SYNTHESES OF POLYMER-SUPPORTED AMIDOPHOSPHATES AND INVESTIGATING THEIR DIVALENT METAL ION AFFINITY

by

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A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

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ABSTRACT

SYNTHESES OF POLYMER-SUPPORTED AMIDOPHOSPHATES AND INVESTIGATING THEIR DIVALENT METAL ION AFFINITY

by

Amanda N. Pustam

Advisor: Professor Spiro D. Alexandratos

Functionalized polymers are of interest because of their wide applications in areas of separation science, sensor design and organic synthesis. This research, divided into two parts, focused on designing complexants for immobilization onto polymers for the purpose of metal ion sequestration and secondly, for the removal of methyl-*t*-butyl ether (MTBE) from aqueous solutions.

In the first part of this project, the polymers investigated contained amide and phosphate ester groups. These functional groups were chosen as they contain coordination sites for metal ion chelation. The prepared polymers were characterized and evaluated for their divalent metal ion affinities at pH 2. Divalent metal ion affinity was found to follow the sequence Pb(II) > Cu(II) > Cd(II) > Zn(II) > Ni(II). The effect of a spacer chain between the ligand's binding sites on metal ion affinities was investigated. Increasing the length of the hydrocarbon spacer elicited a decrease in metal ion affinities.

When the spacer chain contained a donor atom, an increase in divalent metal ion affinity was observed compared to its absence. Some results with trivalent metal ions such as Fe(III), Eu(III), Al(III) were included. Uptake of these metal ions by 2-(2-amidoethoxy)ethyl phosphate resins were about the same, although Fe(III) sorption was the highest. A mechanism that explained how metal ion complexation may occur was proposed.

Characteristics of polymer-supported reagents important for MTBE removal were identified. Polymer-supported calixarenes and polymers with p-cresol sorbed in its pores can be potential candidates for further studies. A procedure for plugging pores was found which has potential in improving separations of extraction chromatographic resins.

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experimented with NYC culture out of the lab. Thanks to Lauren Wickstrom, Dionne Miller and Tara Nath for staying in touch even when circumstances separated us.

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Above all, I thank God for giving me the health, courage and wisdom to pursue and complete this research.

Dedicated to Mum, Dad, Grandmas Agie and Nanny, Grandpas Aja and Nanna

- you have inspired me to become who I am.

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LIST OF ACRONYMS / ABBREVIATIONS

AcSty	4-acetoxystyrene
AEE	2-(2-aminoethoxy)ethanol
AN	acetonitrile
BPO	benzoyl peroxide
BTEX	benzene, toluene, ethylbenzene and xylene
CAAA	clean air act amendments
D	distribution coefficient
DECP	diethyl chlorophosphate
DIGLYME	bis(2-methoxyethyl) ether
DMF	dimethylformamide
DVB	divinylbenzene
EXC	extraction chromatographic resin
FID	flame ionization detector
GC	gas chromatography
GAC	granular activated carbon
IIP	ion imprinted polymers
$K_H^{25°C}$	Henry’s law constant at 25°C
K_{oc}	water/soil partition coefficient
LUST	leaking underground storage tanks
4M2P	4-methyl-2-pentanol
MR	macroreticular
MTBE	methyl-t-butyl ether
N. A.	not applicable
N. D.	not determined
NMP	N-methyl pyrrolidone
ppb	parts per billion
PS	polystyrene
RIEX	reactive ion exchangers
RSD	relative standard deviation
R. T.	room temperature
RFG	reformulated gasoline
TBA	tertiary-butyl alcohol
TEG	triethylene glycol
TEGME	triethylene glycol monomethyl ether
TPGME	tripropylene glycol monomethyl ether
THF	tetrahydrofuran
VOC	volatile organic compound
VBC	(vinylbenzyl) chloride

1 INTRODUCTION

1.1 Background and Significance

The selective removal of toxic metal ions from the aqueous environment remains a daunting task. This issue has been addressed by the development of a number of innovative methods for sequestering these metal ions. Some of the existing technology include solvent extraction, precipitation, electrodeposition, membrane separation, ion exchange and coordination using natural sorbents and modified synthetic materials.

Research in the area of metal ion separations is ongoing to meet the stringent environmental regulations imposed by government agencies that permit water containing only very low levels of toxic contaminants for human and animal consumption. Additionally, there is a global impetus towards a reduction of metal ion waste collected from any site for treatment and/or storage at landfills. This can be achieved through recycling and reusing the metal ion. One concern, for example, is to identify ways of separating trivalent lanthanides from transplutonium actinides, metals that exhibit similar chemical behavior.[1]

Pollution of water in the environment is mainly from anthropogenic sources such as run-off from industrial effluents. At this point, contaminants enter the groundwater and accumulate in the food chain.

The techniques mentioned above are useful for specific applications, and not without shortcomings. For example, while liquid – liquid extraction may be efficient for separations involving high concentrations of metal ions, some loss of extractant into the aqueous phase poses an environmental hazard. In addition to which, large quantities of secondary waste would be generated through management of large quantities of diluents. Ion exchangers are attractive alternatives as the extractant is bound to a solid phase making metal ion separation simple and easy, yet they exhibit poor metal ion selectivity. The advent of coordination or chelating polymers since the 1950's has allowed for the synthesis of ion-selective resins.[2] Chelating polymers offer enhanced selectivity for separation and concentration of metal ions at trace levels by forming complexes with specific metal ions.[3] The varying stability constants of metal ion complexes under different solution conditions allow for metal ion selectivity and separations. It is found that chelating resin complexes often times have higher stability constants compared to their corresponding monomer complexes. This has been attributed to the polymer entropy effect (a large change in entropy due to the proximity of functional groups and the high local concentration of ligands within the resin) and lower dielectric constant of the resin matrix.[4] Chelating resins may contain multiple or single ligating groups, such as iminodiacetic acid resins.[5, 6] N-substituted hydroxylamine functionalized resins,[7] and N-methyl-D-glucamine resins[8, 9] are but just a few.

The design of effective ligands for metal ion complexation with the objective of enhanced selectivity is applicable to polymer-supported reagents. A fundamental understanding of the mechanisms involved in selective metal ion complexation is therefore necessary. A study of the mechanism(s) involved in complexation of polymer-supported reagents with some heavy and transition metal ions in particular, will be considered here.

1.2 Synthesis of polymer-supported reagents

These materials are most commonly synthesized by modification of a crosslinked copolymer with a complexing group. This method of preparation is known as post-functionalization. Typical polymers used for modification include polystyrene, poly(vinylbenzyl) chloride and poly(glycidyl methacrylate). The polymers are generally prepared by suspension polymerization. The crosslinking molecule is usually divinylbenzene or ethylene glycol dimethacrylate. Polymer-supported reagents can also be prepared by pre-functionalization. In this method, a functional monomer (containing the complexing group) is prepared and then copolymerized with a crosslinking molecule and maybe another polymer.[10]

1.3 Selectivity of polymer-supported reagents

Selectivity is a property of some polymer-supported reagents that refers to its ability to complex a specific metal ion in the presence of other metal ions. Selective polymers are useful for applications such as water treatment, chromatographic separations, sensor development and metal ion recovery, as mentioned above. For example, the separation of low concentrations of toxic metal ions when present among large concentrations of innocuous metal ions, commonly found in natural environments, is one of the problems encountered. Economically, these resins are more efficient and can be used for longer periods before becoming saturated and requiring regeneration.

Research in this area has benefitted from solvent extraction studies, theoretical studies involving molecular mechanics calculations and X-ray crystallography.[11] Generally, metal ion selectivity in resins have been enhanced in the following ways:

1. Immobilization of ligands with multiple coordinating sites such as bifunctional polymers
2. Immobilization of low-molecular weight complexing agents, e. g. triazole
3. Preparation of Ion Imprinted Polymers (IIP)
4. Preparation of Reactive Ion Exchangers (RIEX)
5. Immobilizing ligands that are biomimetically relevant
6. Immobilizing specific donor groups through application of Pearson's hard-soft acid-base theory
7. Immobilizing macrocycles e. g. crown ethers, calixarenes, resorcinarenes

1.4 Factors affecting affinity and selectivity of polymer-supported reagents

Polymer-supported reagents containing different functionalities have been prepared and their interaction with metal ions studied. The extent of these studies varied. While all of the studies reported metal ion affinities, not many offered explanations of a possible mechanism. Before alluding to possible mechanisms related to the chemistry of the ligand immobilized on the polymer, it must be noted that there are several "external" factors found to influence metal ion affinities. For example, the speciation of the metal ion plays a significant role in the complexation of the metal ion to the ligand. Metal ion speciation is related to the solution conditions i. e. the pH of the solution as well as the type of counter ions present. The polymer backbone has also been implicated as well as the hydrophobicity of the polymer / ligand system. A study involving polyacrylamide supported glycines showed that the percent crosslinking can affect metal ion specificity.[12]

When these "external" factors are kept constant, metal ion affinities and selectivities are governed by the compatibility of the ligand and the metal ion. This means that the properties (electronic and / or physical) of the ligand and metal ion should be similar. Thus, to successfully design ligands for enhanced selectivity, attention is given to the choice of ligand (donor group properties) and the metal ion (acceptor group properties) for complexation.[13] This concept is expressed in several published reviews where ligands that are selective for specific metal ions are identified.[14] It is also possible to correlate the selectivity for a metal ion by a ligand, against a property of that ion.

The Irving – Williams series is one example of a trend elicited by certain first row transition divalent metal ions. This trend is not unique to polymer-supported reagents but is exhibited by proteins and small molecules. The affinity order followed, i. e. Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II), is related to the stability of the metal ion complex formed.[15]

The following section introduces the metal ion properties that have been found to influence sorption by polymer-supported reagents, with emphasis on transition and heavy metals. Examples of polymer-supported reagents will be added to illustrate the metal ion property – selectivity relation. Note that this information is compiled based on the author's interpretation of the achievement of selectivity in polymer-supported reagents from a literature review of resins and their metal ion affinity studies.

1.4.1 Ionic radius

Evidence for ionic size contributions in complexation was found in studies of small molecule complexes of metal ions, particularly in macrocyclic polydentates.[16-20] Macrocyclic complexes coordinate metal ions by encapsulating them into their cavities. Hence, ionic radius in combination with metal ion polarisability (discussed in the next section), was found to be related to the stability of the resultant complex metal ion and influenced which metal ion gets complexed. In one example, the lanthanide(III) complexes of 1,4,7,10-tetrakis(carbamoylmethyl)-1,4,7,10-tetraazacyclodecane (TCMC) showed an increase in stability constants across the lanthanide series with the optimum stability observed for Sm(III) complex followed by a decrease to Lu(III).[21] Metal ion interactions with small molecules were usually good indicators of the behavior of ions with ligands on a solid sorbent.[22, 23] The following examples of some functionalized polymers illustrated the relation between ionic size and complex formation.

A lead-selective resin was obtained by immobilization of calix[4]arene tetracarboxylic acid on polyallylamine, PAA.[23] The resulting resin, PAA-Calix (Figure 1.1), exhibited the selectivity order Pb >> Cu >> Zn = Ni = Co. The maximum sorption of lead occurred at a pH of 4.5. Control resins of unfunctionalized PAA showed that the absorption behaviour of PAA-Calix was due to the calix[4]arene component and not to the free amino groups of the PAA. The extractant p-t-octylcalix[4]arene tetracarboxylate shows the same selectivity for lead as seen with the resin. In addition to the size of the lead ion matching the size of the coordinating sites of the calixarene derivative, the polarisability of the lead ion and the corresponding oxygen-rich sites were

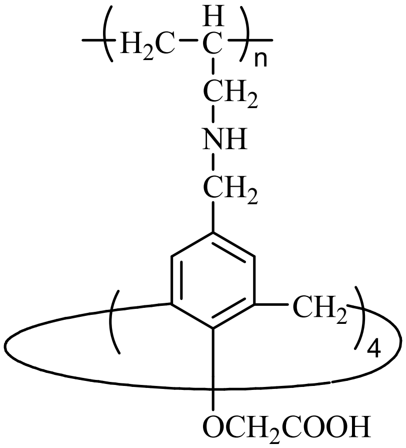


Figure 1-1 Calix[4]arene tetracarboxylic acid immobilized on polyallylamine (PAA-Calix)

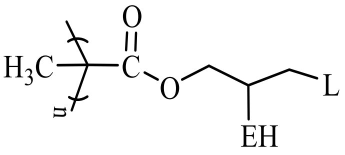
favorable. This was consistent with crown ether-type macrocyclic ligands which demonstrate similar behavior for lead ions.

A sandwich complex, N-(4-vinylbenzyl)-1,4,7-triazacyclononanezinc (II) was copolymerized in the presence of divinylbenzene.[24] A 2 : 1 ratio of TACN : Zn^{2+} in the polymer matrix was obtained. This resin was then treated with 6 N HCl to remove the Zn^{2+} template ions. The demetallated resin was selective for Zn(II) in the presence of Ni^{2+}, Co^{2+} and Mn^{2+} and absence of Cu^{2+}, that is, $Mn^{2+} < Ni^{2+} < Co^{2+} <<< Zn^{2+}$ at pH 4.5. The 2 : 1 ratio of TACN : Zn^{2+} described was maintained. However, when Cu(II) ions were present, the resin was more selective for Cu(II) compared to Zn(II) at the same pH (Cu(II) and Zn(II) ions have similar ionic radii). The competition between Cu^{2+} and Fe^{3+} ions were also studied at pH 2. A high selectivity was noted for Cu(II) relative to Fe(III). This selectivity was attributed to the differences in ionic radii between Cu(II) and Fe(III).

Another similar complex was prepared with mercury ions.[25] The demetallated polymerized sandwich complex of [{mono-N-(4-vinylbenzyl)-1,4,7-triazacyclononane (TACN)}$_2$ Hg](OTf)$_2$, displayed selectivity for mercuric ions at pH 2. High selectivity coefficients, $K_{Hg^{2+}/M^{n+}}$ were noted for mercury in the presence of metals with small ionic radii (Fe^{3+}, Cu^{2+}, Cd^{2+}) and large ionic radii (Pb^{2+}, Ag^{+}). In the absence of mercuric ions, the demetallated resin was able to abstract small amounts of other metal ions (0.87, 41.2 24.1 and 130.6 μmol/g Pb^{2+}, Fe^{3+}, Ag^{+} and Cu^{2+} ions respectively). A 1:1 ratio of TACN : Hg^{2+} was observed upon contacting the resin with a solution of mercury ions. This implied that the mercury-templated resin behaved independently of the sandwich arrangement possibly because of the large ionic radius of Hg^{2+} (compared to the zinc templated resin). Random arrangement of TACN ligands on PS-DVB demonstrated a lower selectivity for Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Mn^{2+} and a high selectivity for Hg^{2+}. In summary, good selectivity for metal ions of smaller ionic radii may be achieved through formation of a "spatial sandwich arrangement of TACN ligands in a templated polymer matrix". Note that, parameters such as softness of Hg^{2+} ions and affinity for nitrogen atoms, as well as the geometry of TACN ligands were cited as possible explanations for the uptake of Hg^{2+} by these resins. Additionally, the large ionic radius of Hg^{2+} was implicated for the deviation (from sandwich-like arrangement of ligands) observed.

Copolymerization of styrene and uranyl vinylbenzoate in the presence of divinylbenzene, the crosslinking agent, and 2-methoxyethanol, the porogen, produced a molecularly imprinted uranyl ion exchange resin.[26] This resin had a high capacity for uranyl ions upon its removal from the polymer. This polymer showed preference for UO_2^{2+} compared to Ni^{2+}, Cd^{2+}, Cu^{2+}, Fe^{3+} at pH 3.5. Control experiments carried out with a nickel-imprinted polymer and a non-imprinted polymer at pH 3.5 and 5.3, supported the observed selectivity and enhanced capacity. This can be explained by incompatible size of the cavity from nickel imprinting for the target ion, which could not be accommodated. In addition, the orientation of the functional groups inside the cavity may also contribute to recognition. This concept of ion imprinted polymers (IIP) would be discussed more fully in section 1.4.3.

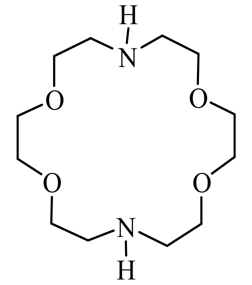
A metal ion sorption study with a series of aza crown ethers immobilized on poly (glycidyl methacrylate-co-ethylene glycol dimethacrylate), (p(GMA-O)), and its sulfur thiirane analogue, (p(GMA-S)) was conducted (Figure 1-2).[27] The ligands investigated



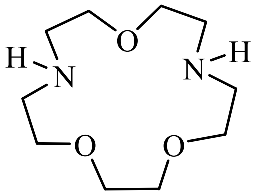
E=O, S

Figure 1-2 General structure of p(GMA-O) and p(GMA-S) upon immobilization of ligand L

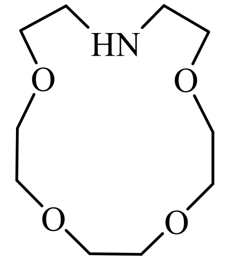
(For examples of L see Figures1-3, 1-4 and 1-5)



[18]aneN_2O_4



[15]aneN_2O_3



[15]aneNO_4

Figure 1-3 Aza crown ethers

were [15]aneNO_4, [15]aneN_2O_3 and [18]aneN_2O_4 (Figure 1.3). Selectivity for Ag^+ was shown for p(GMA-O)-[15]aneNO_4 in comparison to Cd^{2+}, Cu^{2+}, Zn^{2+} from solutions of pH 3 through 7. The metal ion affinity of p(GMA-O)-[15]aneN_2O_3 resin generally decreased with decreasing metal ion radii: $Ag^+ > Pb^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} \sim Ni^{2+}$ (exceptions were Ag^+ and Cu^{2+}). The involvement of pendent hydroxy groups of the resin was implicated in the observed size selectivity. The hydroxy groups may destabilise the complexes of small metal ions compared to those of larger metal ions. Note that the order described above was not observed for p(GMA-O)-[16]aneNS_4[33] or for p(GMA-S)-[15]aneN_2O_3. Resin p(GMA-S)-[15]aneN_2O_3 showed a reversal in the selectivity of Cd^{2+} and Cu^{2+}.

Different amounts of metal ions were complexed for ligands of different ring sizes. The effect was more pronounced for smaller ions such as Cu^{2+} and Zn^{2+}, where fewer of these ions were accommodated by the larger cavity size of p(GMA-O)-[18]aneN_2O_4 compared to p(GMA-O)-[15]aneN_2O_3. Uptake of larger ions such as Ag^+ and Pb^{2+} were found to be similar for [15]aneN_2O_3 and [18]aneN_2O_4.

1.4.2 Metal ion polarizability

Polarizability, α, refers to the ability of an atom or ion to be distorted by an electric field.[28] Polarizability is related to softness: atoms which hold on to their electrons less firmly, are more polarizable and are described as “soft”. “Hard” indicates low polarizability – the electron cloud of the atom is less easily deformed. According to the Lewis concept of acids and bases, the metal ion of a metal ion-ligand complex or coordination compound is the electron pair acceptor or Lewis acid while the ligand is the electron pair donor or a Lewis base. Soft acids prefer to coordinate with soft bases while hard acids preferred hard bases. This concept of hard and soft acid and base (HSAB), proposed by Pearson in 1963, can be used to predict the stability of compounds.[29]

In 1967, Klopman correlated the HSAB theory with the frontier orbital energies of the reactants. When soft acids and soft bases, interact for example, the energy difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO-LUMO) is small, so that electron transfer occurs and covalent bonding results.[30] On the contrary, a large HOMO-LUMO band gap occurs in hard-hard interactions and bonding is electrostatic.

First mention of classification of Lewis acids and bases into class “a” and class “b” was based on their preferential binding. Later, class “a” donors and acceptors were defined as “hard” and class “b” as “soft”.[28] Molecules and ions of intermediate character were termed “borderline”.[29]

Polarizability is related to electronegativity of the atom, highly electronegative atoms are hard, for example; softness decreases from carbon to fluorine across the second row of the periodic table. Polarizability is also a function of atomic number / size, larger atoms are softer than smaller atoms of similar electronegativity. The charge on an atom influences polarizability: metal cations become harder as the oxidation number increases. Table 1-1 gives examples of metal ions and atoms / molecules categorized following the HSAB theory. There have been attempts made to quantify hardness/softness with some physical parameter(s). A parameter known as absolute hardness, η was identified.[31] Absolute hardness was calculated from ionization potential and electron affinity values.

Table 1-1 Classification of Lewis Acids[29]

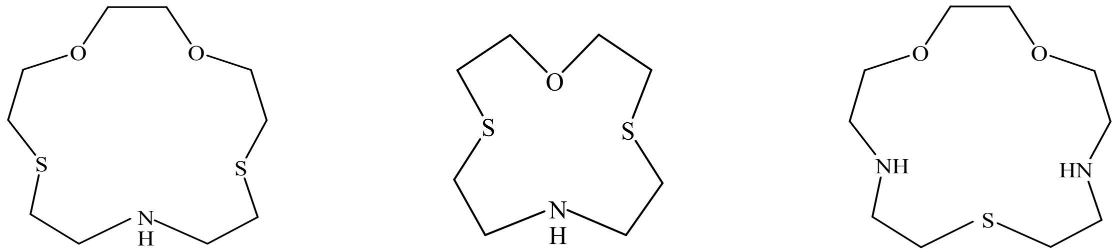
Class a or Hard	**Class b or Soft**	**Borderline**
H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Sn^{2+}, Al^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, As^{3+}, Ir^{3+}, Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, Pu^{4+}, VO^{2+} UO_2^{2+}, $(CH_3)_2Sn^{2+}$, $BeMe_2$, BF_3, BCl_3, $B(OR)_3$, $Al(CH_3)_3$, RPO_2^+, $ROPO_2^+$, RSO_2^+, $ROSO_2^+$, SO_2, R_3C^+, RCO^+, CO_2, NC^+	Cu^+, Ag^+, Au^+, Tl^+, Hg^+, Cs^+ Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, CH_3Hg^+ Tl^{3+}, $Tl(CH_3)_3$, BH_3 RS^+, RSe^+, RTe^+ I^+, Br^+, HO^+, RO^+, I_2, Br_2, ICN, etc. Trinitrobenzene, etc. Chloranil, quinones, etc. Tetracyanoethylene, etc. O, Cl, Br, I, R_3C(?) M^0 (metal atoms) Bulk metals	Fe^{3+}, Co^{2+}, Ni^{2+} , Cu^{2+}, Zn^{2+}, Pb^{2+}, $B(CH_3)_3$, SO_2, NO^+

R = alkyl or aryl group

However, determination of absolute hardness for polyatomic ions would not be accurate, making the ranking of acids and bases according to the degree of hardness difficult. The following examples relate polarizabilities of Lewis acids / ligands based on Pearson's theory.

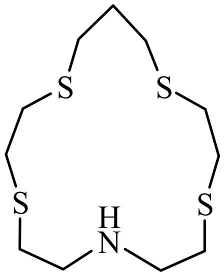
The immobilization of mixed crown ethers containing N, S and O atoms (Figure 1-4) on copolymers of glycidyl methacrylate and ethylene glycol dimethacrylate (p(GMA-O), (Figure 1-2) produced resins that were selective for Ag^+ over divalent nitrates, (Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}) for pH 1 to 6.[32] This was pronounced in those resins where there were two sulfur atoms in the macrocycle, as compared to the one that contained one sulfur atom (Figure 1-4). Substitution of S for N or O in the ether affected the stability of the metal complexes formed. Results for the resin containing one S atom, $[15]aneN_2O_2S$, indicated that Ag^+ uptake was pH dependent. When the corresponding sulfur analogues of p(GMA-O), p(GMA-S) were compared (Figure 1-2), Cu^{2+} was preferred among divalent chlorides, (Cu^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}), the capacity for which increased with increasing solution pH, and the maximum capacity for Cu^{2+} at pH 5.5. Note that the selectivity for Cu^{2+} was greater when the rings contained two S atoms as compared to one S atom.

