing 24.12 g Vim, 7.34 g DVB, 1.13 g azobis(isobutyronitrile) (AIBN), and 23.06 g toluene into a 100 mL graduated cylinder. A small stir bar was added and the solution was stirred five minutes. The solution was then sparged with N_2 five

minutes.. 10.0 g xerogel polystyrene beads were weighed into a 150 mL beaker and the monomer solution was added. The beaker was covered and the beads were allowed to swell for 1.5 h. The excess solution was removed from the beads using a Büchner funnel and the solution was measured with a graduated cylinder. This volume was used to calculate the theoretical capacity of the resin. An aqueous phase was prepared using 134.96 g aqueous phase for every 10 g polystyrene. For every 80 mL aqueous phase 41.7 g $CaCl_2 \bullet 2H_2O$, and PVA (1.5 wt% based on monomer weight) were added. 160 mL aqueous phase was prepared by first dissolving 0.84 g poly(vinylalcohol) (PVA) in 80 mL H_2O then adding 85.5 g $CaCl_2 \bullet 2H_2O$ and enough H_2O to make the total volume 160 mL. The aqueous phase was stirred until all solids were dissolved. 134.96 g aqueous phase was added to a 250 mL 3-neck round bottom flask fitted with a condenser, overhead stirrer, and thermometer with Theromowatch. The aqueous phase was heated to 60°C and the Büchner filtered beads then added. The mixture was heated to 80°C and held there 12 h. The beads were washed four times with hot water and Büchner dried and extracted in a Soxhlet apparatus 17 h with methanol. The beads were washed with water then transferred to a glass fritted column and conditioned by elution with 1 L each (at a rate of 1 L/hour): H_2O, 4 wt% NaOH, H_2O, 4 wt% HCl, and H_2O until a neutral drip was obtained.

Characterization Methods

Büchner Drying of Resins

Excess water was removed from those resins stored under water using a Büchner funnel and aspiration at 710 mm Hg (a five cm difference) for five minutes. The funnel was covered with latex held in place by a rubber band. Such Büchner dried resins are referred to as "wet" resins.

Percent Solids

An oven dried scintillation vial was accurately weighed on the analytical balance. A 1.0 to 1.5 g sample of Büchner dried (wet) resin was weighed (to the fourth decimal place) into the vial. The resin was dried in a 110°C oven for 17 h. The sample was cooled in a desiccator then weighed and the weight of the dry resin determined.

$$\% \ Solids = \frac{dry \ wt. \ of \ sample}{wet \ wt. \ of \ sample} \ x \ 100$$

Dry Weight of Resins

For most analyses the weight of the resin is given in terms of dry weight. For those resins stored under water the dry weight was calculated using Büchner dried (wet) resin and the percent solids.

$$g\ dry\ resin = \frac{(g\ wet\ resin)(\%\ solids)}{100}$$

Acid Capacity

A 1.0 to 1.5 g sample of Büchner dried (wet) resin was accurately weighed (to the fourth decimal place) into a 250 mL Erlenmeyer flask with a ground glass joint. A stir bar and 200.0 mL of 0.1 N NaOH / 5 wt% NaCl (standardized to the fourth decimal place with potassium hydrogen phthalate (KHP)) were added, the flask stoppered, and the mixture stirred on a multipoint stirplate at 350 rpm for 17 h. Two 50.0 mL samples were withdrawn and titrated with 0.1 N HCl (standardized with the above described NaOH) to a phenolphthalein endpoint. The acid capacities were reported in units of (mequiv/g dry resin).

$$Acid\ Capacity = \frac{(mL\ NaOH)(N\ NaOH) - 4(mL\ HCl)(N\ HCl)}{g\ dry\ resin}$$

Base Capacity

A 1.0 to 1.5 g sample of Büchner dried (wet) resin was accurately weighed (to the fourth decimal place) into a 250 mL Erlenmeyer flask with a ground glass joint. A stir bar and 200.0 mL of 0.1 N HCl (standardized with the below described NaOH) were added, the flask stoppered, and the mixture stirred on a multipoint stirplate at 350 rpm for 17 h. Two 50.0 mL samples were withdrawn and titrated with 0.1 N NaOH / 5 wt% NaCl (standardized to the

fourth decimal place with potassium hydrogen phthalate (KHP)) to a phenolphthalein endpoint. The base capacities were reported in units of (mequiv/g dry resin).