Similar results were obtained when a 16-membered azathiacrown ether (Figure 1-5), 7-aza-1,4,10,13-tetrathiacyclohexadecane ($[16]aneS_4N$) was immobilized on p(GMA-O) and its sulfur analogue, p(GMA-S).[33] The oxirane resin showed a high capacity and selectivity towards Ag^+ ions were obtained in the presence of the nitrates of Cu^{2+}, Zn^{2+} and Cd^{2+} ions with low capacities of the latter metal ions. In the absence of Ag^+, chlorides of Cd^{2+} and Cu^{2+} were extracted; Cd^{2+} at pH 1-2 and Cu^{2+} at pH 3-6. The high



[15]aneNO_2S_2 [12]aneNOS_2 [15]aneN_2O_2S

Figure 1-4 Crown ethers containing nitrogen, oxygen and sulfur



L = [16]aneS_4N

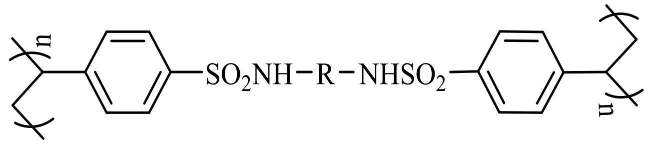
Figure 1-5 Another azathia crown ether

affinity for soft Ag^+ ions has been attributed to the presence of soft sulfur donor atoms on these resins. A substitution of the sulfur atoms of [16]aneS_4N with oxygen and / or nitrogen were shown to decrease the stability of corresponding Ag^+ complexes.[34] There was also some influence of the lariat ether on the backbone, on the sorption of metal ions.

In another study, a series of N-sulfonylpolyamine chelating resins (Figure 1-6) were synthesized and the sorption capacities for lead, cadmium, copper and zinc noted.[35] Metal sorption was studied from pH 1 through pH 7 and was at its optimum at pH 5.5 for Cu(II) and Zn(II), and at pH 6.0 for Cd(II) and Pb(II). In all resins, copper and zinc were preferred over cadmium and lead. It was concluded that the degree of hardness / softness of the resins' donating groups and the metal ion polarisability were comparable. Lead and cadmium are softer metal ions compared to copper and zinc. Nitrogen and oxygen are borderline ligands.

A novel chelating resin containing S, N, and O atoms (Figure 1-7) that has a high affinity for mercury(II) ions from a solution of mercury nitrate buffered at a pH of 5.4 was investigated.[36] Uptake of Hg(II) ions by poly(2-hydroxyethylmercaptomethylstyrene – diethanolamine) (PSME-EDA), involved both N and S atoms on the resin as demonstrated by X-ray photoelectron spectroscopy (XPS) analysis. This was supported by Hg(II) having a strong affinity to S and N electron donors.

Vinyl 2-hydroxyethyl sulfide homopolymer and vinyl 2-hydroxyethyl sulfide-acryl amide copolymer crosslinked with N,N-methylenebisacrylamide were studied.[37] These polymers (Figure 1-8) were selective for Au(III), Ag(I) and Hg(II). Au(III) and



I : R= $(CH_2)_2$
II : R= $(CH_2)_3$
III : R= $(CH_2)_2NH(CH_2)_2$

Figure 1-6 Structure of N-sulphonyl polyamine resins

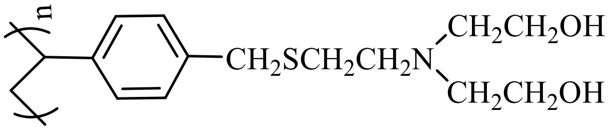


Figure 1-7 Structure of poly(2-hydroxyethylmercaptostyrene – diethanolamine), (PSME-EDA)

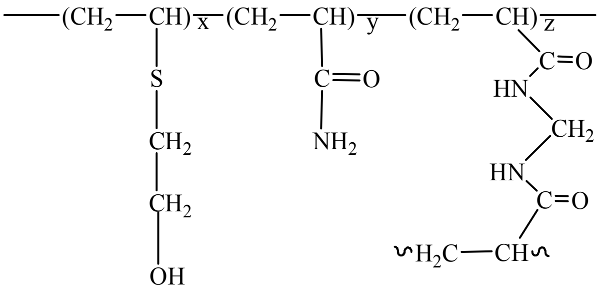


Figure 1-8 Structure of copolymer of vinyl (2-hydroxyethyl) sulfide and acrylamide crosslinked with methylene bisacrylamide.

Ag(I) were adsorbed under high acidities, i.e. 0.1 – 5 M HCl and 1 – 2 M HNO_3 respectively for the homopolymer. Metals such as copper and iron, were not adsorbed in appreciable amounts at pH 1 or in solutions of more than 3 M HCl. Mercury sorption was studied at pH 1 to pH 6 in nitrate and acetate solutions.

1.4.3 Coordination geometry of the metal ion

Correlations of metal ion specificity of polymer-supported reagents and preferred coordination number and geometry of metal ion have been found. This relation was also true for small molecule chelators of metal ions such as oligomers,[38] as well as for larger molecules such as proteins and transition metal ions in solution.[39] Evidence was obtained experimentally from single crystal x-ray diffraction (XRD) and extended x-ray absorption fine structure (EXAFS) data of complexes of molecules in the solid state, or from computer modeling calculations of complex formation.[40] Information from IR spectra was used to identify the ligands that participate in complexation by observing shifts in the frequencies of the bonds (those bonds that complexed the metal ion) upon complexation with metal ions.

The coordination number is defined as the number of ligand donor atoms connected to the central atom or ion. Coordination geometry refers to the spatial arrangement of the ligands around the central atom or ion. It is possible for a metal ion with a particular coordination number to have more than one geometrical arrangement. Metal ion selectivity of polymer-supported reagents can be enhanced by creating pre-organized binding sites or fixing the position of the binding site so that a given metal ion can adopt a preferred coordination number and geometry. This was best achieved through IIP.[41, 42] In this process, a monomer – metal ion complex was initiated and polymerized.

On removal of the metal ion, “memory” of the templated ion was induced. This implied that the specific geometric configuration for a particular metal ion was retained. If the ion-imprinted polymer was now contacted with a solution of metal ions, the metal ion which best fits the geometric requirements of the binding site formed (i. e. the templated ion), will be preferentially complexed. Covalent and non-covalent interactions make it possible to fix binding sites and improve selectivities and stabilities of metal ion binding. Some examples of the above concept would be described below. The imprinted polymer was more selective for the templated metal ion compared to the non-imprinted polymer for the same metal ion. Note that there has been some implication of the size of metal ion correlated to the size of the cavity of the template, as shown earlier.

A surface-templated resin was prepared by emulsion polymerization using monomers, dioleyl phosphoric acid and divinylbenzene in the presence of copper acetate. To this mixture, L-glutamic acid dioleylester ribitol was added as a co-surfactant.[43] The resulting resin was washed with 1 M HCl to remove the bound copper and then used to investigate the affinity of the resin for Cu(II). To further test this technique, a Zn^{2+} imprinted polymer and a non-imprinted polymer were made and their affinity to Cu^{2+} examined. It was found that the copper-imprinted resin removed 100 % Cu^{2+} compared to the reference (non-imprinted) and Zn^{2+} imprinted resin, which both sorbed about 50 % Cu^{2+} at pH 6.0. It was suggested that the effect of copper imprinting was to arrange the dioleyl phosphoric acid groups so that a desirable coordination (possibly square planar) around the Cu^{2+} ion was formed when they interact with Cu^{2+}. This organization of groups was not met by the Zn^{2+} imprinted nor the reference resin which had a random arrangement of groups.

A Cu(II)-selective ion imprinted polymer, poly(ethylene glycol dimethacrylate-methacryloylamidohistidine / Cu(II)) or p(EGDMA-MAH/Cu(II)), was successfully developed and studied under competitive conditions.[44] In the presence of Zn(II), Ni(II) and Co(II), at pH 7 and at temperatures of 25°C, Cu(II) was preferentially sorbed. The ratios of selectivity coefficient were compared with imprinted and non-imprinted matrices: $Cu^{2+} / Zn^{2+} = 7.4$, $Cu^{2+} / Ni^{2+} = 9.5$ and $Cu^{2+} / Co^{2+} = 12.3$ times greater for imprinted than for the non-imprinted polymers.

Metal ion specific binding sites can be designed using acyclic, multidentate ligands. Cu(II) selectivity was obtained by synthesis and polymerization of a Cu(II)-triethylenetetramine complex.[45] The prepared ligand was a mono- or di-subsituted vinylbenzyl chloride triethylenetetramine complex (Vb-TETA or DVb-TETA) which could bind to Cu(II) through its nitrogen donor sites (Vb-TETA-Cu or DVb-TETA-Cu). Copolymerization of the copper complex with 2-ethyl-2-(hydroxymethyl)propane-1,3-diol trimethacrylate (TRIM) created a macroporous polymer with enhanced kinetics. In the presence of Zn(II), the uptake of Cu(II) was unaffected. Electronic (UV-visible) spectra data indicated that the geometry of the Cu(II) – ligand complex was retained when polymerized; for the monosubstituted TETA – Cu(II) complex, a square planar geometry and for the divinylbenzyl - TETA – Cu(II) complex, a distortion of the planar geometry was observed. After several cycles of metal-ion removal / loading, the spectra of the polymers indicated that the binding sites of the polymers were retained.

Polymer-supported catechol ligands showed selectivity for Fe^{3+} at pH 1 - 3 in the presence of divalent (Cu^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Mg^{2+}) and trivalent metal ions (Al^{3+}, Cr^{3+}).[46]

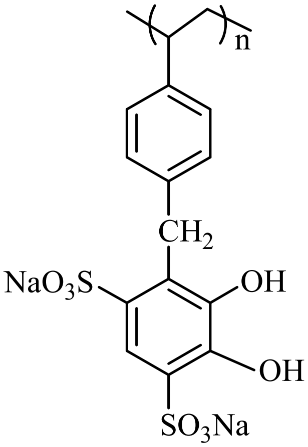


Figure 1-9 Polystyrene-supported sulfonated catechol,
(PS-CATS)

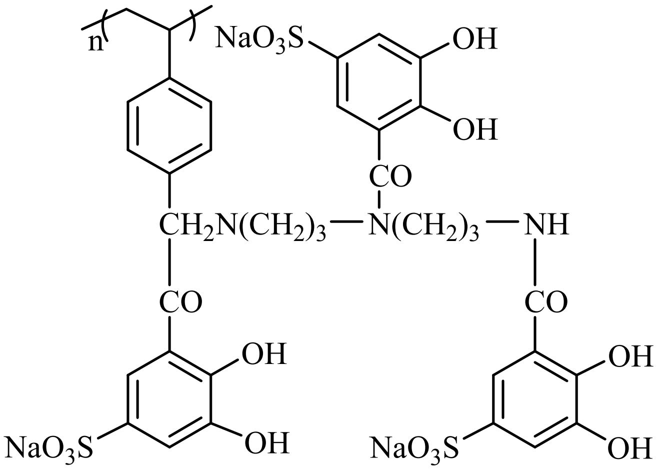


Figure 1-10 Polystyrene-supported sulfonated 3,3-linear tris(catechol)amide,
(PS-3,3-LICAMS)

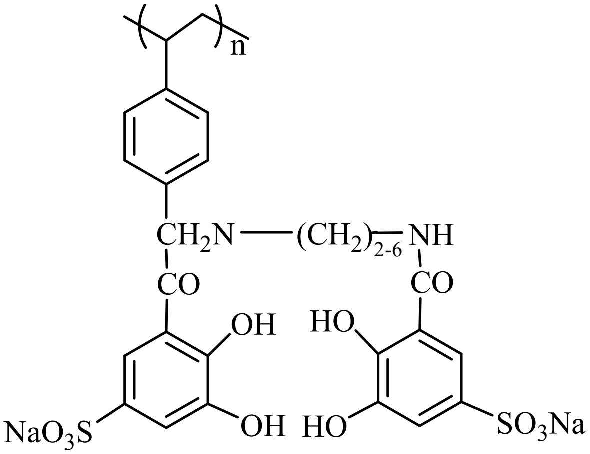


Figure 1-11 Polystyrene-supported sufonated bis(catechol) linear amide, (PS-2—6-LICAMS)

This selectivity was about 11 times greater when the ligand, sulfonated catechol (Figure 1-9) was changed to sulfonated 3,3-linear tris(catechol) amide (PS-3,3-LICAMS), a ligand that was predisposed for octahedral geometry (Figure 1-10).

The catechol functional group was involved in metal ion chelation since the sulfonated and unsulfonated polymers (PS-CATS and PS-CAT) had similar selectivities for Fe^{3+} from aqueous solution. Immobilization of the ligand, sulfonated bis(catechol) linear amide (PS-2—6-LICAMS) in figure 1-11, also showed a high selectivity for trivalent ions. When the divalent ion affinity of PS-2—6-LICAMS, a potentially square planar ligand, was compared to PS-3,3-LICAMS and PS-CATS, PS-2—6-LICAMS was found to be the most selective for divalent metal ions, although no selectivity was observed with any specific divalent metal ion. Note that changing the cavity size (from two CH_2 groups to six CH_2 groups) on the linear amide chain between the two catechol groups in PS-2—6-LICAMS had no effect on the order of selectivity.

In an example where separation of Cu(II) from aqueous solutions containing Fe(III) was desired, it was postulated that ligands which preferably permit tetrahedral disposition of the donor lone pairs would favor complexation of Cu(II) over Fe(III). Fe(III) most commonly forms 6-coordinate octahedral complexes. Chelating ligands based on the derivatives of a tetradentate ligand, N,N′-bis(2-pyridylmethyl)-2,2′-diaminobiphenyl, and on the derivatives of a tridentate ligand, N-(2-pyridylmethyl)-2,2′-diaminobiphenyl, were synthesized and immobilized on chloromethylated cross-linked polystyrene.[47] (Small molecule chelate complexes of the tetradentate ligand were prepared with Cu(II) and Pd(II)). The N-alkylated polymers (Figures 1-12 and 1-13) however, showed low capacity for Cu(II) and it was difficult to distinguish between

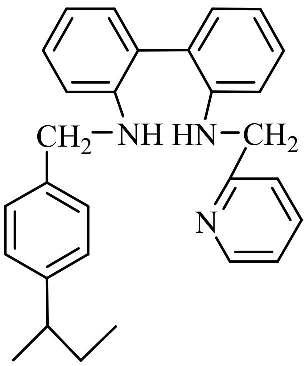


Figure 1-12 N-alkylated polymer of N-(2-pyridylmethyl)-2,2'-diaminobiphenyl (tridentate)

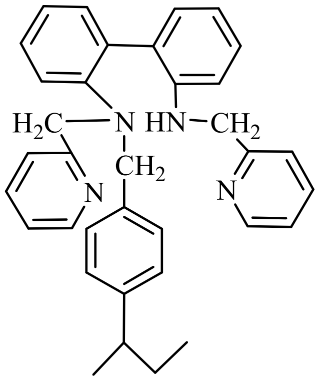


Figure 1-13 N-alkylated polymer of N, N'-bis(2-pyridylmethyl)-2,2'-diaminobiphenyl (tetradentate)

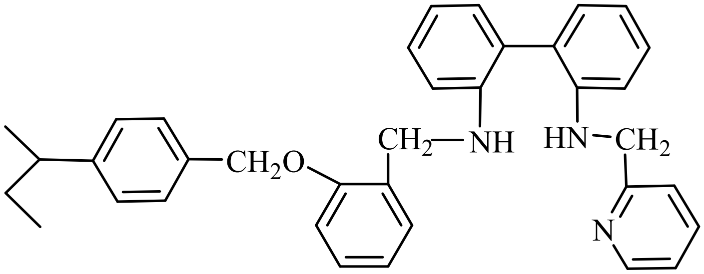


Figure 1-14 O-Alkylated polymer of N-(2-pyridylmethyl)-2,2’-diaminobiphenyl

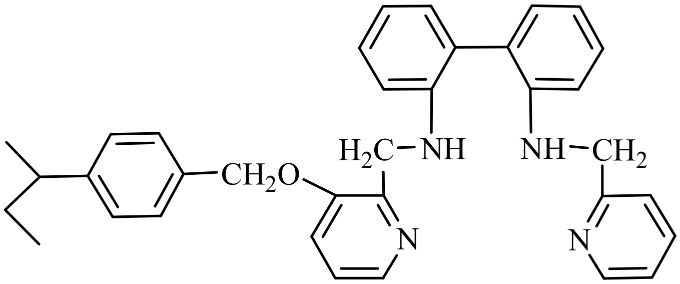


Figure 1-15 O-Alkylated polymer of N, N’-bis(2-pyridylmethyl)-2,2’-diaminobiphenyl (tetradentate)

Cu(II) and Fe(III). This occurred perhaps because the N-benzyl groups were parts of the polymer backbone and also parts of the coordination sites so that there would be some distortion involved upon metal ion chelation.

This was addressed by introducing a phenolic group into one of the phenyl rings of the ligands in the ortho, para and meta positions and immobilizing the ligand to the support via the –OH group (O-alkylated polymers), see figures 1-14 and 1-15. When the ligand were anchored in this way, polymers with considerable binding affinities for Cu(II) were obtained. This was dependent upon the point of attachment of the ligand to the polymer. Also, the tridentate polymers showed a low Cu(II) capacity when the polymer's benzyloxy group was ortho to the ligand's methylamino group compared to the tetradentate polymers, which displayed high affinity for Cu(II) when the ligand was similarly attached. There was an exception in this observation for the tetradentate polymers: the introduction of methyl groups ortho to the pyridine donor atoms on the ring reduced the affinity for Cu(II). It was questionable as to whether the methyl groups had an effect on the stereochemistry of the ligand or simply bulk shielding of the ion cavity.

1.5 Introduction to research in this thesis

This research focuses on designing and investigating novel chelating polymer-supported reagents, containing amide and phosphate ester ligands. Bifunctional polymers bearing these ligands have not been given much attention as regards divalent metal ion sorption. Related ligands such as carbamoylphosphonate (CMPO) and their derivatives have been widely studied for their complexing ability of lanthanides and actinides in the TRUEX process.[48] Immobilization of these moieties on cavitands[49] and macrocycles[50] enhanced their extraction efficiency. Various phosphate-containing ligands, for example tributyl phosphate (TBP) are useful extractants.[51] [52] The immobilisation of phosphorus groups on sorbents produced selective sorbents. Ketophosphonate resins[53, 54], phosphonic acid resins[55-57] pentaerythritol phosphate[58] are some of the phosphorus containing resins. Some research has been conducted with alkyl substituted amides, such as derivatives of oxydiacetic acid for actinide separations.[59]

This project defines the components of a bifunctional ligand[60] and then explores how metal ion affinities and selectivities may be enhanced. An amidophosphate ligand is synthesized on a polymer support. The support is a PS - 2 % DVB copolymer. The ligand is designed such that the binding sites for metal ion coordination are separated by a spacer group. The binding sites are carbonyl oxygen and phosphoryl oxygen and the spacer group is a series of aminoalcohols of different chain lengths.

The nitrate of one of the lanthanide elements, Eu(III) is considered in this work, and there will be some mention of the chemistry of the lanthanide.

1.6 References

1. Hudson, M. J. Some new strategies for the chemical separation of actinides and lanthanides. *Czech J. Phys.* **2003**, *53* (Suppl. A, Pt. 1), A305-A311.

2. Kaliyappan, T.; Kannan, P. Co-ordination polymers**.** *Prog. Polym. Sci.* **2000**, *25*, 343-370.

3. Pennington, L. D.; Williams, M. B. Chelating ion-exchange resins**.** *Ind. Eng. Chem*. **1959**, *51*, 759-762.

4. Sahni, S. K.; Reedijk, J. Coordination chemistry of chelating resins and ion exchangers. *Coord. Chem. Rev*. **1984**, *59*, 1-139.

5. Yuchi, A.; Sato, T.; Morimoto, Y.; Mizuno, H.; Wada, H. Adsorption mechanism of trivalent metal ions on chelating resins containing iminodiacetic acid groups with reference to selectivity. *Anal. Chem.* **1997**, *69*, 2941-2944.

6. Pesavento, M.; Biesuz, R.; Riva, F. D.; Alberti, G. Investigation of the complexation properties of a natural water towards copper(II), manganese(II) and aluminum(III), based on sorption of metal ions on a complexing resin. *Polyhedron* **2002**, *21*, 1343-1350.

7. Rahman, M. Z. Ab; Rahman, L.; Silong, S.; Yunus, W. M. Z. W.; Ahmad, M.; Haron, M. J. Poly(amidoxime) chelating resin used for separation of metal ions in aqueous media. *Orient. J. Chem.* **2001**, *17*, 205-208.

8. Zhu, X.; Alexandratos, S. D. Affinity and Selectivity of Immobilized N-Methyl-D-glucamine for mercury(II) ions. *Ind. Eng. Chem. Res*. **2005**, *44*, 7490-7495.

9. Dambies, L. Salinaro, R.; Alexandratos, S. D.; Immobilized N-methyl-D-glucamine as an arsenate-selective resin. *Environ. Sci.Technol*. **2004**, *38*, 6139-6146.

10. Denizli, A.; Garipcan, B.; Karabakan, A.; Say, R.; Emir, S.; Patir, S. Metal-complexing ligand methacryloylamidocysteine containing polymer beads for Cd(II) removal. *Sep. Purif. Technol*. **2003**, *30*, 3-10.

11. Hay, B. P.; Zhang, D.; Rustad, J. R. Structural criteria for the rational design of selective ligands. 2. Effect of Alkyl substitution on metal ion complex stability with ligands bearing ethylene-bridged ether donors. *Inorg. Chem.* **1996**, *35*, 2650-2658.

12. George, B.; Mathew, B.; Effect of the degree of crosslinking on the metal ion specificity of polyacrylamide-supported glycines. *J. Macromol. Sci., Pure Appl. Chem.* **2001**, A*38*, 429-449.

13. Czerwinski, K. R.; Draye, M. Favre-Reguillon, A.; Foos, J.; Guy, A.; Lemaire, M. Ion selective resins: development and applications for nuclear waste management. *Materials Research Society Symposium Proceedings*, **1999**, *556*, 1277-1284.

14. Bilba, D.; Bejan, D.; Tofan L. Chelating sorbents in inorganic chemical analysis, *Croat. Chem. Acta* **1998**, *71*, 155-178.

15. Irving, H. M.; Williams, R. J. P. The stability of transition-metal complexes. *J. Chem. Soc.* **1953**, *637*, 3192-3210.

16. Williams, S. M.; Brodbelt, J. S.; Marchand, A. P.; Cal, D.; Mlinaric-Majerski, K. Metal complexation of thiacrown ether macrocycles by electrospray ionization mass spectrometry. *Anal. Chem.* **2002**, *74*, 4423-4433.

17. Blakemore, J. D.; Chitta, R.; D'Souza, F. Synthesis and study of crown ether-appended boron dipyrrin chemosensors for cation detection. *Tetrahedron Lett.* **2007**, *48*, 1977-1982.

18. Hancock, R. D.; Maumela, H.; de Sousa, A. S. Macrocyclic ligands with pendent amide and alcoholic oxygen donor groups. *Coord. Chem. Rev.* **1996**, *148*, 315-347.

19. Zhang, X. X.; Izatt, R. M.; Bradshaw, J. S.; Krakowiak, K. E. Approaches to improvement of metal ion selectivity by cryptands. *Coord. Chem. Rev.* **1998**, *174*, 179-189.

20. Hancock, D. Chelate ring size and metal ion selection: the basis of selectivity for metal ions in open-chain ligands and macrocycles. *J. Chem. Educ.* **1992**, *69*, 615-621.

21. Voss, D. A. Jr.; Farquhar, E. R.; Horrocks, W. D. Jr.; Morrow, J. R. Lanthanide(III) complexes of amide derivatives of DOTA exhibit an unusual variation in stability across the lanthanide series. *Inorg. Chim. Acta* **2004**, *357*, 859-863.

22. Ohto, K.; Fujimoto, Y.; Inoue, K. Stepwise extraction of two lead ions with a single molecule of calix[4]arene tetracarboxylic acid. *Anal. Chim. Acta* **1999**, *387*, 61-69.

23. Ohto, K.; Tanaka, Y.; Yano, M.; Shinohara, T.; Murakami, E.; Inoue, K. Selective adsorption of lead ion on calix[4]arene carboxylate resin supported by polyallylamine. *Solvent Extr. Ion Exch.* **2001**, *19*, 725-741.

24. Chen, H.; Olmstead, M. M.; Albright, R. L.; Devenyi, J.; Fish, R. H. Metal-ion-templated polymers: synthesis and structure of N-(4-vinylbenzyl)-1,4,7-triazacyclononanezinc(II) complexes, their copolymerization with divinylbenzene, and metal-ion selectivity studies of the demetalated resins-

evidence for a sandwich complex in the polymer matrix. *Angew. Chem. Int. Ed.* **1997**, *36*, 642-645.

25. Lo, H. C.; Chen, H. Fish, R. H. Metal-ion-templated polymers, 3. Synthesis of a [{mono-N-(4-vinylbenzyl)-1,4,7-triazacyclononane}2Hg](OTf)$_2$ sandwich complex, polymerization of this monomer with divinylbenzene, and Hg^{2+} ion selectivity studies with the demetallated resin. *Eur. J. Inorg. Chem.* **2001**, *9*, 2217-2220.

26. Kimaro, A.; Kelly, L. A.; Murray, G. M. Synthesis and characterization of molecularly imprinted uranyl ion exchange resins. *Sep. Sci Technol.* **2005**, *40*, 2035-2052.

27. Van de Water, L. G. A.; Driessen, W. L.; Reedijk, J.; Sherrington, D. C. Metal-ion extraction by immobilized aza crown ethers. *Eur. J. Inorg. Chem.* **2002**, 221-229.

28. Ahrland, S.; Chatt, J.; Davis, N. R. The relative affinities of ligand atoms for acceptor molecules and ions. *Quart. Rev.* **1958**, *12*, 265-276.

.

29. Pearson, R. G. Hard and soft acids and bases *J. Am. Chem. Soc.* **1963**, *85*, 3533-3539.

30. Klopman, G. Chemical reactivity and the concept of charge- and frontier-controlled reactions. *J. Am. Chem. Soc.* **1968**, *90*, 223-234.

31. Parr, R. G.; Pearson, R. G. Absolute hardness: Companion parameter to absolute electronegativity. *J. Am. Chem. Soc.* **1983**, *105*, 7512-7516.

32. Van de Water, L. G. A.; Driessen, W. L.; Glenny, M. W.; Reedijk, J.; Schroder, M. Selective and reversible extraction of heavy metal-ions by mixed-donor crown ether-modified oxirane and thiirane resins. *React. Funct. Polym.* **2002**, *51*, 33-47.

33. Van de Water, L. G. A.; Ten Hoote, F.; Driessen, W. L.; Reedijk, J.; Sherrington, D. C. Selective extraction of metal ions by azathiacrown ether-modified polar polymers. *Inorg. Chim. Acta* **2000**, *303*, 77-85.

34. Adam, K. R.; Baldwin, D. S.; Duckworth, P. A.; Lindoy, L. F.; McPartlin, M.; Bashall, A.; Powell, H. R.; Tasker, P. A. Macrocyclic ligand design. Effect of donor-set and ring-size variation on silver(I) / lead(II) discrimination within an extended series of dibenzo substituted rings. *J. Chem. Soc. Dalton Trans*. **1995**, *7*, 1127-1131.

35. Bakir, J. A. Jeragh, Abdel-Zaher A. Elassar, Ali El-Dissouky. Ligating behavior and metal uptake of N-sulphonylpolyamine chelating resins anchored on polystyrene-divinylbenzene beads. *J. Appl. Polym. Sci.* **2005,** *96*, 1839-1846.

36. Sun, C.; Qu, R.; Ji C.; Wang, Q.; Wang, C.; Sun, Y. Cheng, G. A chelating resin containing S, N and O atoms: synthesis and adsorption properties for Hg(II). *Eur. Polym. J.* **2006**, *42*, 188-194.

37. Anpilogova, G. R.; Vorob'eva, A. I.; Onina, S. A.; Khisamutdinov, R. A.; Murinov, Y. I.; Monakov, Y. B. Vinyl 2-hydroxyethyl sulfide polymers and their sorption properties with respect to transition metals. *Russ. J. Appl. Chem.* **2006**, *79*, 1593-1599.

38. Yanagida, S.; Takahashi, K.; Okahara, M. Metal-ion complexation of noncyclic poly(oxyethylene) derivatives. III. Complexation in aprotic solvent and isolation of their solid complexes. *Bull. Chem. Soc. Jpn*. **1978**, *51*, 3111-3120.

39. McCall, K. A.; Fierke, C. A. Probing determinants of metal ion selectivity in carbonic anydrase using mutagenesis. *Biochemistry* **2004**, *43*, 3979-3986.

40. Pesonen, H.; Sillanpaeae, A.; Aksela, R.; Laasonen, K. Density functional complexation study of metal ions with poly(carboxylic acid) ligands. Part 2. Poly(acrylic acid - co - maleic acid), poly(methyl vinyl ether - co - maleic acid), and poly(epoxy succinic acid). *Polymer* **2005**, *46*, 12653-12661.

41. Shea, K. J. Molecular imprinting of synthetic network polymers: the de novo synthesis of macromolecular binding and catalytic sites. *Trends in Polymer. Science* **1994**, 2, 166-173.

42. Rao, T. P.; Kala, R.; Daniel, S. Metal ion-imprinted polymers – Novel materials for selective recognition of inorganics. *Anal. Chim. Acta* **2006**, *578*, 105-116.

43. Maeda, M.; Murata, M. Template dependent metal absorptivity of dialkyl phosphate type resins prepared by surface template polymerization technique. *Anal. Sci.* **1994**, *10*, 113-115.

44. Say, R.; Birlik, E.; Ersoz, A.; Yilmaz, F.; Gedikbey, T.; Denizli, A. Preconcentration of copper on ion-selective imprinted polymer microbeads. *Anal. Chim. Acta* **2003**, *480*, 251-258.

45. Singh, A.; Puranik, D.; Guo, Y.; Chang, E.L. Towards achieving selectivity in metal ion binding by fixing ligand-chelator complex geometry in polymers. *React. Funct. Polym.* **2000**, *44*, 79-89.

46. Huang, S-P.; Li, W.; Franz K. J.; Albright, R. L.; Fish, R. H. Polymer pendant ligand chemistry. 3. A biomimetic approach to selective metal ion removal and recovery from aqueous solution with polymer-supported sulfonated catechol and linear catechol amide ligands. *Inorg. Chem.* **1995**, *34*, 2813-2819.

47. Melby, L. R. Polymers for Selective Chelation of Transition Metal Ions. *J. Am. Chem. Soc*. **1975**, *97*(14), 4044-4051.

48. Ozawa, M.; Sano, Y.; Tanaka, Y. CMPO-TRUEX process and its application in the separation of actinides from high-level liquid wastes. *Miner. Process. Extr. Metall. Rev.* **2000**, *21*, 249-275

49. Boerrigter, H.; Verboom, W.; Reinhoudt, D. N. Novel Resorcinarene cavitand-based CMP(O) cation ligands: synthesis and extraction properties. *J. Org. Chem.* **1997**, *62*, 7148-7155.

50. Arnaud-Neu, F.; Boehmer, V.; Dozol, J.-F.; Gruettner, C.; Jakobi, R. A.; Kraft, D.; Mauprivez, O.; Rouquette, H.; Schwing-Weill, M.-J.; Simon, N.; Vogt, W. Calixarenes with diphenylphosphorylacetamide functions at the upper rim. A new class of highly efficient extractants for lanthanides and actinides. *J. Chem. Soc. Perkin Trans. 2* **1996**, *6*, 1175-1182.

51. Kulkarni, P. G.; Gupta, K. K.; Gurba, P. B.; Janardan, P.; Changrani, R. D.; Dey, P. K.; Manchanda, V. K. Solvent extraction behaviour of some fission product elements with N,N-dihexyl octanamide and tri-n-butyl phosphate under simulated PUREX process conditions**.** *Radiochim. Acta* **2006**, *94*, 325-329.

52. Obaseki, O. O.; Ipinmoroti, K. O.; Ajayi, O. O. Separation of copper and zinc cations from each other in aqueous acid sulfate solution using tri-n-butyl phosphate (TBP). *Global J. Pure Appl. Sci.* **2006**, *12*, 93-97.

53. Alexandratos, S. D.; Hussain, L. A. Synthesis of α-, β- and γ-ketophosphonate polymer supported reagents: the role of intraligand cooperation in the complexation of metal ions. *Macromolecules* **1998**, *31*, 3235-3238.

54. Alexandratos, S. D.; Trochimczuk, A. W.; Crick, D. W.; Horwitz, E. P.; Gatrone, R. C.; Chiarizia, R. Synthesis and Ion-Complexing Properties of a Novel Polymer-Supported Reagent with Diphosphonate Ligands. *Macromolecules* **1996**, *29*, 1021-1026.

55. Alexandratos, S.D.; Trochimczuk, A. W.; Horwitz, E. P.; Gatrone, R. G. Synthesis and characterization of a bifunctional ion exchange resin with polystyrene-immobilized diphosphonic acid ligands. *J. Appl. Polym. Sci.* **1996**, *61*, 273-278.

56. Yamabe, K; Ihara, T. Jyo, A. Metal ion selectivity of macroreticular chelating cation exchange resins with phosphonic acid groups attached to phenyl groups of a styrene-divinylbenzene copolymer matrix. *Sep. Sci. Technol.* **2001**, *36*, 3511-3528.

57. Egawa, H.; Yamabe, K.; Jyo, A. Studies on selective adsorption resins. XXXIII. Behavior of macroreticular chelating resins containing phosphinic or phosphonic acid groups in the adsorption of trivalent lanthanides. *J. Appl. Polym. Sci.* **1994**, *52*, 1153-1164.

58. Alexandratos S. D.; Zhu, X.; Bifunctional Coordinating Polymers: Auxiliary Groups as a Means of Tuning the Ionic Affinity of Immobilized Phosphate Ligands. *Macromolecules* **2005**, *38*, 5981-5986.

59. Rao, L.; Tian, G. LBNL-5924, **2006**.

60. Alexandratos, S. D.; Hong, M.-J**.** Enhanced metal ion affinities by supported ligand synergistic interaction in bifunctional polymer-supported aminomethylphosphonates. *Sep. Sci. Technol.* **2002**, *37*, 2587-2605

2 AMIDE AND PHOSPHONATE DIESTER RESINS – SYNTHESIS AND METAL CONTACT STUDIES

2.1 Introduction

Polymer-supported reagents with ion complexing groups are useful as sorbents for metal ion separations and preconcentration.[1, 2] Rational design of ligands for polymer immobilization is essential for preparing new effective sorbents and improving existing materials. As is apparent in Chapter 1, much study is dedicated to ligand design: one can find a vast collection of polymer-supported reagents suitable for different applications.[3, 4]

Two monofunctional resins were synthesized. Monofunctional resins, resins containing one type of complexing group capable of metal ion coordination, do not always have a high capacity for metal ions from acidic media (e. g. pH 2.0). Generally however, resins that are capable of ion-exchange such as phosphonic acid resins, can have high and indiscriminate sorption capacities under these conditions.[5]

Neutral ligands, such as those used in solvent extraction studies, for example, phosphonate and amide type ligands can be effective metal ion complexants.[6, 7] Monofunctional resins bearing these ligands were synthesized. The purpose of their syntheses was to investigate metal uptake by resins containing neutral ligands when one functional group is present so as to compare them to resins in which both functionalities occur together. Knowledge of the interaction of these monofunctional resins with metal ions would be important when proposing a mechanism by which bifunctional neutral resins (Chapter 3) complex metal ions.

Functionalization of resins is easily performed by modification of a poly(vinylbenzyl) chloride – 2 % divinylbenzene copolymer. This method of preparation of polymer-supported reagents enhances the probability of a complete reaction by ensuring that reaction sites would be accessible to reagents.

2.2 Experimental Procedures

A summary of the experimental procedures is presented below. Chapter 5 contains the complete procedures and description of the analysis techniques used in characterizing the resins.

2.2.1 Synthesis of copolymers

Vinylbenzyl chloride (VBC) was synthesized by suspension polymerization with 2 % divinylbenzene (DVB) as the crosslinking agent.[8] The gel resins prepared were sieved with U.S. standard sieves so that the diameter of beads used was 250-425µm.

2.2.2 Synthesis of acid chloride resin

This resin was prepared by chlorination of carboxylic acid resin using thionyl chloride.[8] The synthesis of carboxylic acid resin from VBC - 2 % DVB copolymer followed a standard procedure.[2] This resin was analyzed for its acid capacity. A chlorine elemental capacity was also determined. The resin was then chlorinated and the effectiveness of this step was examined by determination of the chlorine content. In addition, an acid capacity determination of the acid chloride resin upon esterification with methanol also confirmed whether the acid chloride step was complete. (Acid chlorides were found to react fully with methanol and ethanol). For example, an acid chloride resin having a Cl capacity of 5.0 mmol/g was found to have a negligible acid capacity upon its reaction with methanol. (Note that it was difficult to accurately determine the percent functionalization of acid chloride resin using chlorine capacity results since the acid capacity of the carboxylic acid resin, the precursor resin, was 5.7 mmol/g, and not the theoretical value 6.2 mmol/g.) An acid capacity of zero indicated that all of the initial carboxylic acid groups were chlorinated, all acid chloride groups formed were esterified and that the ester bond was stable. The latter method was a convenient way to determine whether the reaction with thionyl chloride was complete.

2.2.3 Esterification of acid chloride resin

About 1 g of freshly prepared acid chloride beads was transferred to a 250 mL round bottom flask. The flask was then set up with an overhead stirrer. Fifty milliliters of methanol were added and the beads stirred for 2 h. The beads were washed with water and filtered (3 times) before evaluating the acid capacity of the resin. This procedure was adopted in the washing treatment of acid chloride resins after a reaction e. g. upon amidation as in section 2.2.4.

2.2.4 Synthesis of carboxamide resin

Acid chloride beads were reacted with diethylamine in acetonitrile at room temperature. Nitrogen elemental was determined for this resin.

2.2.5 Synthesis of phosphonate ester resin

The Arbusov reaction was utilized to prepare this resin.[9] Triethyl phosphite was used as the solvent and reactant. The resin was characterized by its phosphorus capacity.

2.2.6 Treatment of resins that were synthesized from acid chloride resins

The standard treatment employed was stirring the resin with 50 mL methanol for 2h, filtering and then stirring with 50 mL water for 15 minutes. This treatment ensured that any unreacted acid chloride was esterified.

2.2.7 IR spectroscopy of resin

IR spectra were obtained by preparing KBr disc of the resin sample and using a Bomem FTIR spectrophotometer.

2.3 Results and Discussion

2.3.1 Characterization of polymer support

Vinylbenzene - 2 % divinylbenzene (2 % VBC-DVB) copolymer was prepared. The copolymer had average chlorine capacities of 6.0 mmol/g (theoretical = 6.3 mmol/g). In the IR spectrum of VBC (Figure 2-1), a band at 703 cm^{-1} characteristic of C-Cl stretch[10, 11] and one at 1265 cm^{-1} which was assigned to a methylene wagging mode of benzyl chlorides were found.[12]

2.3.2 Characterization of carboxylic acid, acid chloride and carboxamide resins

Conversion of -CH_2Cl groups on the polymer chain to -COOH functional groups was quantitative. Carboxylic acid resins were characterized by acid capacity determinations and IR spectroscopy. Average acid capacities of 5.7 mmol/g (theoretical acid capacity = 6.2 mmol/g) were obtained. The chlorine capacity of the modified polymer was found to be negligible, indicating that there were no available alkyl chloride side chains (% conversion $\geq$ 90 %). Conversion of the carboxylic acid to acid chloride with thionyl chloride was 100 % complete. This was concluded from control experiments by esterification of acid chloride resin with methanol (discussed in sections 2.2.2 and 2.2.3). It was found that alcohols such as methanol and ethanol can react completely with acid chlorides, forming esters at room temperature after 2 hours of contact time with methanol and acid chloride resin. IR spectra confirmed the preparation of carboxylic acid (Figure 2-2) and acid chloride resins (Figure 2-3). The locations of the carbonyl group stretching frequencies at 1700 cm^{-1} for the carboxylic acid and 1772 cm^{-1} for the acid chloride fell within the expected range of frequencies.[13, 14] Additionally the spectrum of benzoyl chloride showed C=O stretches at 1763 cm^{-1} and 1724 cm^{-1}, which compared well with those found in the acid chloride resin spectrum at 1772 cm^{-1} and 1733 cm^{-1}.

Reaction at the carbonyl group was enhanced by conversion of carboxylic acid to acid chloride group. Substitution of –Cl by diethylamine to produce the carboxamide (Figure 2-4) occurred readily, with a nitrogen capacity of 3.40 mmol/g indicating that the resin was 83 % functionalized (based on N capacity). The IR spectum of the carboxamide resin indicated a C=O stretch at 1626 cm^{-1} (Figure 2-5). Another band at 1718 cm^{-1} can be the C=O of an ester, possibly as a result of unreacted acid chloride reacting with methanol for 2 hours. Note that the standard treatment of washing acid chloride resins after a reaction such as amidation, involved removal of the reactants and stirring the resin with methanol by stirring for 2 h. Any hydrolysis of unreacted acid chloride can be avoided (section 2.2.3). Table 2-1 gives the elemental analyses results of carboxylic acid, acid chloride and carboxamide.

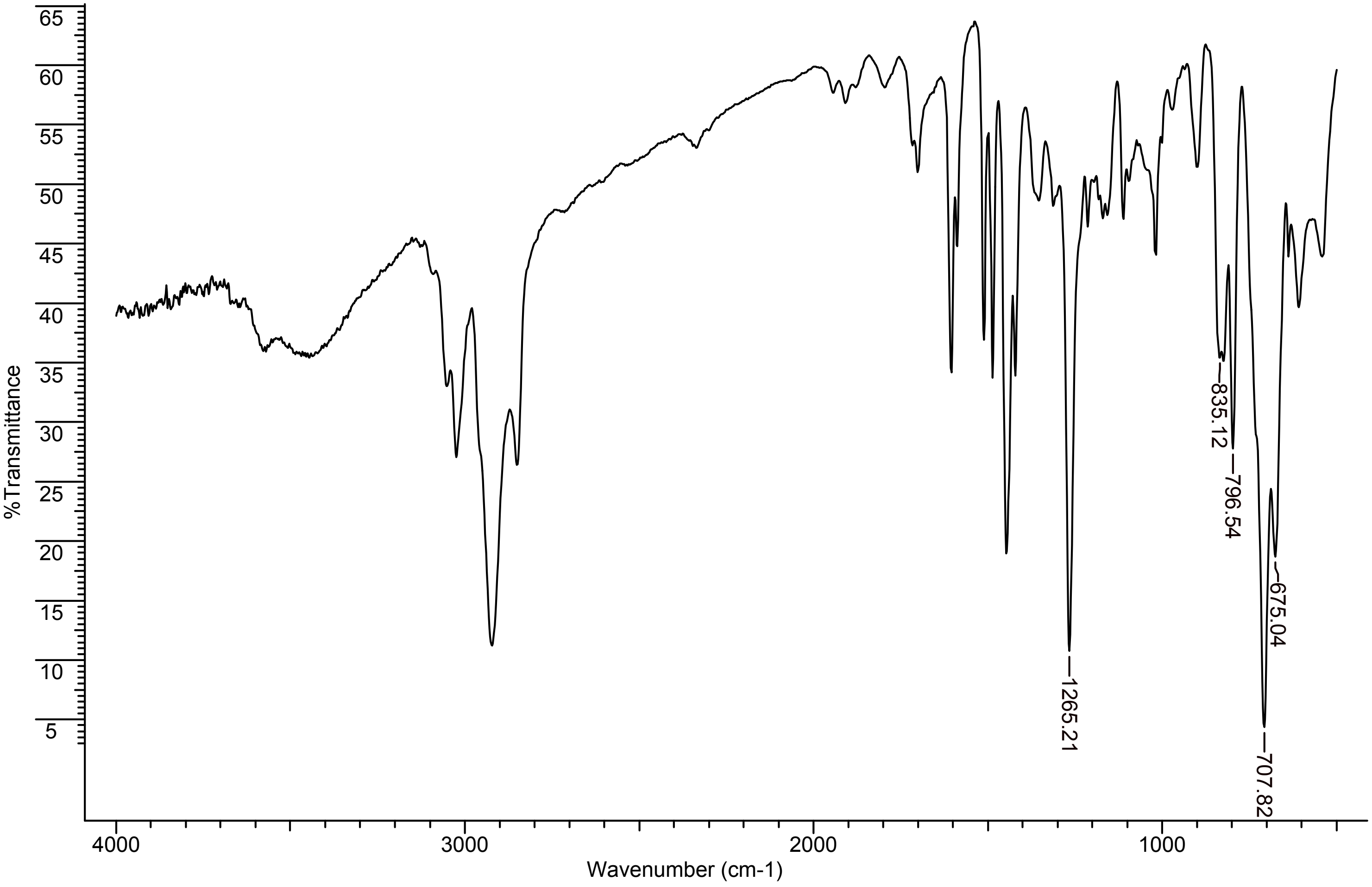


Figure 2-1 VBC - 2% DVB gel copolymer IR spectrum

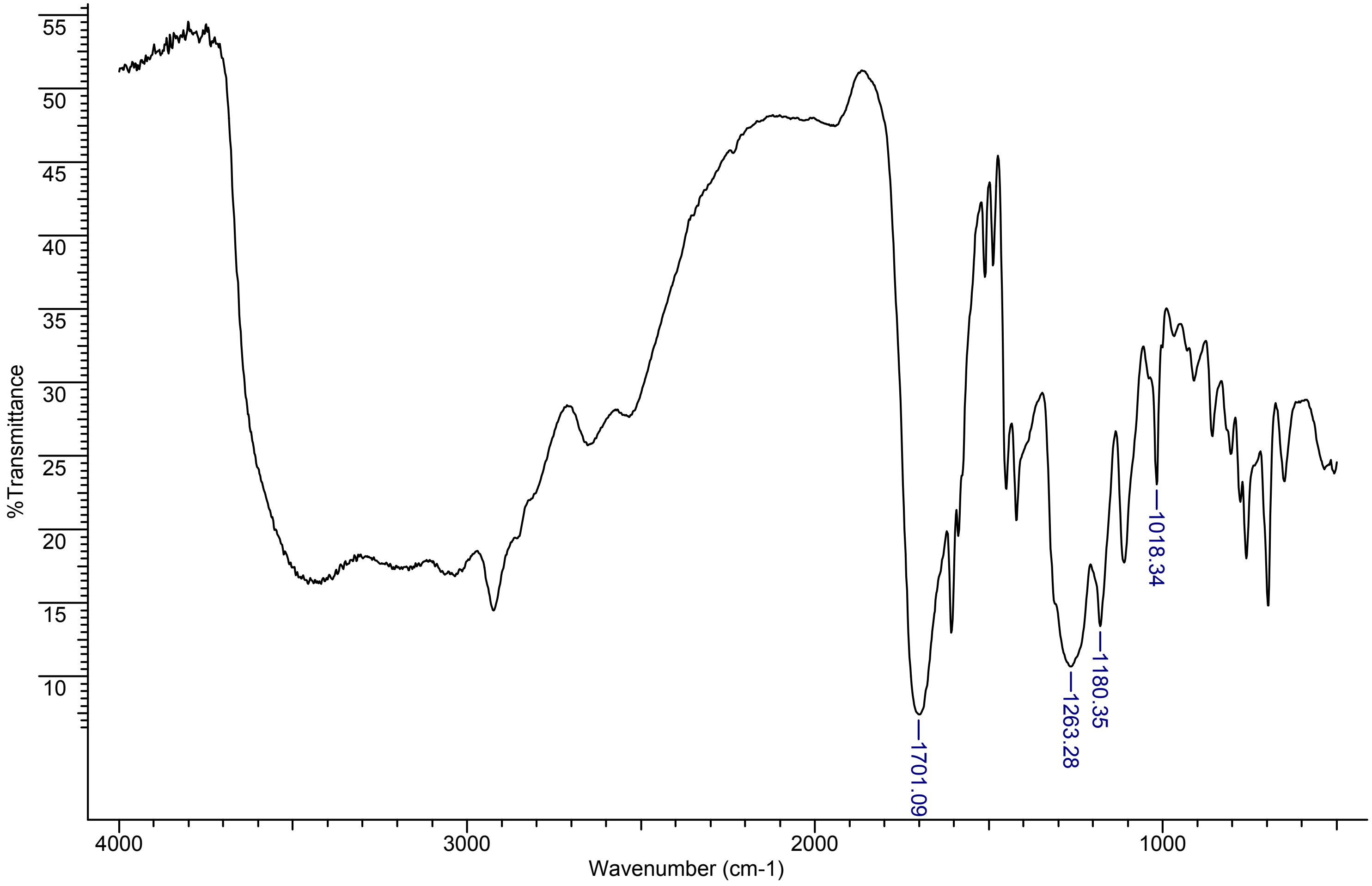


Figure 2-2 FTIR spectrum of carboxylic acid resin.