$$Base\ Capacity = \frac{(mL\ HCl)(N\ HCl) - 4(mL\ NaOH)(N\ NaOH)}{g\ dry\ resin}$$

Nitrogen Capacity

A 0.2 g sample of oven dried resin was accurately weighed (to the fourth decimal place) into a 500 mL 3-neck round bottom flask fitted with a full length West condenser and two stoppers. 0.25 g $CuSO_4$, 10 g K_2SO_4, 25 mL concentrated H_2SO_4, and several carbon boiling chips were then added. The mixture was heated using a heating mantle with a variac setting of 50 for one hour. The variac setting was then increased to 85 and the mixture heated for an additional eight hours. After cooling the inside of the condenser and one stopper were carefully rinsed into the flask with a small amount of distilled water and removed. A stirbar and 100 mL distilled water were added and the flask was fitted with a 250 mL addition funnel and a distillation apparatus to which a funnel was attached by tubing. 50.0 mL standardized 0.1 N HCl was pipetted into a 600 mL beaker and the funnel positioned to just below the surface of the HCl. 150 mL 6 N NaOH was transferred to the addition funnel and the funnel stoppered. The NaOH was added over five minutes with stirring. With the stopcock fully open, the mixture was heated with variac setting of 94. After a

distillation time of one hour the distillate was checked with pH paper to confirm a neutral pH. The funnel was rinsed into the beaker with distilled water and the HCl solution transferred quantitatively to a 250 mL volumetric flask and diluted to the mark with distilled water. Two 100 mL aliquots were then titrated with standardized 0.1 N NaOH to a bromocresol green endpoint. The nitrogen capacities were reported in (mequiv N/g dry resin).

$$\textit{Nitrogen Capacity} = \frac{(mL\ HCl)(N\ HCl) - 2.5(mL\ NaOH)(N\ NaOH)}{g\ dry\ resin}$$

Phosphorus Capacity

Phosphorus capacities were determined by two methods. The second method was preferred due to elimination of the perchloric acid digestion.

Method 1: In duplicate, a 0.020 to 0.025 g sample of oven dried resin was accurately weighed (to the fourth decimal place) into a 125 mL Erlenmeyer flask. 5 mL concentrated HNO_3 and 10 mL $HClO_4$ (70%) were added and the mixture heated gently on a hot plate until the solution was clear and no bead particles remained, approximately 3 - 4 hours. The mixture was then boiled 2 minutes under constant supervision to ensure the solution was NOT evaporated to dryness. After cooling the solution was transferred quantitatively to a 100 mL volumetric flask and diluted to the mark with distilled water. A 5.0 mL aliquot was transferred to a 50 mL volumetric flask to which 3.5 mL $HClO_4$ (70%), 4.5 mL freshly prepared amidol solution (1 g 2,4-diaminophenol dihydrochloride

(recrystallized), 10 g Na_2SO_3, 2.7 g concentrated H_2SO_4, and 90 g H_2O), and 3.5 mL ammonium molybdate solution (4.4 g $(NH_4)_6Mo_7O_{24}\bullet 4H_2O$ and 50 g H_2O). The mixture was diluted to the mark with distilled water and allowed to develop 30 minutes. The absorbance was measured on a Bausch and Lomb Spectronic 21 which was zeroed at 700 nm with a blank containing the amidol, $HClO_4$, and ammonium molybdate solutions. An absorbance vs. concentration curve was generated using a series of K_2HPO_4 standards from which the slope of the line was calculated in mL/mg. The phosphorus capacities were reported in units of (mequiv P/g dry resin).

$$Phosphorus\ Capacity = \frac{(Absorbance)(1000mL)}{(g\ dry\ resin)(30.974\ mg/mequiv)(slope)}$$

Method 2: In duplicate, a 0.020 to 0.025 g sample of oven dried resin was accurately weighed (to the fourth decimal place) into a 125 mL Erlenmeyer flask. 400 µL 0.5 M $CuSO_4$ and 10 mL concentrated H_2SO_4 were added and the mixture heated on a hot plate at a medium setting for two hours. The mixture was cooled to room temperature at which time 75 mL H_2O and 2.0 g $K_2S_2O_8$ were added. The hot plate temperature setting was lowered to "3" and the mixture heated an additional two hours. The solution was cooled and 50% NaOH added until slightly cloudy. A 2% H_2SO_4 solution was added until the solution was again clear. The solution was checked with pH paper to validate neutrality. The solution was then transferred quantitatively to a 100 mL

volumetric flask and diluted to the mark with distilled water. A 25 mL aliquot was transferred to a 50 mL volumetric flask to which 10 mL vanadate-molybdate solution* was added. The solution was diluted to the mark with distilled water and allowed to develop 15 minutes. The absorbance was measured on a Bausch and Lomb Spectronic 21 which was zeroed at 470 nm with a blank containing the vanadate-molybdate solution. An absorbance vs. concentration curve was generated using a series of K_2HPO_4 standards from which the slope and y-intercept of the line were calculated. The phosphorus capacity was reported in units of (mequiv P/g dry resin).