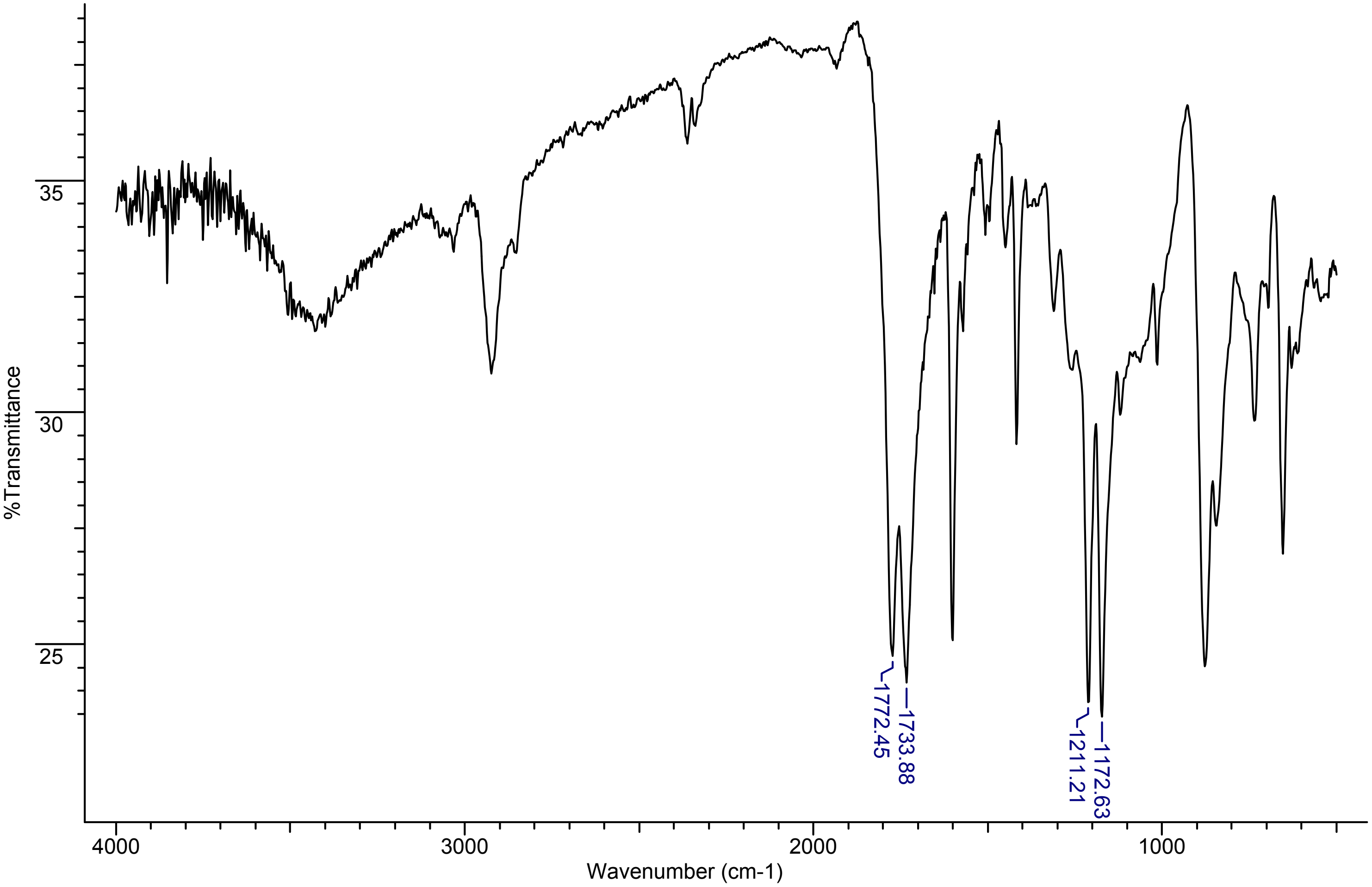
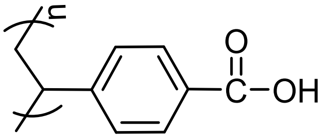
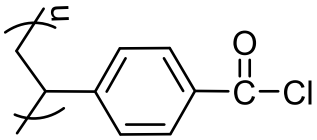


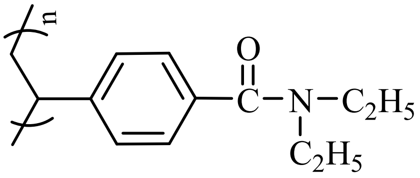
Figure 2-3 FTIR spectrum of Acid chloride resin



Carboxylic acid resin



Acid chloride resin



Carboxamide resin

Figure 2-4 Structures of carboxylic acid, acid chloride and carboxamide resins

Table 2-1 Elemental analysis of carboxylic acid, acid chloride and carboxamide of a sample of resins

Resin code (AP #)	**Functional group**	**Acid capacity, mmol/g Actual (theoretical)**	**Nitrogen capacity, mmol/g Actual (theoretical)**	**Chlorine capacity, mmol/g Actual (theoretical)**	**[a]% solids**
5-045	-COOH	5.68 (6.30)	N. A.	0.00	48.3
5-053		5.71	N. A.	N. D.	52.3
5-091		5.99	N. A.	0.00	46.4
3-139	-COCl	N. A.	N. A.	4.55 (5.78)	N. A.
3-191		N. A.	N. A.	5.42	N. A.
3-204		N. A.	N. A.	4.94	N. A.
3-221		N. A.	N. A.	4.34	N. A.
4-299b	$-C(O)N(C_2H_5)_2$	0.07 (0.00)	3.86 (4.10)	N. D.	73.1
5-001[a]		0.28	3.40	N. D.	66.3

([a] % solids = $g_{dry}/\, g_{wet} \times 100$)
N. A. = not applicable
N. D. = not determined

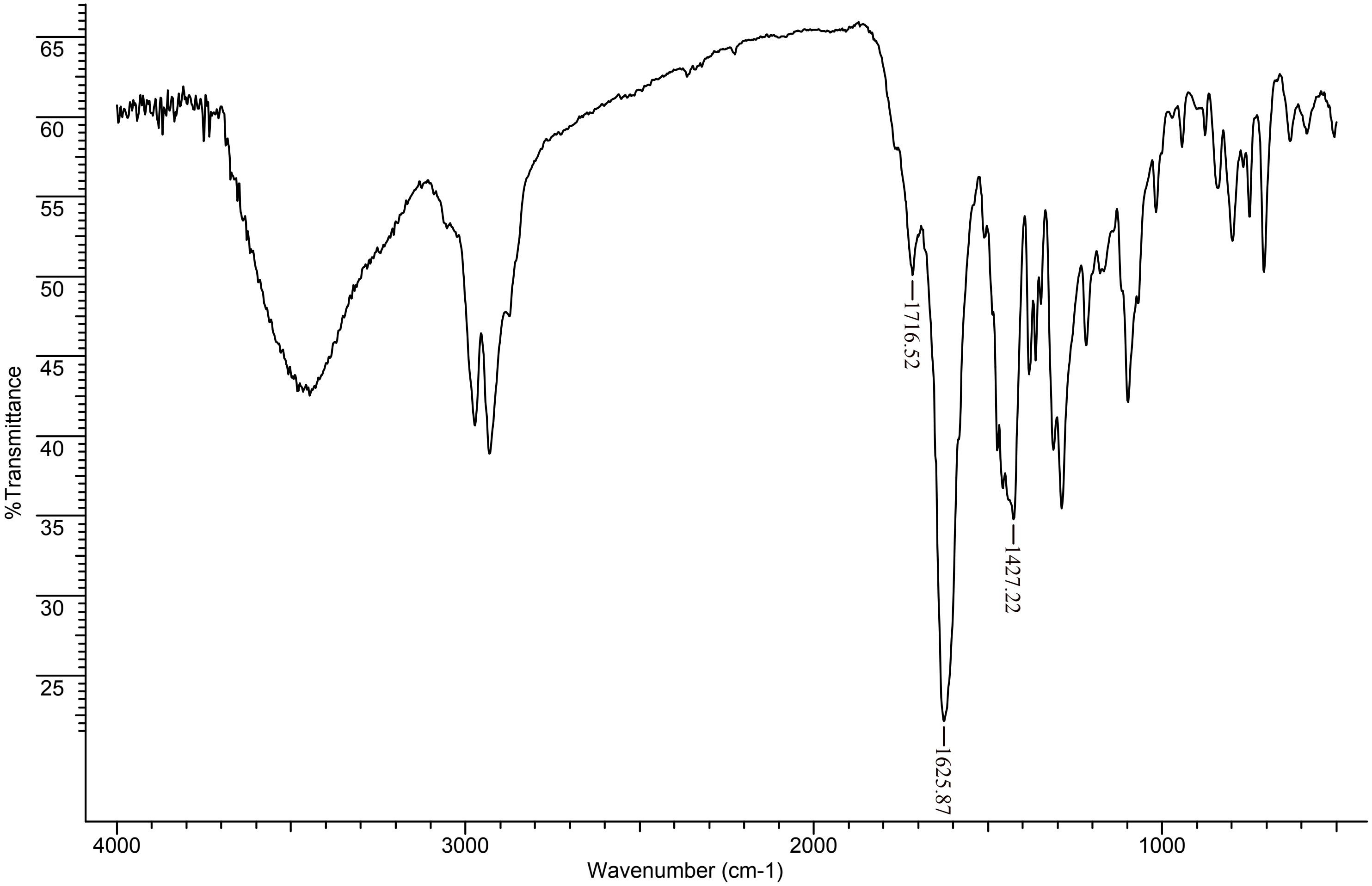


Figure 2-5 FTIR spectrum of carboxamide resin (AP 5-001a)

Attempts were made to prepare the carboxamide by refluxing acid chloride beads with N, N-dimethyl formamide.[15] However, high acid capacities and lower N capacities were obtained. Figure 2-4 illustrate the structures of carboxylic acid, acid chloride and carboxamide resins.

2.3.3 Characterization of phosphonate diester resin

The Michaelis-Arbusov reaction was used for the introduction of the phosphonate group. Near-theoretical phosphorus capacities were obtained with an average phosphorus capacity of 3.71 mmol/g (theoretical = 3.94 mmol/g, see Table 2-2). This resin has a P=O functional group at 1234 cm^{-1} and P-O stretches at 1054, 1024 and 964 cm^{-1} as shown in Figure 2-6.

Table 2-2 Elemental analysis of phosphonate diester resin

Resin code (AP #)	P cap., mmol/g Actual (Theoretical)	Acid cap., mmol/g	% solids
4-274	3.90 (3.94)	0.00	72.7
4-282	3.57	0.08	68.6
4-042	3.81	0.09	69.4

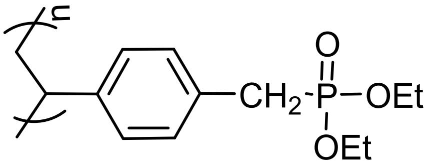


Figure 2-6 Phosphonate diester resin

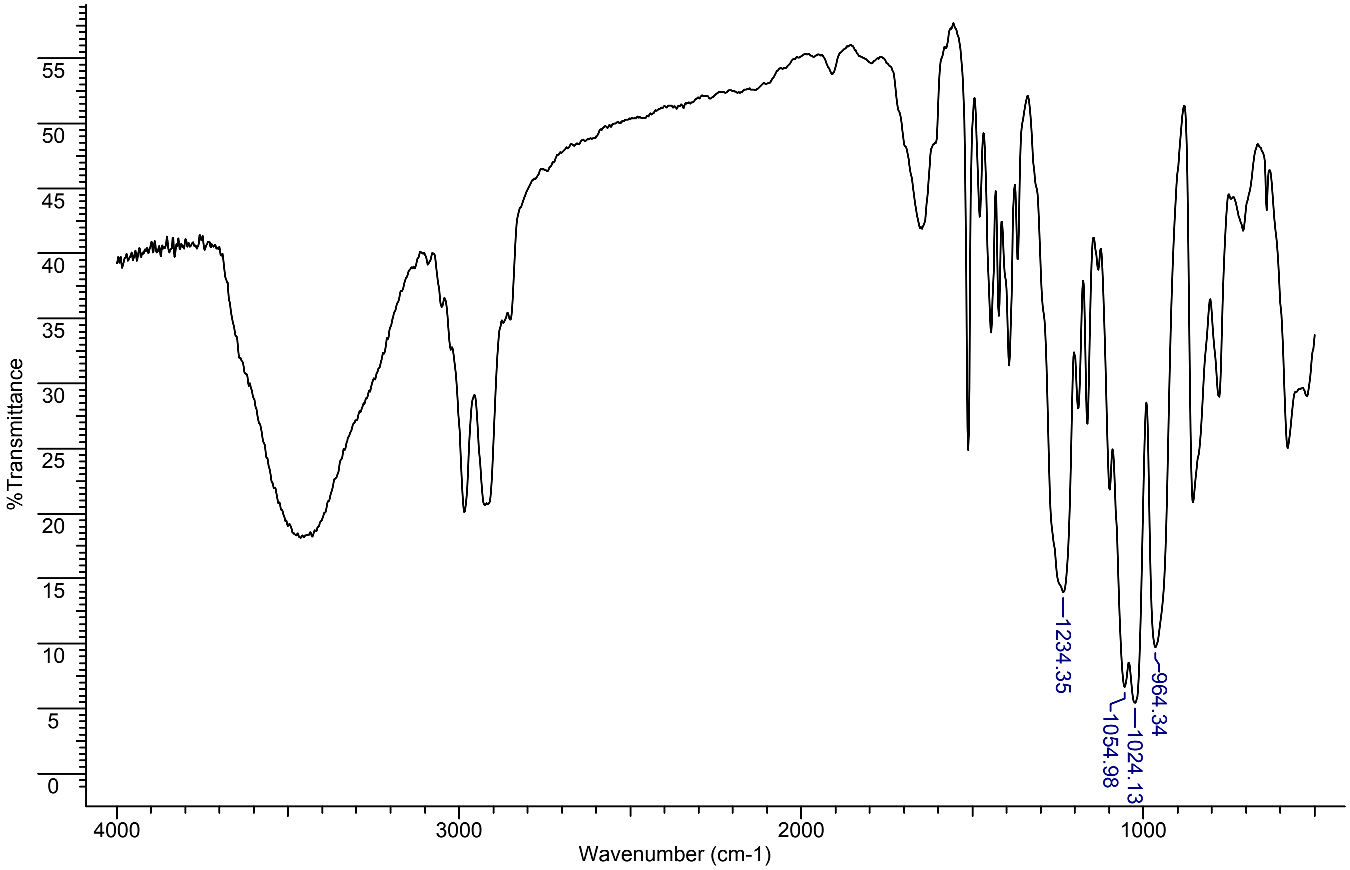


Figure 2-7 Representative FTIR spectrum of phosphonate diester resin (AP 4-042)

2.3.4 Metal contact study results

Tables 2-3 and 2-4 show the metal contact study results of carboxamide and phosphonate diester resins at pH 2.0, with divalent and trivalent ions respectively. The results were expressed in terms of percent metal ion complexed and distribution coefficient (D) values. The percent metal ion complexed referred to the amount of metal ion on the resin compared to initial amount of the metal ion in solution used, expressed as a percentage, while the D values are defined as the ratio of the number of millimoles of metal ion on the resin per gram of resin to the number of millimoles of metal ion in the solution per mL of solution. The results indicate that resins containing either ligand alone do not have high affinities for metal ions. Carboxamide resins have similar affinities for divalent and trivalent metal ions. Although phosphonate diester resins have low affinities for divalent and trivalent metal ions, larger amounts of trivalent ions are complexed compared to divalent ions.

The ability to complex metal ions is related to the basicity of the complexing group.[16] The carbonyl oxygen of amides and phosphoryl oxygen of esters have low basicity and hence are not good complexants on their own.[17, 18] The phosphoryl group is a stronger complexant and the higher affinity for trivalent metal ions may be due to the charge density of the ion. Higher charge density of ions allows for stronger interactions.[19]

2.4 Conclusions

The results indicate that neutral resins containing one coordinating site per ligand (either carbonyl or phosphoryl oxygens) are weak complexants at pH 2.0. The competition for a proton is stronger and so the ligand prefers this acceptor. Adjusting the background solution to higher pH's may result in higher sorption.

Table 2-3 Divalent metal ion study results of carboxamide and phosphonate diester resins from 1×10^{-4} N metal nitrate solutions in a background solution of 0.01 N nitric acid

		Pb(II)		**Cd(II)**		**Cu(II)**		**Ni(II)**		**Zn(II)**	
Resin code AP#	**Functional group**	**%[a] complexed**	**D[b]**	**% complexed**	**D**	**% complexed**	**D**	**% complexed**	**D**	**% complexed**	**D**
5-001a, 4-299b	$-C(O)N(CH_3)_2$ carboxamide	4.63	1.34	2.70	0.78	4.55	1.28	2.95	0.82	2.50	0.88
4-274, 4-282	$-P(O)(OEt)_2$ phosphonate ester	8.43	2.65	5.08	1.77	4.37	1.25	2.15	0.61	5.78	1.66

[a] $\%\ M^{n+}$ complexed = $\{([M^{n+}_{(aq)}]_{initial} - [M^{n+}_{(aq)}]_{equilibrium}) / [M^{n+}_{(aq)}]_{initial}\} \times 100$

[b] $D = ([\text{mmol } M^{n+}]_{resin}/g_{resin})/([\text{mmol } M^{n+}]_{soln}/mL_{soln})$

Table 2-4 Trivalent metal ion study results of carboxamide and phosphonate diester resins from 1×10^{-4} N metal nitrate solutions in a background of 0.01 N nitric acid.

Resin code AP#	**Functional group**	**Eu(III)**		**Fe(III)**		**Al(III)**	
		% complexed	**D**	**% complexed**	**D**	**% complexed**	**D**
5-001a, 4-299b	$-C(O)N(CH_3)_2$ Carboxamide	4.87	1.37	1.90	0.52	0.00	0.00
4-274, 4-282	$-P(O)(OEt)_2$ phosphonate ester	24.4	9.33	39.9	18.1	21.8	8.18

2.5 References

1. Ivanova, E.; Todorova, O. Immobilized organic reagents and their use in analytical chemistry. *Izvestiya po Khimiya* **1989**, *22*, 78-93.

2. Sherrington, D. C. Polymer-supported reagents, catalysts, and sorbents: evolution and exploitation-a personalized view**.** *J. Polym. Sci., Part A: Polym. Chem*. **2001**, *39*, 2364-2377.

3. Alexandratos, S. D. New polymer-supported ion-complexing agents: Design, preparation and metal ion affinities of immobilized ligand**s.** *J. Hazard. Mater.* **2007**, *139*, 467-470.

4. Taylor, P. Removal of trace concentrations of heavy metals using complexing ion-exchange resins. *Sep. Sci. Technol*. **2006**, *41*(11), 2575-2579.

5. Merdivan, M.; Buchmeiser, M. R.; Bonn, G. Phosphonate-based resins for the selective enrichment of uranium (VI). *Anal. Chim. Acta* **1999**, *402*, 91-97.

6. Zhao, J.; Bai, Y. Li, D.; Li, W. Extraction of rare earths(III) from nitrate medium with di-(2-ethylhexyl)-2-ethylhexyl phosphonate and synergistic extraction combined with 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5. *Sep. Sci. Technol.* **2006**, *41*, 3047-3063.

7. Berthon, C.; Chachty, C. NMR and IR spectrometric studies of monoamide complexes with plutonium(IV) and lanthanide(III) nitrates. *Solvent. Extr. Ion Exch*. **1995**, *13*, 781-812.

8. Stine, C. L. Ph.D. Dissertation, University of Tennessee. Knoxville **2002.**

9. Alexandratos, S. D.; Hussain, L. A. Synthesis of α-, β- and γ-ketophosphonate polymer supported reagents: the role of intraligand cooperation in the complexation of metal ions. *Macromolecules* **1998**, *31*, 3235-3238.

10. Chattopadhyay, S. Assignments of the vibrational frequencies of some benzyl compounds. *Indian Journal of Physics* **1967**, *41*, 759-770.

11. Bird, C. W.; Carbon-halogen stretching frequencies of some benzyl chlorides and bromides. *Spectrochim. Acta, Part A: Molecular and Biomolecular Spectroscopy* **1968**, *24*, 1666-1667.

12. Mannion, J.; Wang, T. S. An infrared study of the CH_2Cl group in benzyl chloride and derivatives. *Spectrochim. Acta* **1964**, *20*, 45-49.

13. Condit, D. A.; Craven, S. M.; Katon, J. E.; Vibrational spectra of some benzoyl halides. Benzoyl chloride, benzoyl-d5 chloride and benzoyl bromide, *Appl. Spectrosc*. **1974**, *28*, 420-426.

14. Wilhelm, C.; Gardette, J. L. Infrared identification of carboxylic acids formed in polymer photooxidation. *J. Appl. Polym. Sci*. **1994**, *51*, 1411-1420.

15. Lee, W. S.; Park, K. H.; Yoon, Y.-J. N, N-dimethylamination of acid chloride with DMF. *Synth. Commun*. **2000**, *30*, 4241-4245.

16. Alexandratos, S. D.; Zhu, X.; High-affinity ion-complexing polymer-supported reagents: Immobilized phosphate ligands and their affinity for the uranyl ion. *React. Funct. Polym*. **2007**, *67*, 375-382.

17. Boehme, C.; Wipff, G. Carbamoylphosphine oxide complexes of trivalent lanthanide cations: role of counterions, ligand binding mode, and protonation investigated by quantum mechanical calculations. *Inorg. Chem*. **2002**, *41*, 727-737.

18. Schurhammer, R.; Erhart, V.; Troxler, L.; Wipff, G. Interaction of M^{3+}cations with phosphoryl containing $(alkyl)_3P{=}O$ versus $(alkyl\text{-}O)_3P{=}O$ ligands: steric effects are more important than basicity effects. *J. Chem. Soc., Perkin Trans 2* **1999**, 2423-2431.

19. Miyaza, A.; Barnes, R. M. Complexation of some transition metals, rare earth elements, and thorium with a poly(dithiocarbamate) chelating resin. *Anal. Chem*. **1981**, *53*, 299-304.

3 PHOSPHORYLATED AMIDOALCOHOL AND OTHER BIFUNCTIONAL RESINS – SYNTHESES AND METAL ION CONTACT STUDIES

3.1 Introduction

Multifunctional resins contain more than one complexing group. These resins have been given significant attention over the past decades because of improved metal ion selectivities and capacities. The complexes formed are more stable than those formed with monofunctional resins as the metal ion can coordinate to more than one ligand or binding site forming a chelate or ring.

Molecules containing multiple coordinating sites may cooperate to enhance metal ion complexation. Some common examples of neutral molecules that behave in this manner are carbamoylmethyl phosphine oxide (CMPO),[1] carbamoylmethyl phosphonates (CMP)[2] and malonamide derivatives.[3, 4] In the first two molecules, carbonyl oxygen and phosphorus oxygen are the coordinative sites, while malonamide molecules contain two carbonyl oxygens for complexation. These molecules are widely used as extractants for separations of waste containing trivalent lanthanides and actinides from highly acidic media.[5] Their superiority over monodentate ligands arise because of their unrivaled selectivity for targeted metal ions under the conditions found in liquid wastes from processing nuclear fuels.[6]

Steric preorganization of molecules on suitable platforms such as resorcinarene cavitands[7] and calix[4]arenes[8, 9] enhance extraction efficiencies. The rigidity of the platform and orientation of coordinating groups contributed to improved selectivities. For example, the immobilization of CMPO ligands on a resorcinarene cavitand promoted greater selectivity of Eu(III) over UO_2(II) and Fe(III) compared to simple CMPO derivatives.[7]

This chapter delves into the design and synthesis of novel polymer-supported reagents containing amide and phosphate ester groups with the aim of investigating whether cooperation of ligands for enhanced metal ion affinities can occur between these groups. To understand the mechanism of complexation of this bifunctional resin, several “control” resins were synthesized. Two of these resins, monofunctional carboxamide and phosphonate diester were discussed in Chapter 2. The remaining resins, in addition to the phosphorylated amidoalcohol, would be part of this chapter. These resins would be 2-(2-aminoethoxy)ethanol, and phosphorylated 2-(2-aminoethoxy)ethanol, benzoyl phosphonate and polymer-supported amidoalcohol.

Research on metal ion removal with amide and phosphonic acid groups immobilized on vinylbenzyl chloride-styrene-divinylbenzene copolymers had been explored by another group under buffered conditions.[10] The mechanism of complexation proposed was different from what was found here.

3.2 Experimental

A summary of the experimental procedures is presented below. A complete account is found in Chapter 5 along with a description of the techniques used in analysis and characterization of the resins.

3.2.1 Synthesis of 2-(2-aminoethoxy)ethanol resin

These beads were obtained by heating VBC copolymer in N-methyl pyrrolidone (NMP) at 80 °C in the presence of 2-(2-aminoethoxy)ethanol. The temperature was slowly increased to 80 °C. Substitution of –Cl by primary amine was the favored reaction.

3.2.2 Synthesis of 2-(2-aminoethoxy)ethylphosphate resin

A standard reaction of introducing phosphate groups into the resin was employed. Diethyl chlorophosphate (DECP) was introduced into a flask containing beads in NMP. The resin was characterized by phosphorus and nitrogen analyses.

3.2.3 Synthesis of benzoyl phosphonate ester resin

This resin was synthesized by a modification of Michaelis - Arbuzov reaction, from acyl chlorides and trialkyl phosphites.[11, 12]

3.2.4 Synthesis of amidoalcohol resins: (2-(2-amidoethoxy)ethanol resin)

This resin and other amidoalcohol resins were prepared by first modifying the VBC copolymer to acid chloride resin. The acid chloride resin was reacted with the corresponding aminoalcohol at 60 °C for 10 h in acetonitrile (used for preparation of 2-(2-amidoethoxy)ethanol resin) or dioxane (used for preparation of other amidoalcohols) as the solvent.

3.2.5 Synthesis of phosphorylated amidoalcohols

These resins were prepared by phosphorylation of the –OH functional group using DECP as the phosphorylating agent in the presence of pyridine. Pyridine is used to remove the HCl produced in the reaction and prevent hydrolysis of ester. The resins were characterized by phosphorus and nitrogen elemental analyses. Phosphorylation of other amidoalcohols was performed in a similar manner.

3.3 Results and Discussion – Section I

3.3.1 Preparation and characterization of polymer-supported 2-(2-aminoethoxy)ethanol

Immobilization of 2-(2-aminoethoxy)ethanol (AEE) occurred by substitution of the amine part of the aminoalcohol molecule at the $–CH_2Cl$ side chains of the VBC copolymer (VBC - co - 2 % DVB). Nitrogen capacities of polymer-supported 2-(2-aminoethoxy)ethanol, Figure 3-1, were lower than expected, (expected = 4.36 mmol/g, actual = 3.40 mmol/g), despite implementing common solvents and reaction conditions[13, 14] used for amination (Table 3-1). N-methyl pyrrolidone (NMP) was chosen as the most suitable solvent since it was inert and a good swelling solvent for the VBC copolymer. Note that, while in some cases, comparable nitrogen capacities were obtained when other solvents were used, in other cases e. g. dimethylformamide (DMF), the nitrogen capacities were lower than usual. The reaction proceeded similarly in the absence of any solvent.

Two possible reasons can account for the lower nitrogen capacity. Secondary crosslinking has been found to occur in reactions involving dimethylamine or aminoalcohols and chloromethylated divinylbenzene-styrene copolymers.[15, 16] In addition,

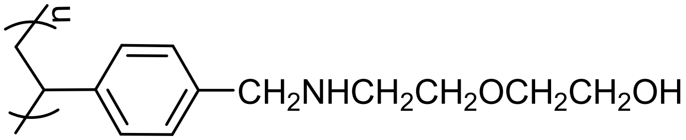


Figure 3-1 Structure of 2-(2-aminoethoxy)ethanol resin

Table 3-1 Investigation of the Immobilization of 2-(2-aminoethoxy)ethanol (AEE) on VBC copolymer

AP #	**Solvent**	**Reaction conditions**	**N capacity, mmol/g**
5-029	none	VBC (2g), 70 mL AEE, swell 1h. Heat to 80 degrees, 17h	3.44
5-071	Acetonitrile	VBC (2g), 50 mL acetonitrile, swell 1h. Add 20 mL AEE, reflux, 17h	3.30
4-279	DMF	VBC (2g), 100 mL DMF, swell 1h. Add 10 mL AEE, 40 degrees, 17h	2.64
4-273B	Dioxane	VBC (2g), 100 mL dioxane, swell 1h. Add 10 mL AEE, reflux, 17h	3.38
5-34B	THF	VBC (2g), 42 mL THF, swell 1h. Add 21 mL AEE , 42 mL THF reflux, 17h	3.28
5-34A	Water	VBC (2g), 10 mL water, swell 1h. Add 70 mL AEE, heat to 80 degrees, 17h	2.73
4-273A	NMP	VBC (2g), 100 mL NMP, swell 1h. Add 10 mL AEE, heat to 70 degrees, 17h	3.40
5-078	NMP	VBC (6g), 100 mL NMP, swell 2h. Add 50 mL AEE + 50mL NMP, heat to 80 degrees, 17h	3.44
4-214	NMP	VBC (6g), 100 mL NMP, swell 2h. Add 10 mL water + 20mL AEE, Heat to 70 degrees, 17h	2.78 (H+)

Table 3-2 Elemental analysis of some polymer-supported (aminoethoxy)ethanol resins

AP #	Nitrogen capacity, mmol/g	Acid capacity, mmol/g	% solids	Chlorine elemental, mmol/g
4-078	2.96	2.94	N. D.	0.76
5-046	3.30	n.d.	N. D.	0.57
5-066	3.29	n.d.	N. D.	1.00
5-078	3.44	2.94	38.3	N. D.
5-095	3.42	3.07	34.7	N. D.
5-115	3.14	2.90	44.6	N. D.
5-123	3.14	N. D.	N.D.	0.77

(N. D. = not determined)

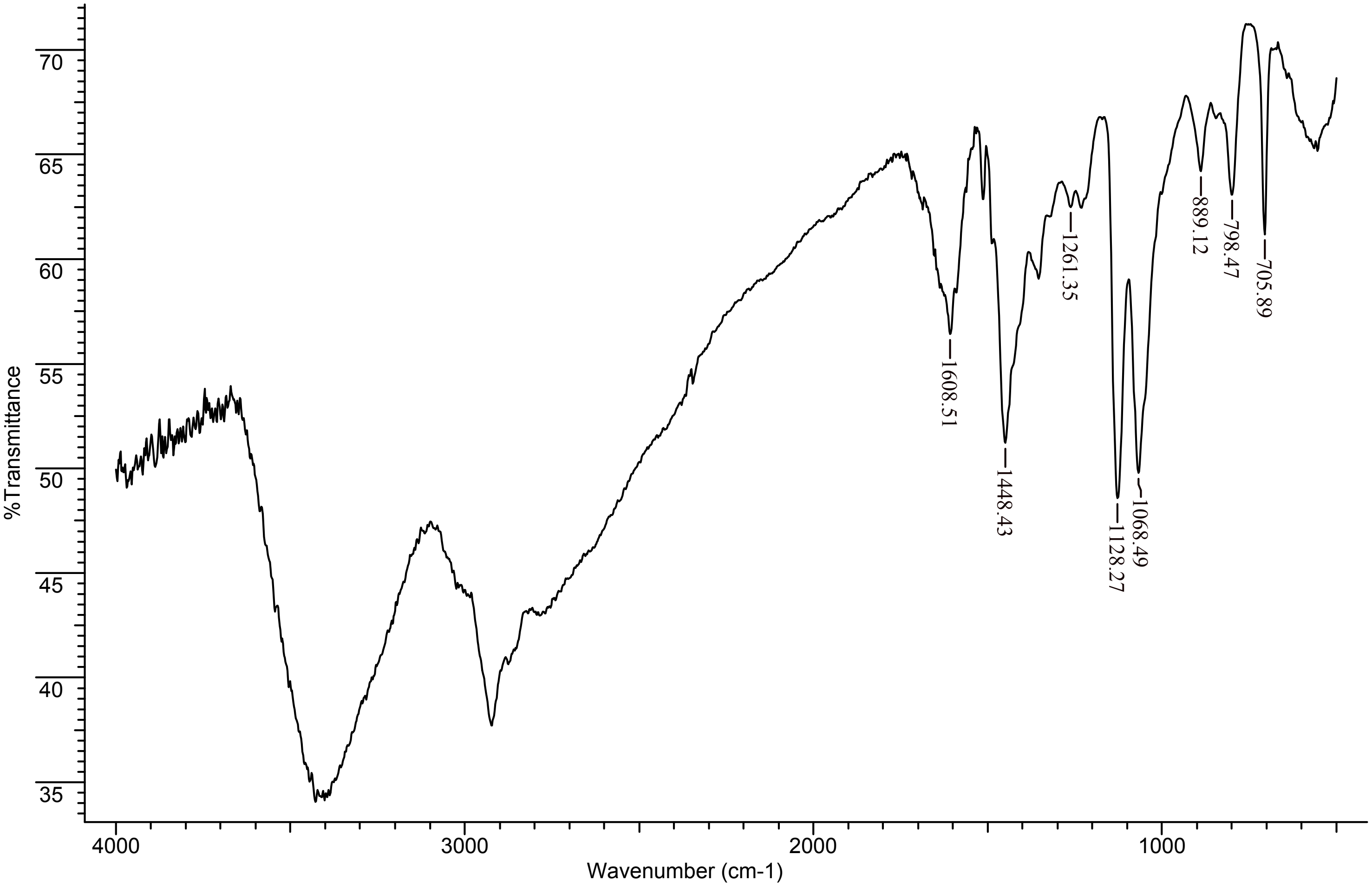


Figure 3-2 FTIR spectrum of 2-(2-aminoethoxy)ethanol resin (AP 4-078)

ethanolamine can be alkylated to the tertiary aminoalcohol.[17] There is evidence of slow reactivity of aminoalcohols with chloromethylated polystyrene.[18]

Secondly, there is experimental evidence of incomplete reaction as indicated by a small amount of chlorine on the resin (Table 3-2). Further characterization showed agreement between the acid capacity and the experimental nitrogen capacity. This means that all the nitrogen atoms can be protonated. The IR spectrum of this resin in Figure 3-2 indicated bands at 1448 cm^{-1}, 1128 cm^{-1} and 1068 cm^{-1} corresponding to N-H bending, C-O(C) and C-O(H) stretching frequencies, respectively.

3.3.2 Preparation and characterization of polymer-supported phosphorylated 2-(2-aminoethoxy)ethanol

It was established that basic conditions (resin and the reaction mixture) were necessary for this reaction to proceed, (see entry AP # 5-088, Table 3-3). Heating a reaction mixture containing the phosphorylating reagent, DECP, in the absence of a base can permit hydrolysis of the phosphate ester with limited immobilization of the phosphorus group. DECP (used in five molar excess of –OH sites) was found to be sufficient for a complete reaction. Thus, concentration of DECP and the presence of a base were the two important variables for consideration.

Nitrogen and phosphorus capacities of the phosphorylated (aminoethoxy)ethanol were similar, within experimental error. However acid capacities were always lower than nitrogen capacities (Table 3-4). One possible reason was that upon introduction of the phosphorus group, steric hindrance about the crosslinked amine sites may affect their protonation.

Table 3-3 Phosphorylation of polymer-supported 2-(2-aminoethoxy)ethanol

AP #	**Variables Examined**	**Reaction conditions**	**P capacity, mmol/g**	**N capacity, mmol/g**	**Acid capacity, mmol/g**
5-112	Reaction time	1g beads, 50 mL dioxane, 4 mL NMP, 5 mL DECP, 17 h, RT	1.46	2.57	1.95
		1g beads, 50 mL dioxane, 4 mL NMP, 5 mL DECP, 65 h, RT	1.60	2.57	1.92
5-114	# moles of Base, DECP	1g beads,100 mL dioxane, 8 mL NMP, 10 mL DECP, 17 h, RT	1.16	N. D.	2.02
5-116	Temperature	1g beads, 50 mL dioxane, 4 mL NMP, 5 mL DECP, 17 h, heat to 40 degrees	1.31	N. D.	2.24
5-117	Concentration	1g beads, 25 mL dioxane, 4 mL NMP, 5 mL DECP, 17 h, RT	1.96	2.66	1.84
5-103	Volume of NMP	1g beads, 50 mL dioxane, 2 mL NMP, 5 mL DECP, 17 h, RT	1.38	2.87	1.76
		1g beads, 50 mL dioxane, 4 mL NMP, 5 mL DECP, 17 h, RT	1.44	2.32	1.74
		1g beads, 50 mL dioxane, 8 mL NMP, 5 mL DECP, 17 h, RT	1.63	2.51	1.54
5-088	Absence of base	1g beads, 50 mL dioxane, 5 mL DECP, 17 h, RT	0.91	N. D.	2.24
	Absence of base and heating	1g beads, 50 mL dioxane, 5 mL DECP, 17 h, reflux	1.98	N. D.	3.03
5-087	Solvent and base	1g beads, 50 mL dioxane, 7 mL pyridine, 5 mL DECP, 17 h, RT	2.77	2.28	N. D.

Table 3-4 Elemental analysis of polymer-supported phosphorylated 2-(2-aminoethoxy)ethanol

AP #	Nitrogen capacity, mmol/g	Acid capacity, mmol/g	% solids	Phosphorus elemental, mmol/g
5-163	2.55	1.52	44.1	2.15
5-165	2.54	1.83	42.6	1.84
5-169	2.27	1.61	43.8	1.95

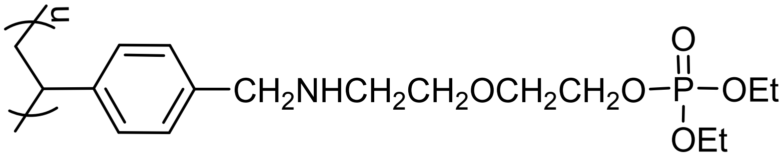


Figure 3-3 Structure of phosphorylated 2-(2-aminoethoxy)ethanol resin

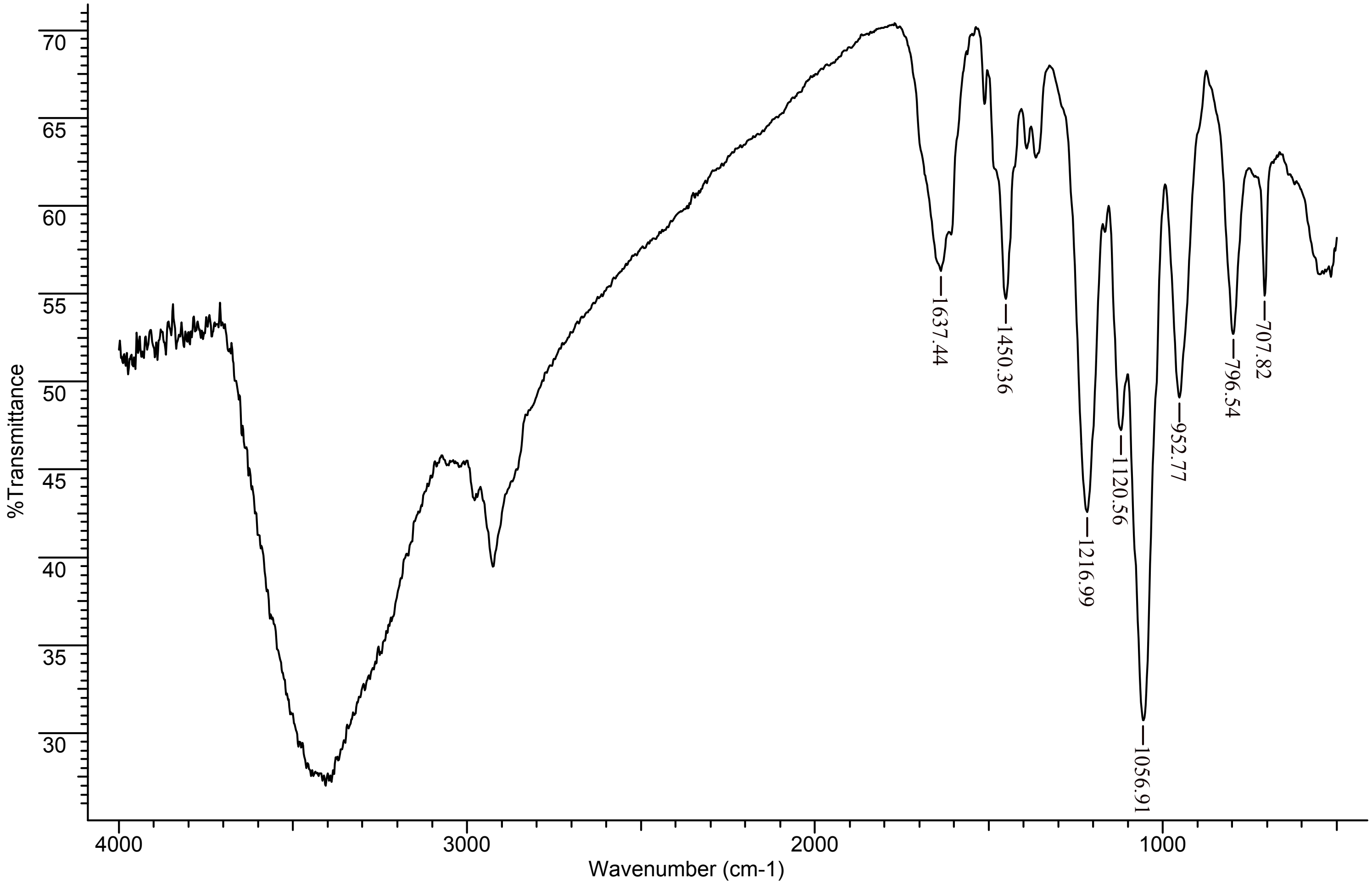


Figure 3-4 FTIR spectrum of phosphorylated 2-(2-aminoethoxy)ethanol resin

Introduction of phosphorus was evident on the IR spectrum of this resin. In Figure 3-4, it is clear that P=O and P-O stretching frequencies occur at 1217cm^{-1} and 1057cm^{-1} respectively.

3.3.3 Preparation and characterization of polymer-supported benzoyl phosphonate ester resin.

The preparation of this resin (Figure 3-5), involved the application of the Michaelis-Arbusov reaction to acid chlorides. Small molecule synthesis of acyl phosphonates have been carried out.[11, 12] Functionalization was complete as observed from phosphorus capacities (Table 3-5) where theoretical phosphorus capacity was 3.75 mmol/g compared to actual phosphorus capacity (average) which was 3.72 mmol/g. A small amount of acid capacity was determined, possibly arising from incomplete reaction of triethyl phosphite and acid chloride beads.

The IR spectra (Figure 3-6) indicated that the phosphorus group was immobilized as the P=O given the band at 1234 cm^{-1}. It must be pointed out that the IRs obtained in each instance were all different with respect to position of the P=O stretch. This could be related to the hydrogen bonding within the resin in relation to the position of the P=O in the molecule.