$$mg\ P = \frac{(Absorbance - Intercept)}{Slope}$$

$$Phosphorus\ Capacity = \frac{(4)(mg\ P)}{(30.974\ mg/mequiv)(g\ dry\ resin)}$$

*Vanadate-molybdate Solution - 25 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was dissolved in 300 mL distilled water. In a separate vessel 1.28 g NH_4VO_3 was dissolved in 300 mL H_2O by heating to boiling. After cooling to room temperature 330 mL concentrated HCl was carefully added. Both solutions were quantitatively transferred to the same 1 L volumetric flask and diluted to the mark with distilled water.

Chlorine Capacity

Two methods were used in the determination of chlorine capacities. The second method was preferred for safety reasons.

Method 1: A sample of oven dried resin was accurately weighed (to the fourth decimal place) into 15 X 160 mm pyrex test tube. To this 2 g sodium metal and 1 mL xylene were added. Approximately 0.5 g sodium metal was added to a second test tube of the same dimensions. A gas transfer tube of 7 mm soft glass tubing was prepared in a square "U" configuration with one arm long enough to reach the bottom of the tube containing only the sodium metal, and the other arm long enough to fit through a # 1 stopper and slightly into the test tube containing the sample. The sodium metal in the test tube without the sample was melted and the long end of the transfer tube was heated and inserted into the molten metal. The rubber stopper, with the tubing inserted, was then affixed to the sample test tube, the sodium melted, and the xylene driven off. Once it had been confirmed that the gas was traveling through the transfer tube and up through the molten sodium in the second test tube, the sample was slowly decomposed. After complete decomposition of the sample, 2 - 4 minutes, both test tubes were heated strongly for 15 minutes insuring that the soot was burned from the transfer tube and tops of both test tubes. The apparatus was allowed to cool at which time all glass was crushed into a beaker containing 100 mL dry methanol. The methanol was evaporated on a hot plate and the resulting solids dissolved in approximately 100 mL H_2O. The

solution was transferred quantitatively into a 250 mL volumetric flask, the glass being removed by gravity filtration. Two 50 mL aliquots were prepared by adding one drop concentrated HNO_3 then 0.3 M NaOH to a methyl orange endpoint. (Note: If nitrogen was contained in the samples the aliquots were boiled in the hood for 15 minutes upon acidification for the removal of HCN.) The aliquots were then titrated with 0.05 N $AgNO_3$ to an orange/red K_2CrO_4 endpoint. Chlorine capacities were reported in units of (mequiv Cl/g dry resin).

$$Chlorine\ Capacity = \frac{(5)(mL\ AgNO_3)(N\ AgNO_3)}{g\ dry\ resin}$$

Method 2: A 0.05 to 0.8 g sample of oven dried resin (based upon anticipated % chlorine by weight) was accurately weighed (to the fourth decimal place) into a Parr bomb capsule. An amount of mineral oil was added so the total weight contained by the capsule was approximately 0.8 g, see Table 7.2. Under no circumstances did the total weight exceed 1.0 g. 5 mL 5% $NaCO_3$ was added to the bomb cylinder and swirled to insure complete wetting of the interior. The capsule was placed in the holder and a 10 cm nickel alloy fuse wire was threaded through the stem holes and adjusted to touch the surface of the oil. The bomb was assembled and filled with oxygen to a pressure of 30 atm. The bomb was degassed and refilled two times. The bomb was placed into a water bath and ignited. The bomb was held in the water bath 10 minutes then removed and dried. The solution was quantitatively transferred to a 400 mL