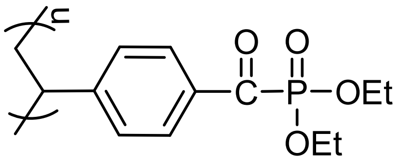


Figure 3-5 Benzoyl phosphonate resin

Table 3-5 Elemental analysis of benzoyl phosphonate resins

AP #	**P capacity, mmol/g Actual (Theoretical)**	**Acid capacity, mmol/g**	**% Solids**
3-269	3.97 (3.75)	0.82	72.6
4-065	3.65	0.57	59.7
4-242	3.55	0.65	68.1

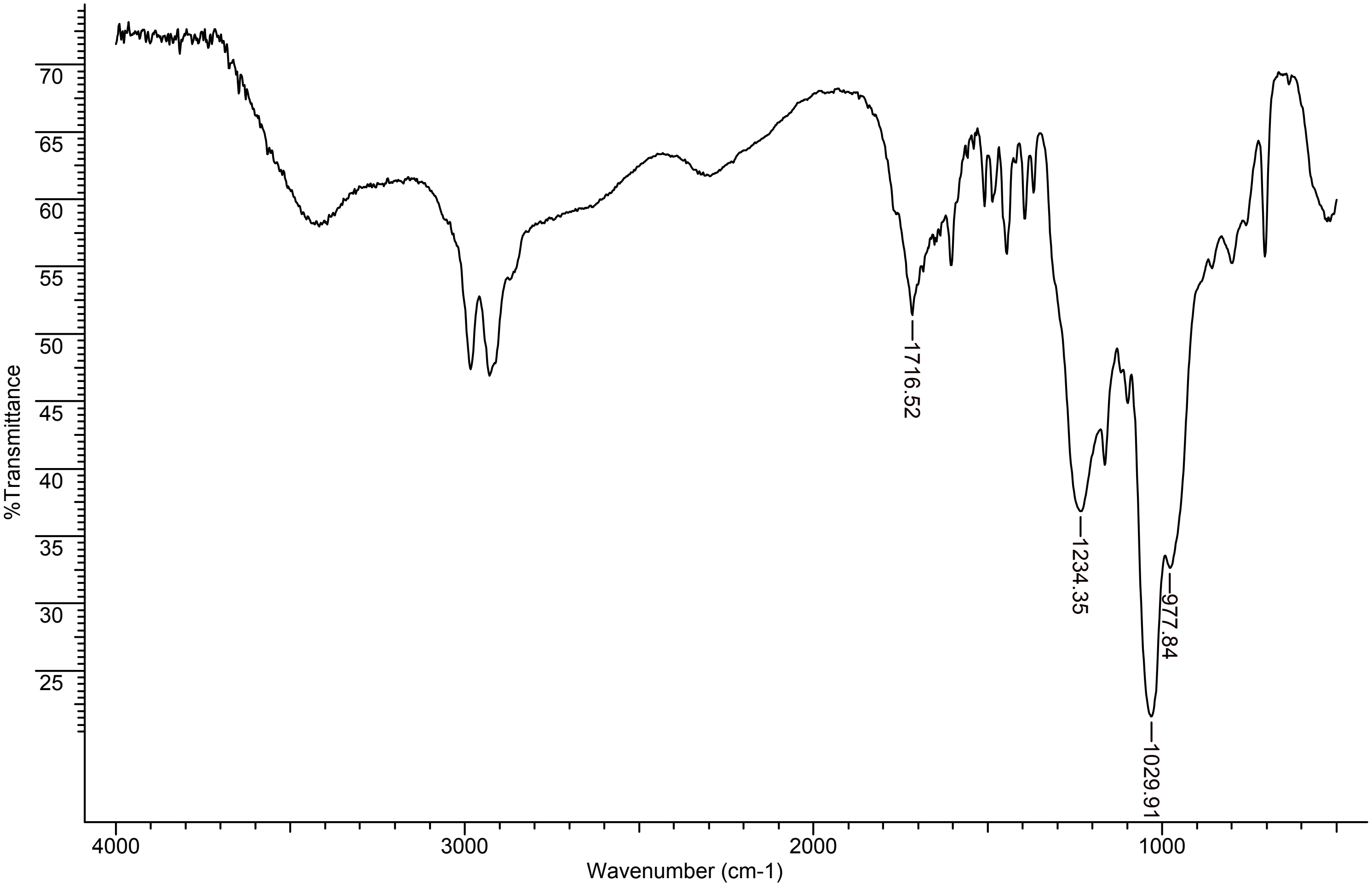


Figure 3-6 FTIR spectrum of benzoyl phosphonate ester.

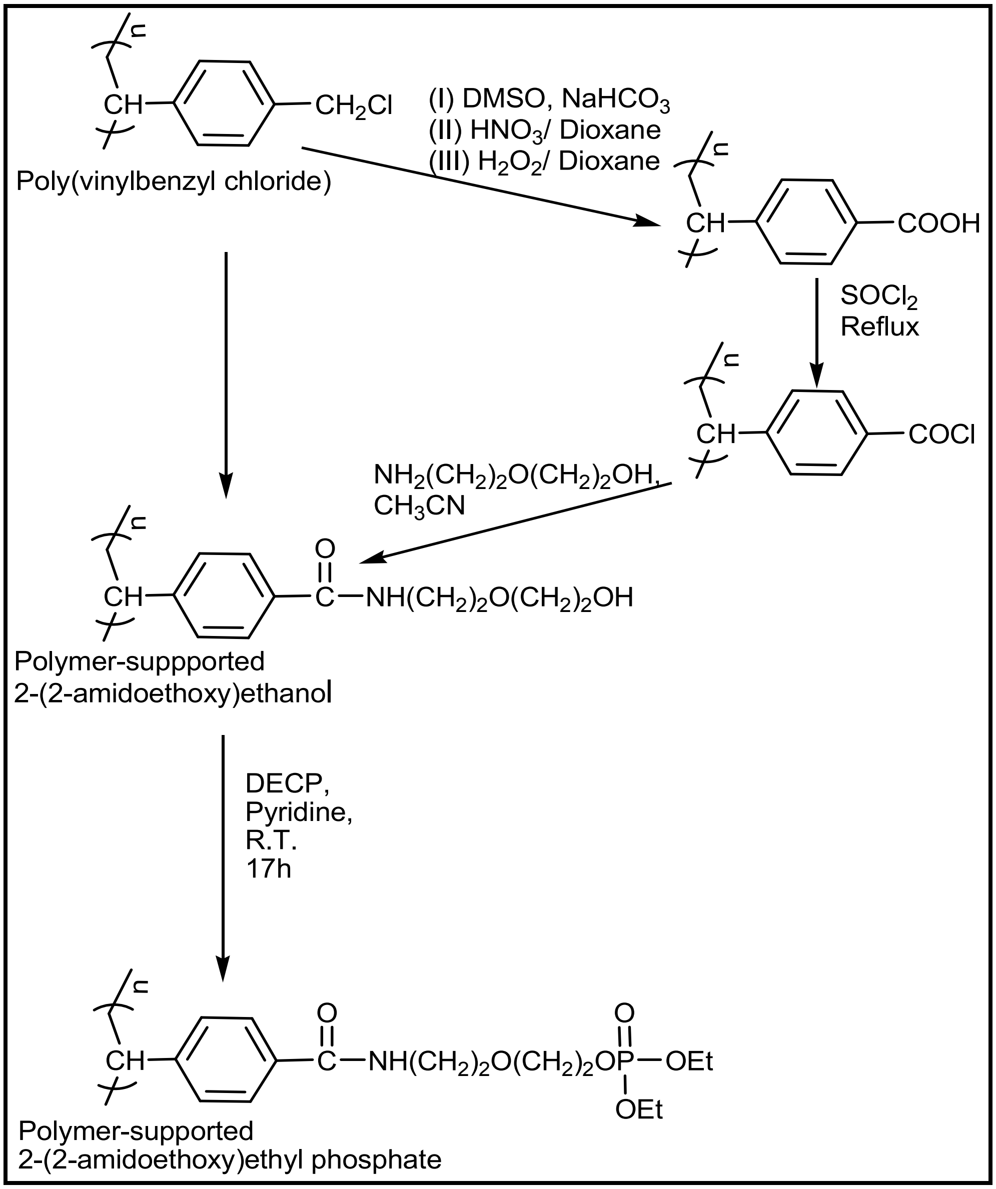


Figure 3-7 Reaction scheme for preparation of phosphorylated amidoalcohol resins (Immobilisaton and phosphorylation of 2-(2-aminoethoxy)ethanol is used as an example)

3.3.4 Preparation of glycol esters

The reactivity of acid chloride resins with diols, e. g. ethylene glycol, to form the corresponding ester was investigated. Application of conventional methods of esterification of acid chlorides with alcohols in solution to the reaction with acid chloride resins and diols proved unsuitable.[19, 20] For example, it was evident that the acid chloride groups reacted with the base present (pyridine and triethylamine) so that there was some extraneous nitrogen present in the polymer despite carrying out the reaction in the presence of ethylene glycol. A base was used to neutralize the HCl that would be produced when the ethylene glycol reacts with the acid chloride.

Reaction of acid chloride resins with ethanol and 2-methoxyethanol were compared to reaction with diols. It was found that acid chloride resins were easily esterified with ethanol (Table 3-6). The percent conversion to the corresponding ester was calculated after determination of the acid capacities of the products formed. The acid capacities were negligible. This implied that there were no acidic sites on the resin either from incomplete reaction or hydrolysis of ester. It was later discovered that milder conditions than those described in Table 3-6 were sufficient for ester formation (2 h stirring at room temperature with methyl or ethyl alcohol for the methyl or ethyl ester respectively). In addition, IR spectra (Appendix section IV) confirmed the formation of the ester. The band at 1716 cm^{-1} indicated the presence of C=O stretch and 1284 cm^{-1}, for the C-O-(C) stretch. The high percent solids indicated that a more hydrophobic resin was produced.

Table 3-6 Reactivity of acid chloride beads with alcohols

AP #	**[a]Reactant**	**% solids**	**Acid capacity, mmol/g**	**% conversion to ester**
3-048	2-methoxyethanol	80.9	0.06	100
3-049	Ethanol	79.3	0.07	100

[a] (Reaction conditions – In a 250 mL RBF, 1 g of beads, swell 2 h in 100 mL dioxane, 20 mL reactant, reflux 17 h)

Optimal conditions for ester formation with ethylene glycol were determined by varying conditions of temperature, solvent and reaction time, as well as surface area and porosity of the polymer, as outlined in Tables 3-7 to 3-10. The success of the reaction was inferred from acid capacity determinations and IR spectroscopy. An acid capacity of 0.15 mmol/g, for example, suggested that there was 100 % conversion of acid chloride to the ester (i. e. all -Cl sites are replaced with –OH from diol), within experimental error. This was achieved when the product was washed with solvent (dioxane) and then with water instead of methanol followed by water.

Several solvents were used (Table 3-9), and dioxane was found to be the most suitable. Dioxane swelled the beads, was non-reactive, and miscible with ethylene glycol, the reactant. Reaction time and temperature were among the factors that were found to be more effective (Tables 3-8 and 3-10) in affecting the amount of immobilization. The effect of reactant concentration and surface area were inconclusive (Tables 3-7 and 3-10). The low acid capacity of gel compared to macroporous resins in Table 3-7 can be attributed to a higher degree of crosslinking for macroporous beads, making them more rigid. Unreacted acidic groups can be esterified with triethyl orthoformate.[21] It was not possible to obtain a high degree of immobilization of ethylene glycol on acid chloride resins in repeated trials. The unreactivity of ethylene glycol may be attributed to hydrogen bonding between the –OH groups of diols which increased the solution's viscosity and reduced accessibility of the reactant to the active sites in the resin.

One possible hypothesis that has not been explored to enhance reactivity would be to enhance the nucleophilicity of the reactant. This can be achieved by preparing the sodium salt of ethylene glycol and then reacting this with the acid chloride resins in the

Development of optimum conditions for obtaining the ester of ethylene glycol

Table 3-7 Effect of bead porosity on the esterification of acid chloride beads.

AP #	**Polymer support**	**% solids**	**% conversion to ester**
2-066	5% DVB (macroporous beads)	33.8	45.0
2-067	2% DVB (gel beads)	85.0	91.4

(Reaction conditions - solvent = 100 mL dioxane, swell 2h., 4 mL ethylene glycol, heat to 102 °C for 48 h, 1 g beads)

Table 3-8 Effect of reaction time on esterification reaction (using 2% DVB gel beads)

Time, h	**Acid capacity, mmol/g**	**% Solids**	**[b] % conversion**
24	5.06	62.7	0.0
48	3.80	74.5	24.3
7 days	2.13	80.8	57.6

(Reaction conditions – 15 mL ethylene glycol, 110 mL dioxane, 1 g gel beads, stir at RT) ,

[b] The beads were washed with 100 mL dioxane, 100 mL water

Table 3-9 Effect of solvent

Solvent (mL)	**Reaction Conditions**	**% conversion**
Carbon disulphide (100 mL + TEA 3 mL)	Ice bath, 22 h.	13.9
Tetrahydrofuran (120 mL)	R.T., 17 h.	50.4
Dimethylformamide (120 mL)	R.T.,17 h.	4.1
Pyridine (120 mL)	Distilled reactants, 3 h. R.T	48.9
Pyridine (120 mL)	Distilled reactants, 22 h. R.T.	50.1
Dichloromethane (110 mL + TEA 3 mL)	Ice bath, 15 h.	46.2
Dioxane (120 mL + TEA 3.5 mL)	Reflux for 20 h.	69.8
N-methylpyrrolidinone (120 mL)	Heat to 60 °C, 20 h.	12.6

(Resin conditions – 15 mL ethylene glycol, the resins above were washed with ethanol, ethanol/water (1:1) and water)

R. T. = room temperature

Table 3-10 Effect of reaction temperature and reactant concentration on % conversion.

Temperature	Time, h	Volume of ethylene glycol, mL	Acid capacity, mmol/g	% conversion
Reflux	48	13	0.99	82.9
Reflux	96	15	2.98	48.5
Reflux	48	32	0.64	88.9
50°C	48	60	4.07	36.3
50°C	48	30	3.25	49.1
50°C	48	30	1.78	72.1

(Reaction conditions – 1 g Beads, 110 mL dioxane reaction scheme shown in Figure 3-7.

3.3.5 Preparation and characterization of poly(amidoalcohols)

The difficulty of immobilizing diols prompted the preparations of esters of aminoalcohols. Aminoalcohols contain $–NH_2$ and –OH groups. The greater nucleophilicity of amines allowed for greater reactivity with acid chlorides.[22] These reactions were rapid with good yields. The reaction of acid chloride resin with 2-(2-aminoethoxy)ethanol, (AEE) was investigated to determine the reaction conditions as a representative reaction for other aminoalcohols. Various solvents, listed in Table 3-11 were employed to find one that was inert and compatible with the beads regarding polarity and ability to swell the beads. “Clumping” was used to describe the appearance of the beads when they stuck together. Acetonitrile was the chosen as the solvent for the amidation reaction with AEE, because the beads were free-flowing (mixed well) in the reaction mixture upon addition of AEE, and a high degree of immobilization was obtained. The theoretical nitrogen capacity for this resin was 3.69 mmol/g (free base form).

Reactions in dioxane gave high levels of functionalization despite the observed resin clumping. It was concluded then, that dioxane could also be used as a solvent. For reactions with other aminoalcohols, dioxane was the solvent of choice as acetonitrile didn’t improve the resin’s appearance or reactivity. DMF was not used as an unexplained high acid capacity resulted and a different IR was obtained. IRs of some poly(amidoalcohol) resins prepared with different solvents can be found in the Appendix section I.

Table 3-11 Effect of solvent in preparation of polymer-supported 2-(2-amidoethoxy)ethanol

SOLVENT and AEE and resin at R.T.* for 20h	**Acid cap., mmol/g**	**Nitrogen cap., mmol/g**	**Resin appearance on addition of AEE**
Dioxane	0.74	3.25	Clumping
THF (5°C)	0.67, 0.57	2.03, 3.57	Clumping
DMF	3.22	1.70	Clumping absent
Diglyme	1.63	2.95	Clumping
Acetonitrile	0.71	3.26	Clumping absent

* unless otherwise indicated

Some solvents could not be used as they reacted with the chlorinated resin. It was important to choose inert solvents, and the reactivity of solvents was also investigated. These results were compiled in Table 3-12. The evolution of fumes was evidence that some reaction occurred. This was further supported from nitrogen and acid capacity determinations where necessary.

Heating increased the reaction rate, though it had minimal effect above 25°C as shown in Table 3-13. Amidation was complete after 1h (Table 3-14). Nitrogen capacities were quite consistent over the 48 h time studied. There was a small but noticeable trend in acid capacities of reactions carried out for longer times compared to those performed at shorter times: shorter times had higher acid capacities due to incomplete reaction (Table 3-15). A time of 10 h and temperature of 60 °C were chosen as reasonable conditions for immobilization. Resins 4-184, 4-183A, 4-183B of Table 3-10 had the same starting material and this was also true of 4-175A, 4-175B, 4-175C, 4-179A, 4-179B. Each resin in Table 3-15 was prepared independently of the others.

All other poly(amidoalcohol) resins gave reasonable nitrogen capacities when allowed to react at room temperature and when the solvent was dioxane despite some clumping of resin observed upon addition of the aminoalcohol to the solvent containing beads. It was found that acetonitrile was not a better solvent than dioxane for the amidation reactions of other aminoalcohols (the beads clumped together in either solvents) as mentioned before. Dioxane was chosen as the solvent because of its availability.

Table 3-12 Solvent reactivity with acid chloride resin.

SOLVENT and acid chloride resin only at RT	**Acid capacity, mmol/g**	**Nitrogen capacity, mmol/g**	**Observation**
Acetonitrile	0.19	0.16	No fumes
NMP	*N. D.	N. D.	Fumes from flask
Pyridine/Acetonitrile	5.71	0.16	No observable fumes
TEA/Acetonitrile	5.01	0.45	Fumes from flask
Pyridine	N.R.	1.10	Fumes from flask

(The beads were stirred with methanol upon removal of the solvents)
N.D. = not determined

Table 3-13 The effect of temperature on esterification of acid chloride resin with (aminoethoxy)ethanol

[a]**Temperature, °C**	**Acid capacity, mmol/g**	**Nitrogen cap, mmol/g**
0	0.33	0.44
25	0.62	3.42
50	0.55, 0.51	3.73, 3.56
70	0.57	3.57

[a]solvent used – acetonitrile (100 mL), beads swell 1 h, stir at listed temperature for 8 h

Table 3-14 Effect of time on the esterification reaction at 70 °C

Time, h	**Acid capacity, mmol/g**	**Nitrogen cap, mmol/g**
1	0.86	3.40
2	0.90, 0.63	3.69, 3.38
8	0.69	3.25
17	0.74	2.78
34	0.81,0.51	3.70, 3.39
48	0.49	3.69

Table 3-15 Elemental analyses of poly(amidoethoxy)ethanol resins prepared at different reaction times in acetonitrile.

Time, h	Resin code	Acid capacity, mmol/g	Nitrogen capacity, mmol/g
1	4-179A[a]	0.86	3.40
2	4-175A[b]	0.90	3.69
2	4-184[c]	0.63	3.38
8	4-175B[b]	0.69	3.25
17	4-175C[b]	0.74	2.78
34	4-179B[a]	0.81	3.70
34	4-183A[c]	0.51	3.39
48	4-183B[c]	0.49	3.69

Resin codes with the same superscript were reacted on the same day.

The spectra of poly 2-(2-amidoethoxy)ethanol resins show characteristic amide bands at 1637, 1545 and 1305 cm^{-1} corresponding to amide I, II and III bands and C-O-(C), C-O-(H) at 1120, 1066 cm^{-1} respectively. The amide I band, assigned to C=O stretching vibration usually found in the region 1630-1700 cm^{-1}. Amide II and amide III bands corresponded to N-H in-plane deformation with contributions from C-N stretching in the region 1510-1650 cm^{-1} and 1230-1330 cm^{-1} to N-H / C-N deformations respectively.[23-25]

The characteristic bands in the spectra of other poly(amidoalcohol) resins compared well with that obtained for poly 2-(2-amidoethoxy)ethanol resin. The IR bands of poly (amidoalcohol) resins were listed in Table 3-16 and shown in Appendix section II. Table 3-17 contained the identity of the bands of some other amide resins prepared.

IR bands of amide resins (Tables 3-16 and 3-17), showed a shoulder in the region of 1700 cm^{-1}, with the exception of polymer-supported diethylamide. This shoulder may be a result of incomplete reaction between aminoalcohol molecules with acid chloride resin.

Table 3-16 Band frequencies (cm^{-1}) of various polymer-supported amidoalcohols

Ligand	**Amide I (C=O)**	**Amide II (N-H deformation)**	**Amide III (N-H / C-N) deformation**	**C-O-(H)**
$-C(O)NHCH_2CH_2OH$ (amidoethanol)	1635	1545	1306	1063
$-C(O)NHCH_2CH_2CH_2OH$ (amidopropanol)	1637	1545	1306	1041
$-C(O)NHC(CH_3)_2CH_2OH$ (2-amido-2-methylpropanol)	N.D.	N.D.	N.D.	N.D.
$-C(O)NHCH_2CH_2CH_2CH_2CH_2OH$ (amidopentanol)	1639	1541	1306	1053
$-C(O)NHCH_2CH_2OCH_2CH_2OH$ (2-(2-amidoethoxyethanol))	1637	1543	1306	1065

N.D. not determined

Table 3-17 Frequency of bands (cm^{-1}) of some polymer-supported amides

Ligand	**Amide I**	**Amide II**	**Amide III**
-$C(O)NHCH_2CH_2CH_2CH_3$ (amidobutane)	1637	1541	1306
-$C(O)N(CH_2CH_3)_2$ (carboxamide)	1624	N. A.	1288
-$C(O)NHCH_2CH_2NHCH_2CH_2NH_2$ (2-amidoethylenediamine)	1637	1541	1286
-$C(O)NHCH_2CH_2NH_2$ (amidoethylamine)	1635	1539	1307

Table 3-18 Elemental analyses of amidoalcohol resins

Ligand	AP #	N capacity, mmol/g	Acid capacity, mmol/g	% solids
$-C(O)NHCH_2CH_2OH$	4-228	3.87	N. D.	N. D.
	4-103	3.93	0.73	60.4
$-C(O)NHCH_2CH_2CH_2OH$	3-142	4.02 (H+)	0.88	64.8
	5-130	3.72 (OH-)	0.39	68.5
$-C(O)NHC(CH_3)_2CH_2OH$	3-143	3.06	1.67	64.5
$-C(O)NHCH_2CH_2CH_2CH_2CH_2OH$	3-156	3.07	0.81	75.2
$-C(O)NHCH_2CH_2OCH_2CH_2OH$	4-203	3.69	0.58	64.7
	4-223	3.09	0.66	68.1

3.3.6 Phosphorylated poly(amidoalcohol) resin preparation and characterization

Phosphorylation of poly(amidoalcohol) resins were accomplished using diethyl chlorophosphate in the presence of pyridine. The amount of diethyl chlorophosphate used was approximately five times (molar) in excess of active sites (-OH groups) on the resin. Pyridine removed the hydrochloric acid produced as a result of the reaction.

Table 3-19 lists the identity of the bands found in the IR spectra of these resins. These spectra can be found in the Appendix section III.

Table 3-19 Frequency bands (cm^{-1}) of phosphorylated amidoalcohol resins

Ligands	**Amide I**	**Amide II**	**C-O-(P)**	**P=O**
$-C(O)NHCH_2CH_2OP(O)(OEt)_2$	1647	1541	1041	1279
$-C(O)NHCH_2CH_2CH_2OP(O)(OEt)_2$	1639	1541	1040	1278
$-C(O)NHC(CH_3)_2CH_2OP(O)(OEt)_2$	1647	1545	1049	1271
$-C(O)NHCH_2CH_2CH_2CH_2CH_2OP(OEt)_2$	1647	1543	1032	1258
$-C(O)NHCH_2CH_2OCH_2CH_2OP(O)(OEt)_2$	1645	1543	1036	1258

Table 3-20 Elemental analyses of phosphorylated amidoalcohol resins

Ligands	**AP #**	**N capacity, mmol/g (Actual)**	**P capacity, mmol/g (Actual)**	**Acid capacity, mmol/g**	**% solids**
$-C(O)NHCH_2CH_2OP(O)(OEt)_2$	4-238	2.77	2.12	N. D.	75.4
$-C(O)NHCH_2CH_2CH_2OP(O)(OEt)_2$	3-147	2.63	1.95	0.80	72.3
	5-132	2.57	2.14	0.51	69.1
$-C(O)NHC(CH_3)_2CH_2OP(O)(OEt)_2$	3-148	2.28	1.52	1.24	72.3
$-C(O)NHCH_2CH_2CH_2CH_2CH_2OP(O)(OEt)_2$	3-158	2.16	2.11	0.71	80.8
$-C(O)NHCH_2CH_2OCH_2CH_2OP(O)(OEt)_2$	5-013	2.01	2.07	0.60	57.3
	5-016	1.70	2.32	0.55	73.6

3.4 Results and Discussion – Section II

3.4.1 Metal ion contact studies

Phosphate esters of amidoalcohols were synthesized to determine their ability as metal complexing agents because of their multiple chelating sites. To investigate the coordinating ability of a phosphorylated 2-(2-amidoethoxy)ethanol resin, a series of polymers isolating the various functional groups of the phosphorylated resin was synthesized. All polymers were prepared from the modification of poly (VBC) gel copolymer crosslinked with 2 % DVB.

Polymer-supported carboxamide resin (described in Chapter 2), polymer-supported 2-(2-aminoethoxy)ethanol, polymer-supported phosphorylated 2-(2-aminoethoxy)ethanol and polymer-supported 2-(2-amidoethoxy)ethanol were found to complex less than 10 % of divalent or trivalent metal ions from metal nitrate solutions of 1×10^{-4}N initial concentrations at pH 2 (Tables 3-21 and 3-22). Additionally, polymer-supported phosphorylated 2-(2-amidoethoxy)ethanol, polymer-supported benzoyl phosphonate and polymer-supported diethyl phosphonate (the latter for trivalent metal ions only), were the sorbents exhibiting higher metal ion sorption affinities. The metal ion affinity trend for the amidoalcohol phosphates followed the approximate order: Pb(II) > Cu(II) > Cd(II) > Zn(II) > Ni(II) (Table 3-21). In the case of trivalent metal ions studied, iron showed the highest affinity to these resins (Table 3-22).

3.4.2 Metal ion affinity analysis - A. Divalent metal ions.

The phosphoryl oxygen and the carbonyl oxygen were the primary binding sites investigated in the phosphorylated amidoalcohol resins. This was illustrated in Table 2-3

Table 3-21 Percent divalent metal ion complexation and D (distribution coefficients) values, in brackets, for bifunctional resins from metal nitrate solutions of 1×10^{-4} N initial concentration (RSD = 2.3%)

Metal Ion **Ligand**	**Pb(II)**	**Cd(II)**	**Cu(II)**	**Ni(II)**	**Zn(II)**
$-NHCH_2CH_2OCH_2CH_2OH$	4.08 (2.06)	3.47 (1.78)	4.53 (2.27)	4.38 (2.18)	3.33 (1.69)
$-NHCH_2CH_2OCH_2CH_2OP(O)(OEt)_2$	2.34 (0.66)	3.66 (1.12)	3.56 (1.04)	2.65 (0.80)	5.19 (1.57)
$-C(O)NHCH_2CH_2OCH_2CH_2OH$	7.15 (2.22)	7.77 (2.62)	9.30 (3.00)	1.64 (0.60)	1.71 (0.64)
$-C(O)P(O)(OEt)_2$	57.3 (36.1)	30.4 (12.2)	30.8 (12.4)	13.7 (4.37)	20.2 (6.89)
$-C(O)NHCH_2CH_2OCH_2CH_2OP(O)(OEt)_2$	75.3 (78.8)	48.1 (23.4)	56.5 (33.6)	24.8 (8.56)	41.0 (18.8)

Table 3-22 Percent trivalent metal ion complexation and D (distribution coefficients) values, in brackets for bifunctional resins from metal nitrate solutions of 1×10^{-4} N initial concentration

Metal Ion **Ligand**	**Eu(III)**	**Fe(III)**	**Al(III)**
$\mathrm{-NHCH_2CH_2OCH_2CH_2OH}$	2.28 (1.16)	4.43 (2.33)	4.03 (2.06)
$\mathrm{-NHCH_2CH_2OCH_2CH_2OP(O)(OEt)_2}$	5.76 (1.75)	10.36 (3.34)	3.74 (1.20)
$\mathrm{-C(O)NHCH_2CH_2OCH_2CH_2OH}$	0.00 (0.00)	2.60 (0.78)	1.00 (1.02)
$\mathrm{-C(O)P(O)(OEt)_2}$	75.0 (81.1)	79.1(102)	45.5 (23.5)
$\mathrm{-C(O)NHCH_2CH_2OCH_2CH_2OP(O)(OEt)_2}$	64.2 (45.3)	74.0 (85.9)	60.9 (40.8)

and in Table 3-21 where, for example, Pb(II) removal was less than 10 % for resins having only one coordinating group but was 57 % for the benzoyl phosphonate diester resin and 75 % for phosphorylated 2-(2-amidoethoxy)ethanol resin, resins with both coordinating groups in their structures. This indicated that metal ion coordination involved both coordinating sites. Synergism occured when binding sites occur in the same resin and on the same chain. The two ligands cooperate to complex greater levels of Pb(II), for example, than either ligand can alone. This phenomenon of "supported ligand synergistic interaction" was observed when the spacer ligand was an ethyl group, an ethoxyethyl group or when the spacer ligand was absent. Intraligand cooperation had been noted with polymer-supported aminomethylphosphonates,[26] α-, β-, γ-ketophosphonates[11] and phosphonoacetic acid.[27]

Pb(II) ions were the most highly preferred and Ni(II) ions, the least preferred, for the phosphorylated amidoalcohols considered: Pb(II) was the softest metal of the divalent ions investigated, based on Misono softness values.[28] This metal ion affinity trend was observed with some other phosphate resins.[29] This trend was also observed on a silica sorbent containing self-assembled carbamoylphosphonic acid, relating softness to metal ion affinity .[30] An approximate correlation between metal ion polarisability, represented by the Misono softness parameters, and binding affinity of metal ions, determined by their distribution coefficients, can be made. For the resin poly (2-(2-amidoethoxy)ethyl phosphate)) in Figure 3.7, the correlation coefficient was 0.93 with an intercept of 0.22 on x axis and a slope of 449, while resin poly(amidoethyl phosphate) gave a correlation of 0.96, an intercept of 0.22 and a slope of 629. Benzoyl phosphonate diester resin was added for comparison.

Table 3-23 Effect of varying the length of the spacer group on metal ion affinities of divalent metal ions (% divalent metal complexed) from metal nitrate solutions of initial concentrations of 1×10^{-4} N

Metal ion **Ligand structure** **Name**	**Pb(II)**	**Cd(II)**	**Cu(II)**	**Ni(II)**	**Zn(II)**
$-C(O)P(O)(OEt)_2$ *diethyl benzoylphosphonate ester*	57.3	30.4	30.8	13.7	20.2
$-C(O)NHCH_2CH_2OP(O)(OEt)_2$ *phosphorylated amidoethanol*	82.4	63.6	64.3	37.2	50.2
$-C(O)NHCH_2CH_2CH_2OP(O)(OEt)_2$ *phosphorylated amidopropanol*	25.9	7.71	10.7	0.0	3.22
$-C(O)NHC(CH_3)_2\ CH_2OP(O)(OEt)_2$ *phosphorylated 2-amido-2-methyl-1-propanol*	19.4	5.48	10.9	0.0	4.47
$-C(O)NHCH_2CH_2CH_2CH_2CH_2OP(OEt)_2$ *phosphorylated amidopentanol*	19.0	5.62	8.28	0.0	3.59
$-C(O)NHCH_2CH_2OCH_2CH_2OP(O)(OEt)_2$ *phosphorylated amidoethoxyethanol*	75.3	48.1	56.5	24.8	41.0

Table 3-24 Effect of the length of the spacer group on metal ion affinities of trivalent metal ions (expressed as % metal ion complexed) from metal nitrate solutions of initial concentrations of 1×10^{-4} N

Ligand	**Eu(III)**	**Fe(III)**	**Al(III)**
-C(O)P(O)(OEt)$_2$	75.0	79.1	45.5
-C(O)NHCH$_2$CH$_2$OP(O)(OEt)$_2$	44.4	43.1	33.7
-C(O)NHCH$_2$CH$_2$OCH$_2$CH$_2$OP(O)(OEt)$_2$	64.2	74.0	60.9

These correlations can be found in Table 3-25. Similar findings were obtained for monophosphorylated polyols and divalent metal ions.[29] The low linearity observed suggested that polarisability may not be the sole determinant of metal ion coordination.

Polarisability of a metal ion can be a useful indicator for explaining metal ion affinity as seen here and as found in the literature cited in the introduction section. It was observed that the ethylamide phosphate resin had a higher affinity for divalent metal ions and was more selective than the longer chain amidoethoxyethyl phosphate (containing two glycol moieties connected by an ether linkage).

Table 3-25 Correlations of poly(amidoethoxyethyl phosphate), poly(amidoethyl phosphate) and poly(diethyl benzoylphosphonate) resins

Ligands	**Correlation**	**x intercept**	**Slope**
$-C(O)P(O)(OEt)_2$	0.96	0.22	194
$-C(O)NHCH_2CH_2OP(O)(Oet)_2$	0.96	0.22	629
$-C(O)NHCH_2CH_2OCH_2CH_2OP(O)(OEt)_2$	0.93	0.22	449

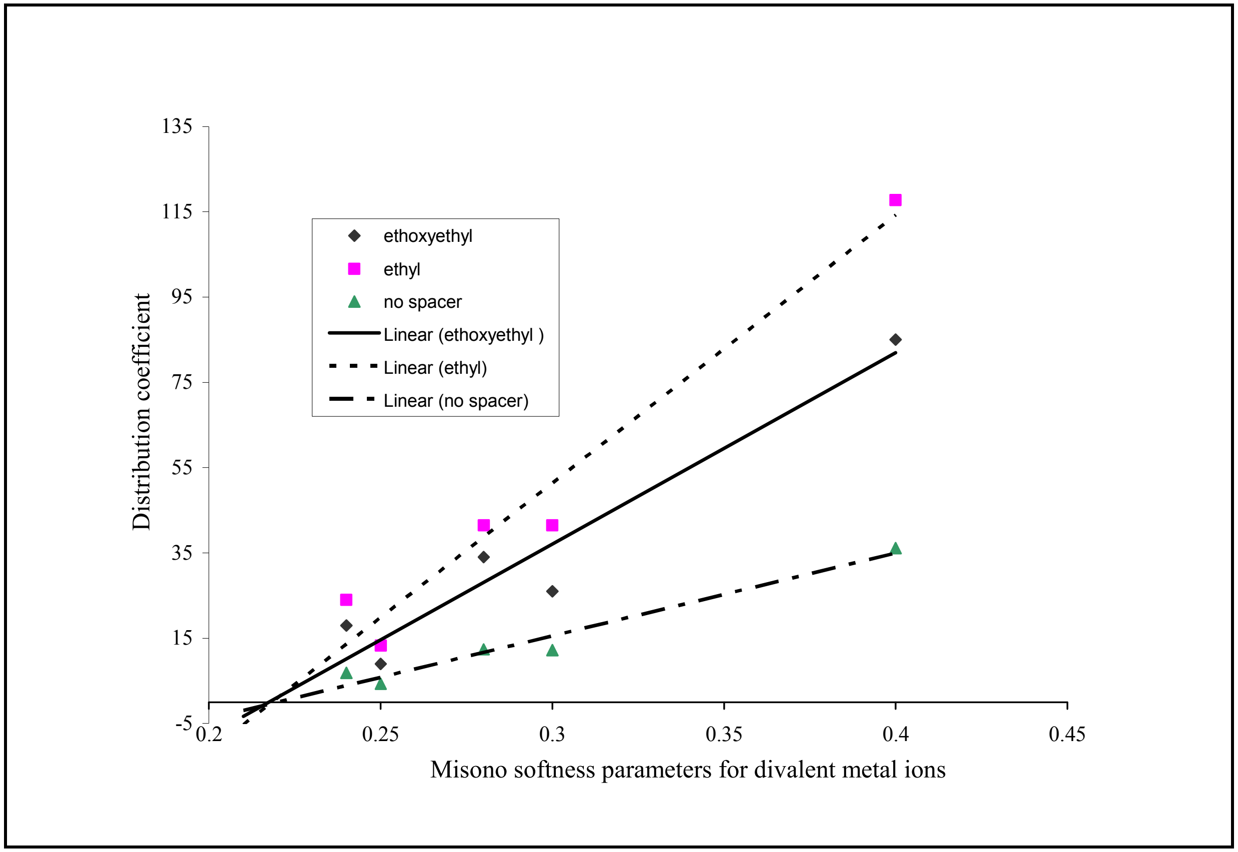
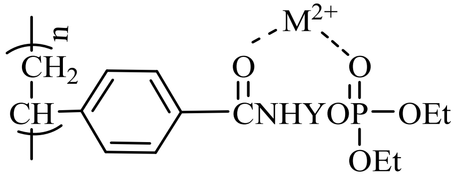


Figure 3-8 Correlation of distribution coefficients with metal ion polarisability for phosphorus containing resins.

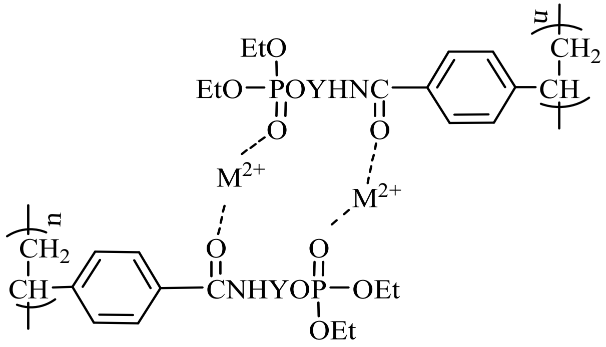
The decreased sorption by phosphorylated amidoalcohol esters with increased chain length is possible as the resin became less hydrophilic, reducing the accessibility of ligands to metal ions. For example, in Table 3-23, as the number of carbon atoms between the carbonyl and phosphoryl oxygen groups is increased from 2 to 3 to 5, the percent removal of Pb(II) decreased from 75% to 26% to 19% when the initial concentration of lead nitrate used was 1×10^{-4} N. Note that phosphorylated 2-(2-amidoethoxy)ethanol and amidopentanol resins possess the same number of atoms i.e. 4 C atoms and 1 O atom between the metal ion binding sites in the former and 5 C atoms in the latter case. The idea of accessibility can be tested by using macroporous resins instead of gel resins. Ether substitutents have been suggested for enhancing resin affinity by improving resin hydrophilicity.[31-34] The influences of spacer group characteristics such as hydrophilicity on chelation had been investigated using piperazine and N, N'-dimethylethylenediamine.[35] The location of the spacer chain may also play a role in determining its function. For instance, spacer chains introduced between the polymer and the functional ligand enhanced flexibility of the ligand resulting in higher metal sorption capacities.[36, 37]

The ether oxygen is weakly basic and can complex metal ions. This role of the ether oxygen participating in metal ion binding is debatable. Invasive studies such as solid state NMR or EPR would clarify how the metal ion binds to the ligand. The geometrical requirements for metal ion coordination would be determined so that orientation of the carbonyl oxygen and phosphoryl oxygen can be known. For example, the orientation afforded by ether oxygen in phosphorylated 2-(2-amidoethoxy)ethanol resins would not be possible for phosphorylated amidopentanol resins.

A. Intra-ligand metal ion complexation, “Y” = spacer chain of varying lengths.



B. Inter-ligand metal ion complexation



When the ligand is AEE, there can be involvement of the ether oxygen of the spacer chain.

Figure 3-9 Mechanism of binding for metal ions for phosphorylated amidoalcohol resins

Poly(benzoyl phosphonate) resins showed a lower percent sorption for divalent metal ions as compared to 2-(2-amidoethoxy)ethyl phosphate resin and amidoethyl phosphate resin. For example, in Table 3-24, sorption of Pb(II) was found to be 57 % for the phosphonate resin while it was 75 % and 82 % for phosphorylated esters of amidoethoxyethanol and amidoethanol respectively (Initial concentration of lead nitrate solution used was 1×10^{-4} N). In addition, poly(benzoyl phosphonate) was less selective among the three resins compared in Table 3-25, with the smallest slope of 194 (slopes for amidoethoxyethyl and amidoethyl phosphates were 449 and 629 respectively). Benzoyl phosphonate resin followed the same order of affinity for divalent metal ions as the phosphorylated amidoalcohols.

Acyl phosphonates contain a carbonyl group adjacent to the phosphonate while the phosphorylated amidoalcohol resins contain O-alkyl groups adjacent to the phosphoryl groups. Although phosphonates are stronger complexing agents compared to phosphates[38], the electron density of the P=O may be reduced by the presence of an electron withdrawing group such as C=O immediately adjacent to it.

Spacer participation in metal ion binding is possible if there is an electron donating group in the spacer chain.[39] Enhanced sorption capacities of gold and palladium were attributed to the hydrophilicity from ethylene oxide and ethylene sulfide units in addition to the coordinating properties of donor atoms in spacers.[40] The length of spacer can provide proper geometry of resin ligand for intramolecular metal complexation.[41, 42] In another example, for several calix[4]crown-4 oligomers synthesized, the extraction of several transition metal ions, (Cu^{2+}, Co^{2+}, Ni^{2+} and Hg^{2+}), were fairly good in comparison with their monomers. The study implicated the presence of polyoxyethylene bridges of the oligomers to account for the differences observed in selectivity and binding.[43] Note that these extraction experiments were carried out with metal picrate salts in chloroform.

3.4.3 Metal ion affinity analysis - B. Trivalent metal ions.

Carbonyl and phosphoryl involvement in metal ion extraction for lanthanides and transition metal ions have been investigated for small molecules[1] and functionalized silica sorbents[30] as well as organic polymer resins[11, 45] and quantum mechanical studies[46] bearing similar functional groups.

The low affinity for trivalent metal ions Fe^{3+}, Eu^{3+} and Al^{3+} by phosphorylated amidoethanol resins occurred because these metal ions were categorized as “hard” metal ions. A similar observation for divalent metal ions was made with the harder metal ions such as Ni^{2+} and Zn^{2+} having lower affinities. Introduction of the longer chain oxyethylene group increased capacity because of possible participation of the ether oxygen in metal ion binding.

Involvement of ether oxygens was proposed for a series of phosphorylated glycol resins interacting with several trivalent metal ions.[44] Resins containing ether linkages, showed a higher affinity for trivalents and almost none for divalents. Increasing chain length of ethers resulted in increased affinities among the trivalents, with a minimum of two glycol units required for high affinities.

Ketophosphonate resins showed better sorption for trivalent than for divalent metal ions. This can be explained by charge density of the trivalent ions compared to divalent metal ions, allowing the interactions between them to be stronger. A crosslinked polystyrene resin containing amine-N,N,N-triacetic acid functional groups generally was found to show a higher affinity for trivalent metal ions compared to divalent metal ion, that is, Ga(III) > In(III) > Cu(II) > Al(III) > Eu(III) > Ni(II) > Zn(II) > Co(II).

3.5 Conclusions

This research highlighted the analysis of resin selectivity with divalent and trivalent metal ions. It was found that determining that property of the metal ion which principally controls metal ion complexation was not always clear. It may be a combination of more than one factor(s). However, what was apparent was that correlations were present between metal ion and the ligand's binding site. For example for the amidophosphates prepared, there was a relation between the polarisability of the metal ion and the coordinative sites at phosphoryl oxygen enhanced by the carbonyl group. This relation was most noticeable in poly(amidoethyl phosphate) and poly (2-(2-amidoethoxyethyl phosphate) where the amount of metal ion complexed was higher.

The role of ligand geometry was investigated when a spacer chain was introduced between the carbonyl and phosphoryl binding sites. Increasing the spacer length made the ligand less able to complex metal ions, except when the spacer contained a donor group as in poly 2-(2-amidoethoxyethyl phosphate). Speculation on the role of the "O" in poly 2-(2-amidoethoxyethyl phosphate) suggested that participation of the donor group (which affect the geometry of metal ion complex) and/or hydrophilicity of the ligand may be responsible for higher metal ion capacities. A comparison of poly (amidopentyl phosphate and poly 2-(2-amidoethoxyethyl) phosphate indicate a clear difference in the metal ion affinities.

The results from the ketophosphonate resin indicate a higher affinity for trivalent metal ions. While this was not unexpected, these results when compared to the 2-(2-amidoethoxy)ethyl phosphate resin cannot be readily explained. Further investigations into the preparation of the ketophosphonate resin may be helpful. as there were unexplained variations noted in the IR spectrum of this compound following the synthesis method proposed.

3.6 References

1. Sano, Y.; Karino, J.; Koyama, T.; Funasaka, H. NMR study of lanthanide(III) nitrate complexes in CMPO/TBP systems. *J. Alloys Compd.* **2000**, *303-304*, 151-156.

2. Someda, H. H.; El-Zahhar, A. A.; Shehata, M. K.; El-Naggar, H. A. Extraction studies of UO_2^{2+} by dihexyl-N,N-diethyl carbamoyl methyl phosphonate (DHDECMP). *J. Radioanal. Nucl. Chem.* **1998**, *228*, 37-41.

3. Rao, L. Tian, G. Complexation of actinides with derivatives of oxydiacetic acid. LBNL-59274, **2006.**

4. Iveson, P. B.; Drew, M. G. B.; Hudson, M. J.; Madic, C. Structural studies of lanthanide complexes with new hydrophobic malonamide solvent extraction agents. *J. Chem. Soc. Dalton Trans: Inorganic. Chemistry* **1999**, *20*, 3605-3610.

5. Gannaz, B.; Chiarizia, R.; Antonio, M. R.; Hill, C.; Cote, G.; Extraction of Lanthanides (III) and Am (III) by mixtures of malonamide and dialkylphosphoric acid. *Solvent Extr. Ion Exch.* **2007**, *25*, 313-337.

6. Manchanda, V. K.; Pathak, P. N. Amides and diamides as promising extractants in the back end of the nuclear fuel cycle: an overview. *Sep. Purif. Technol.* **2004**, *35*, 85-103.

7. Boerrigter, H.; Verboom, W.; Reinhoudt, D. N. Novel Resorcinarene Cavitand-Based CMP(O) Cation Ligands: Synthesis and Extraction Properties. *J. Org. Chem.* **1997**, *62*, 7148-7155

8. Arnaud-Neu, F.; Bohmer, V.; Dozol, J-F.; Gruttner, G.; Jakobi, R. A.; Kraft, D.; Mauprivez, O.; Rouquette, H.; Schwing-Weill, M.-J.; Simon, N.; Vogt, W. Calixarenes with diphenylphosphorylacetamide functions at the upper rim. A new class of highly efficient extractants for lanthanides and actinides. *J. Chem. Soc. Perkin Trans 2* **1996**, *6*, 1175-1182.

9. Arduini, A.; Bohmer, V.; Delmau, L.; Desreux, J- F.; Dozol, J-F.; Carrera, M. A. G.; Lambert, B.; Musigmann, C.; Pochini, A.; Shivanyuk, A.; Ugozzoli, F. Rigidified calixarenes bearing four carbamoylmethylphosphine oxide or carbamoylmethylphosphoryl functions at the wide rim. *Chem. Eur. J.* **2000**, *6*, 2135-2144.

10. Trochimczuk, A. W.; Jezierska, J. New amphoteric chelating/ion exchange resins with substituted carbamylethylenephosphonates; synthesis and EPR studies of Cu(II) complexes. *Polymer* **2000**, *41*, 3463-3470.

11. Alexandratos, S. D.; Hussain, L. A. Synthesis of α-, β- and γ-ketophosphonate polymer supported reagents: the role of intraligand cooperation in the complexation of metal ions. *Macromolecules* **1998**, *31*, 3235-3238.

12. Berlin, K. D.; Hellwege, D. M.; Nagabhushanam, M. Dialkyl esters of acylphosphonic acids. *J. Org. Chem.* **1965**, *30*, 1265-1267.

13. Kawabe, H.; Yanagita, M. Group interactions in polyelectrolytes. I. Amination kinetics of chloromethylated polystyrene. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1518-1524.

14. Alexandratos S. D; Zhu X. Immobilized tris(hydroxymethyl)aminomethane as a scaffold for ion-selective ligands: the auxiliary group effect on metal ion binding at the phosphate ligand. *Inorg. Chem*. **2007**, *46*, 2139-47.