Table 7.2

Chlorine Elemental Sample Preparation

Wt% Chlorine	Sample Wt. (g)	Mineral Oil (g)
< 2	0.8	0.0
2 - 5	0.4	0.4
5 - 10	0.2	0.6
10 - 20	0.1	0.7
20 - 50	0.05	0.7

beaker and rinsed with water until 200 mL were obtained. The solution was then quantitatively filtered into a 250 mL volumetric flask and diluted to the mark with water. Two 25 mL aliquots were transferred to 125 mL Erlenmeyer flasks and prepared by adding 3 mL 2 N HNO_3. Exactly 10 mL 0.0500 N $AgNO_3$ was added to each aliquot and to two clean Erlenmeyer flasks (for standardization of the NH_4SCN). The flasks containing the aliquots were placed onto a hot plate and allowed to come to a boil. The samples were cooled to room temperature (in a dark place) and filtered into clean 125 mL Erlenmeyer flasks. The flask and/or solid were washed thoroughly with a small amount of 0.01 N HNO_3. The $AgNO_3$ samples were then titrated to a faint orange endpoint with 0.05 N NH_4SCN using 3 mL $FeNH_4(SO_4)_2$ solution* as the indicator. This was done to standardize the NH_4SCN. The aliquots were then titrated with the standardized NH_4SCN to a faint orange endpoint using 3 mL $FeNH_4(SO_4)_2$ solution* as the indicator. The chlorine capacities were reported in units of (mequiv Cl/g dry resin).

$$\textit{Chlorine Capacity} = \frac{10[(mL\ AgNO_3)(N\ AgNO_3) - (mL\ NH_4SCN)(N\ NH_4SCN}{g\ dry\ resin}$$

*$FeNH_4(SO_4)_2$ Indicating Solution - A saturated $FeNH_4(SO_4)_2$ solution was prepared by heating excess $FeNH_4(SO_4)_2 \cdot 12H_2O$ in just over 500 mL H_2O. This mixture was cooled to slightly above room temperature and filtered into a

500 mL volumetric flask. This solution and exactly 500 mL 2 N HNO_3 were then combined.

Total Anion Exchange Capacity (TAEC)

A 2.5 to 3.0 g sample of Büchner dried resin was accurately weighed (to the fourth decimal place) and transferred to a glass fritted column. The sample was eluted with 1.0 L 1 N $NaNO_3$ into a 1 L volumetric flask over one hour. Two 50 mL aliquots were prepared by adding one drop concentrated HNO_3 then 0.3 M NaOH to a methyl orange endpoint. The aliquots were then titrated with 0.05 N $AgNO_3$ to an orange/red K_2CrO_4 endpoint. The TAEC's were reported in units of (mequiv/g dry resin).

$$TAEC = \frac{20(mL\ AgNO_3)(N\ AgNO_3)}{g\ dry\ resin}$$

Metal Ion Studies

Due to variations in the procedures for metal ion studies, descriptions are given in individual chapters. All metal ion solutions were analyzed using a Perkin-Elmer 3100 atomic absorption/emission spectrometer. Parameters for analyses are given in Table 7.3.

Table 7.3

Atomic Absorption/Emission Spectroscopy Parameters

Metal	Mode	Wavelength	Flame
Ag	AA	328.1 nm	air/acetylene
Cd	AA	228.8 nm	air/acetylene
Co	AA	240.7 nm	air/acetylene
Cu	AA	324.7 nm	air/acetylene
Eu	AE	459.4 nm	N_2O/acetylene
Fe	AA	248.3 nm	air/acetylene
Pb	AA	283.3 nm	air/acetylene
Zn	AA	213.9 nm	air/acetylene

Infrared Spectroscopy

IR spectra were obtained using a Bio-Rad FTS-7 Fourier transform infrared spectrometer. Oven dried polymer samples were ground to a fine powder and pressed into a KBr pellet at a polymer to KBr ratio of 1:100. A resolution of 8 wavenumbers and 16 to 64 scans were accumulated and adjusted as needed.

^{31}P NMR Spectroscopy

^{31}P NMR were recorded on a Nicolet NT-200 spectrometer. The spectra were obtained at an operating frequency of 80.99 MHz via DP/MAS. A Doty Scientific standard 5-mm VT-MAS probe was used. Wet samples were contained in sapphire rotors with Vespel end caps. The data size was 8K and was collected with a sweep width of ±15 Hz and spin speeds of 3.0-3.6 kHz. DP/MAS spectra were recorded with a pulse width of 3 μsec and a relaxation delay of 10 seconds. 300 to 350 scans were normally obtained. Exponential line broadenings of 30 Hz were used. An external triphenylphosphine sample was used as the reference.

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