15. Vaidya, S. V.; Bapat, S. S.; Kale, A. S.; Mokashi, S. V. Weak base anion-exchange resin: simplification of amination process and control on SBC. *Ion Exch. Adv. Proc. IEX* **1992**, 112-119.

16. Seliger, H. New synthesis of polystyrene and styrene copolymers with primary aromatic amino groups. *Makromolekulare Chemie.* **1973**, *169*, 83-93.

17. Shabanov, A. L. ; Azizov, A. M. ; Sultanzade, S. S. ; Azizova, N. A.; Alieva, N. T. Alkylation of 2-aminoethanol to the corresponding tertiary amino alcohols. *Azerbaidzhanskii Khimicheskii Zhurnal* **1988,** 67-70.

18. Kawabe, H. Group interactions in polyelectrolytes. XIV. Amination of chloromethylated polystyrene with amino alcohols. *Hiroshi. Bull. Chem. Soc. Jpn.* **1981**, *54*, 2886-2892.

19. Kirzecky, N. D.; Thomson, L. M.; Wayne, R. S. Acid chloride to ester formation: mechanism of sulfur dioxide-amine interference. *J. Org. Chem.* **1987**, *52*, 3452-3455.

20. Hubbard, P.; Brittain, W. J. Mechanism of Amine-Catalyzed Ester Formation from an Acid Chloride and Alcohol. *J. Org. Chem.* **1998**, *63*, 677-683.

21. Cohen, H.; Mier, J. D. Esterification of carboxylic acids with triethyl orthoformate. *Chem. Ind*. **1965**, *8,* 349-350.

22. Wade, L. G. Jr. Organic Chemistry, 3rd ed. Prentice-Hall: New Jersey, **1995**, p. 264.

23. Yadav, L. D. S. Organic Spectroscopy, Kluwer Academic: The Netherlands, Anamaya: New Delhi, **2005**; Chapter 3.

24. Diem, M. Introduction to Modern Vibrational Spectroscopy, John Wiley & Sons: New York, **1993**; pp 208–210.

25. Avram, M.; Mateescu, Gh. D. Infrared Spectroscopy: applications in organic chemistry, Wiley-Interscience: New York, **1972**; pp. 444–449.

26. Alexandratos, S. D.; Hong, Min-Jeong**.** Enhanced metal ion affinities by supported ligand synergistic interaction in bifunctional polymer-supported aminomethylphosphonates. *Sep. Sci. Technol.* **2002**, *37*, 2587-2605.

27. Alexandratos, S. D.; Smith, S. D. Intraligand cooperation in metal-ion binding by immobilized ligands: the effect of bifunctionality. *J. Appl. Polym. Sci.* **2004**, *91*, 463-468.

28. Shriver, D. F.; Atkins, P. W. Inorganic Chemistry, 3rd ed. W. H. Freeman: New York **2003**, pp. 167-169

29. Alexandratos, S. D.; Zhu, X. Bifunctional coordinating polymers: Auxillary groups as a means of tuning the ionic affinity of Immobilized phosphate ligands *Macromolecules* **2005**, *38*, 5981-5986.

30. Yantasee, W.; Lin, Y.; Fryxell, G. E.; Busche, B. J.; Birmbaum, J. C. Removal of heavy metals from aqueous solution using novel nanoengineered sorbents: self-assembled carbamoylphosphonic acids on mesoporous silica. *Sep. Sci. Technol.* **2003**, *38*, 3809-3825.

31. Yamada, M.; Kishii, N.; Araki, K.; Shiraishi, S. Extraction and release of divalent metal ions by 6,6'-diamino-2,2'-bipyridine supported on polymer beads. *Nippon Kagaku Kaishi* **1989**, *6*, 988-992.

32. Qu, R.; Sun, C.; Ji, C.; Wang, C.; Zhao, Z.; Yu, D. Synthesis and adsorption properties of macroporous cross-linked polystyrene that contains an immobilizing 2,5-dimercapto-1,3,4-thiodiazole with tetraethylene glycol spacers. *Polym. Eng. Sci.* **2005**, *45*, 1515-1521.

33. Hojjatie, M.; Valiente, M.; Ribas, X.; Freiser, H. "Spacer" modified polymer bonded metal chelating ligands. Iranian *Journal of Polymer Science & Technology* **1994**, *3*, 105-14.

34. Sugii, A.; Ogawa, N.; Harada, K.; Nishimura, K. Metal sorption of macroreticular poly(4-vinylpyridine) resins cross-linked with oligo(ethylene glycol dimethacrylates). *Anal. Sci.* **1988**. *4*, 399-402.

35. Salem, N. M.; Ebraheem, K. A. K.; Mubarak, S. M. The effects of spacer groups on the chelation characteristics of some Mannich polymers containing 8-hydroxyquinoline. *React. Funct. Polym.* **2004**, *59*, 63-69.

36. Nishide, H.; Shimidzu, N.; Tsuchida, E. Chelating resin: Pyridine derivatives attached to poly(styrene) beads with spacer group. *J. Appl. Polym. Sci.* **1982**, *27*, 4161-4169.

37. Kumagai, H.; Inoue, Y.; Yokoyama, T.; Suzuki, T. M.; Suzuki, T. Chromatographic selectivity of rare earth elements on Iminodiacetate-type chelating resins having spacer arms of different lengths: Importance of steric flexibility of functional group in a polymer chelating resin. *Anal. Chem.* **1998**, *70*, 4070-4073.

38. Marcus, Y. Solvent Extraction of Inorganic Species. *Chem. Rev.* **1963**, *63*, 139-170.

39. Topp, K.-D.; Grote, M. Synthesis and characterization of a 1,2,4,5-tetrazine-modified ion-exchange resin. *React. Funct. Polym.* **1996**, *31*,117-136.

40. Sanchez, J. M.; Hidalgo, M.; Salvado, V. The gold (III) and palladium (II) on new phosphine sulphide-type chelating polymers bearing different spacer arms. Equilibrium and kinetic characterisation. *React. Func. Polym.* **2001**, *46*, 283-291.

41. Lauth, M.; Frere, Y.; Prevost, M. Gramain, PH. Complexation properties of a homologous series of linear polythioethers grafted onto macroporous polystyrene matrices. Selective binding of mercury(II) and silver(I). *React. Polym.* **1990**, *13*, 73-81.

42. Lauth, M.; Frere, Y.; Meurer, B.; Gramain, PH.; Prevost, M. Poly(ethylene oxide) grafted onto Polystyrene-divinylbenzene macroporous resins. Covalent binding of mercuric chloride. *React. Polym.* **1990**, *12*, 155-166.

43. Li, H.; Tian, D.; Xiong, D.; Gao, Z. Synthesis of calix[4]crown-4 oligomers containing hard and soft binding sites. *J. Appl. Polym. Sci.* **2007**, *104*(5), 3201-3205.

44. Alexandratos, S. D.; Zhu, X. Immobilized phosphate ligands with enhanced ionic affinity through supported ligand synergistic interaction. *Sep. Sci. Technol.* **Feb. 2008** (submitted)

45. Efendiev, A. A.; Orujev, D. D.; Sidorchuk, I. I. Selective polymer sorbents on the basis of copolymers of dialkyl esters of vinylphosphonic acid and acrylic acid. *React. Polym.* **1983**, *1*, 295-300.

46. Coupez, B.; Boehme, C.; Wipff G. Interaction of bifunctional carbonyl and phosphoryl ligands with M3+ lanthanide cations: how strong is the bidentate effect? The role of ligand size and counterions investigated by quantum mechanics. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5716-5729.

4 MOLECULAR RECOGNITION OF METHYL-t-BUTYL ETHER (MTBE) BY FUNCTIONALIZED POLYMERS

4.1 Introduction

Methyl-t-butyl ether (MTBE) has been detected in significant quantities in groundwater systems and drinking water wells in the U.S.[1-3] Public awareness of and controversy about MTBE began in 1996 when seven wells that supplied 50% of the water to Santa Monica, California were shut down due to high MTBE concentrations (≈ 600 μg/L).[4] MTBE was added to gasoline in the 1970's to improve the octane number as tetraethyl lead, an anti-knock ingredient in gasoline was being phased out. As a fuel oxygenate, MTBE's usage increased, especially in areas with severe ozone pollution and during the winter months. It was added to reformulated gasoline (RFG) to comply with regulations mandated by the 1990 Clean Air Act Amendments (CAAA).[4] Its large scale use was due to its low cost, ease of production, favorable transfer and blending properties with gasoline.[5] Apart from its use as a fuel additive, MTBE was used in medicine for treatment of gallstones and for synthesis of other organic chemicals.[6]

Its presence in the environment was the result of leaking underground storage tanks (LUSTs) and associated piping, and spillage when vehicles and water craft were being refueled. Surface water body entry occurred when there was spillage during manufacture and transport of MTBE and gasoline containing MTBE through underground pipelines. Exhaust from automobiles account for a high percentage of MTBE emissions in air. In some states, such as California and New York, where there have been especially high levels of MTBE reported, MTBE usage has been banned since 2004.[7] A Blue Ribbon Panel was convened by the EPA in 1998 to investigate water and air quality issues from the use of oxygenates in gasoline. Among their recommendations was reducing MTBE usage and removing the stipulation in the CAAA which states that 2% by weight of RFG consist of oxygen.[2]

MTBE has a low molecular weight with a water solubility of 43 - 54.3 g/L and boiling point of 53.6 - 55.2°C.[8] Its Henry's law constant, $K_H^{25°C}$ is 0.026[9] and log K_{oc} is 1.20.[8] These properties make it easily transported and readily distributed in the environment. The concern about its distribution and occurrence as a result of its intensive use has led to the proposition of an acceptable standard for MTBE in drinking water set by U.S. EPA at 20-40 μg/L.[10] The advisory was set to protect against potential health concerns and to establish groundwater cleanup standards. MTBE contaminated waters have an unpleasant taste and a distinct turpentine-like odor[11] detectable at concentrations as low as 2.5 ppb.[12] Testing would be required to determine the long term effects of MTBE exposure. Some animal studies have reported on its carcinogenicity.[13] Although MTBE usage was addressing some air pollution problems by reducing carbon monoxide and ozone emissions, it was also creating new water pollution issues. Besides its occurrence in surface and groundwater, it caused gasoline solubility in water to increase.[14]

Some of the technologies available for MTBE removal include air stripping, advanced oxidation processes (ozone, UV, hydrogen peroxide addition),[15] adsorption with granular activated carbon, membrane separation, pump-and-treat, and soil vapor extraction.[16] Biological treatment of MTBE and tertiary-butyl alcohol (TBA), a degradation product of MTBE and a contaminant of gasoline, has also been explored for MTBE remediation. Research in the area of aerobic and anaerobic biodegradation has been investigated, including the effect of the presence or absence of other contaminants on the degradation of MTBE.[17, 18] Note that it is likely for compounds such as benzene, toluene, ethylbenzene and xylene (BTEX) to be present in areas polluted by MTBE.[19] Not all the above processes are economically viable. Several studies have compared the different methods for MTBE removal with respect to cost and effectiveness.[1, 16, 20, 21]

There is an interest to develop synthetic resin sorbents, as preliminary studies indicate that they can be economically competitive.[22] The resin may be regenerated.[23] In addition, resins can be prepared with surfaces of predetermined characteristics, so that it is possible to design a resin for a specific adsorption application. This chapter reports on some experiments geared towards designing polymer-supported reagents for MTBE removal with high affinities and selectivities. Several approaches were investigated to identify the factors involved in MTBE adsorption. These will be outlined in the next section.

Pore modification of resins was addressed as a means of improving extraction chromatographic resins (EXC), which can be applied in this research. EXC resins were made inefficient because of tailing observed upon elution of the sorbed material.[40] Tailing was believed to be due to the presence of stagnant pores within the resin. Experiments were designed to determine if “plugging” the micropores of the resin would reduce this effect.

4.2 Experimental

A summary of experiments is presented below. Details of the experimental methods and conditions used in analysis can be found in Chapter 5. MTBE sorption with resins was investigated as follows:

1. Investigating resin structure and functional groups – To develop a resin for MTBE sorption, the variables considered were: polymer backbone structure, % crosslink (i. e. % divinylbenzene (DVB)), % porosity and type of complexant.

a. Polymer supports investigated were poly(vinylbenzyl chloride) (VBC), poly(styrene) (PS), poly(butyl acrylate), poly(4-acetoxystyrene) (AcSty), poly(vinylbenzyl chloride): styrene (VBC:sty)

b. Macroporous resins (MR) of different crosslink levels (% DVB) were prepared - 5 % DVB MR, 12 % DVB MR, 40 % DVB MR.

c. Complexants such as calixarenes, phosphorylated calixarenes, hydroxy, phosphonate esters, phosphonic acid, ethers (triethylene glycol (TEG), triethyleneglycol monomethyl ether (TEGME), (tripropyleneglycol monomethyl ether (TPGME)) and amines (N-methyl-D-glucamine, trihexylamine, dimethylamine) were immobilized. Polystyrene was acetylated, nitrated and brominated.

All resins examined were listed in Table 4-1. Batch equilibrium adsorption experiments were performed and the aqueous solution analyzed for MTBE using a GC / FID. Details of the operating conditions of GC / FID can be found in Chapter 5.

2. Solvent extraction studies – I. A series of liquid-liquid extraction experiments using each of the following extractants was carried out: butylbenzene, p-xylene, mesitylene,

chlorobenzene, 4-chlorotoluene, m-nitrotoluene, isooctane, 2-ethyl-1-hexanol and toluene. It was important that the solvents chosen were all liquids at room temperature and pressure and insoluble in water. Ten milliliters of a 150 ppm MTBE solution was contacted with 5 mL of the complexant. The aqueous phase was analyzed for MTBE after a 2 h contact time while shaking on a Burrell Wrist Action Shaker. One microliter of the aqueous phase was removed and injected into the GC. The parameters for analysis with GC / FID were kept the same as for the analysis of the aqueous phase with batch experiments with resins. These experiments were useful for determining the type of complexants that had high affinities for MTBE.

Solvent extraction studies – II. The liquid-liquid extraction experiments were expanded to investigate the effect of MTBE sorption in the presence of a more hydrophobic contaminant such as benzene (quite common in natural environments). This was applicable since in nature, MTBE was found in the presence of contaminants of this type. Fifteen milliliters of a solution (containing 150 ppm benzene and 150 ppm MTBE) was placed in a 20 mL screw capped vial. Five milliliters of the extractant was then added and the mixture shaken for 2 h. The aqueous phase was analyzed for MTBE.

3. Preparation of extraction chromatographic resins

One way of combining the above investigations was to prepare extraction chromatographic resins. One gram vacuum dried XAD-4 was stirred overnight in 100 mL toluene with 20 mL p-cresol. The resin was separated from the solution by filtration and washed with water. The resin was dried for 5 h under the hood and then transferred to the oven and kept for 17 h at 110 degrees. The resin was contacted with 20 mL of aqueous MTBE solution (150 ppm) and shaken for 17 h. The aqueous phase was analyzed for MTBE.

4. Alteration of pore structure of resin and influence on MTBE sorption

The resins used for modification were XAD-4 [Styrene – DVB copolymer, MR, Surface area = 780 m^2/g, pore size = 50 °A, (Supelco, PA)], pre-filter resin, PF-B100-A [polyacrylate, MR (Eichrom Technol., IL)]. Modified resins were analysed with a TriStar 3000 porosimeter for changes in surface area. The samples were first vacuum oven dried at 70 °C for 6 h and then degassed with nitrogen at 50 °C for 2 h. The following were the pore modification experiments undertaken.

Procedure I - 1 g of resin was contacted with 0.5 mL vinylbenzyl chloride (VBC), 10 mL of 1% benzoyl peroxide (BPO) and 10 mL methanol in a capped flask for 24 h. The methanol was removed in a rotary evaporator and then capped before placing in the oven for 24 h at 70 °C. The resin was air dried.

Procedure II - 1 g of resin was contacted with 5 mL VBC and 1% BPO for 24 h in a capped vial. The contents was emptied into a frit funnel for 10 s and 5 mL acetone allowed to pass through, turning on vacuum for another 5 s. The vial was capped and put in the oven for 24 h at 70 °C.

Procedure III - 1g of resin was contacted with 5 mL acrylonitrile containing 1% BPO for 24 h. The solvent was removed with a pipette and the vial capped and placed in an oven set to 70 °C for 24 h.

4.3 Results and Discussion

A method for analysis of MTBE from aqueous media was developed. There were several methods for analysis of volatile organic compounds (VOC), but not all were EPA validated for environmental analysis of highly water soluble ethers such as MTBE. Modification of existing methods was necessary to get accurate results. In addition, factors such as the sample matrix, length of analysis, reliability and instrumentation had to be considered before choosing a method.[24]

Method 8015 was optimized and implemented. This is an EPA SW-846 determinative method for MTBE using a Gas Chromatograph with Flame Ionization Detector (GC/FID) system. A detailed account of the modified method can be found in Chapter 5. It was appropriate to use this method since analysis of the batch equilibrium adsorption experiments contained only MTBE. Initial experiments involved injecting MTBE-spiked samples directly into the GC using a 1 microliter Hamilton 700 series syringe. MTBE was identified by its retention time of 2.28 mins on the chromatogram (Figure 4-0). A modified sample preparation method following the guidelines of EPA Method 5030 enabled the analysis of parts per billion (ppb) levels of MTBE.[25] The method required the attachment of a purge and trap ensemble for extracting the hydrophilic volatile organic compound (VOC) from aqueous solution prior to its entry in the GC. The use of this method would eliminate problems of water injections into GC.[27] See Chapter 5 for method description. A method was developed and a sample chromatogram is presented in the Appendix section V. Note that the results presented in the thesis are representative of analyses in the absence of the purge and trap.

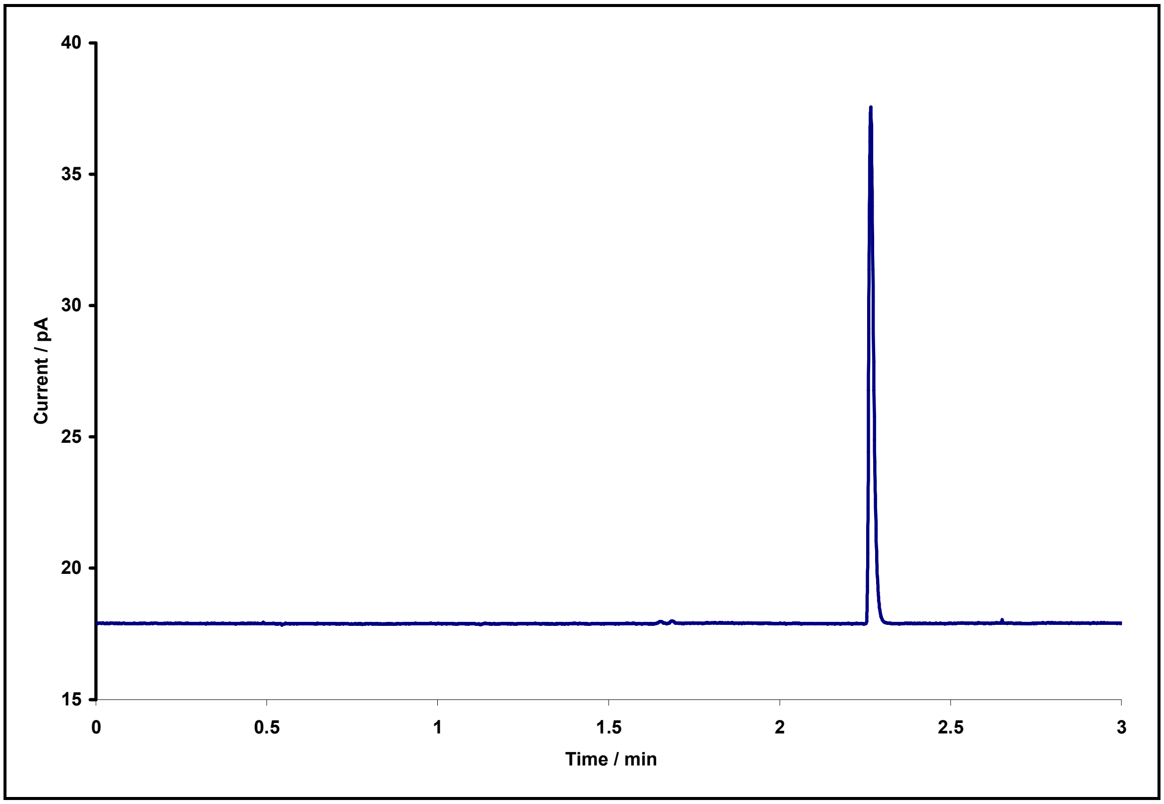


Figure 4-1 MTBE spiked sample (150ppm) analyzed with GC/FID

Hydrophobicity and porosity were key variables in MTBE sorption. XAD-4, a porous, cross-linked polystyrene resin had a high MTBE affinity, while polystyrene resin at lower crosslink levels do not remove MTBE significantly (Table 4-1). 40% DVB poly (VBC) macroreticular (MR) resins performed well. Lowering the percent crosslink makes the support less efficient. However, a polystyrene or a poly(vinylbenzyl chloride:styrene) (poly(VBC:sty)) matrix can be quite efficient at lower crosslink levels compared to other supports. Porosity was also a factor in MTBE sorption and MR resins were prepared and used in this study. MR resins contain pores that allow greater accessibility for MTBE. Ligands were immobilized on supports containing low cross-link levels to investigate whether there can be an interaction between that ligand and MTBE that can account for MTBE sorption.

The complexants investigated (Table 4-1), suggested that none of immobilized ligands significantly affected MTBE sorption, with the exception of phosphorylated calixarene (resin code XZ 01-067). They may form complexes within their cavity structures due to their orientation of the ligands on the polymer. Calixarenes can form complexes with neutral organic molecules in solution (host-guest concept recognition).[26]

The use of sorbents in remediation of water containing organic compounds has been reported.[21, 24] Optipore L493, for example, has proved effective for collecting analytes such as BTEX and chlorinated hydrocarbons. The most common sorbent for MTBE removal is granular activated carbon (GAC). GAC has a high surface area and a large capacity for adsorbing organic compounds. GAC however becomes saturated quickly and needs to be replaced or regenerated.[28] The high costs incurred as a result make its use not economical and the performance of the activated carbon varied.[1, 29]

Table 4-1 Resins and percent removal of MTBE after 17h shaking. (RSD = 6.7%)

Resin code	**Matrix**	**Ligand**	**Characterization**	**Percent removal MTBE**
XZ-01-050	VBC 5% DVB MR	None	N. A.	0.0
LD 02-078	Phenol/ formaldehyde	Hydroxyl	N. A.	6.2
AP 01-040	4 AcSty 12% DVB MR	-C(O)CH_3	N. A.	5.6
AP 01-045	Butylacrylate 12% DVB MR	-$COOC_2H_5$	N. A.	7.7
AP 01-022	VBC 12% DVB MR	None	N. A.	24.5
SN 03-015	VBC 12% DVB MR	None	N. A.	9.2
CL 01-264	VBC 16% DVB MR	None	N. A.	7.0
RB 05-227	VBC 40% DVB MR	None	N. A.	80.7
AP 01-016	25:75 VBC:sty 5% DVB MR	None	N. A.	25.6
AP 01-020	25:75 VBC:sty 12% DVB MR	None	N. A.	0.0
AP 01-018B	PS 12% DVB MR	None	N. A.	19.0

Table 4.1 (cont'd)

Resin code	**Matrix**	**Ligand**	**Characterization**	**Percent removal MTBE**
AP 01-052	4 AcSty 12% DVB MR	Phosphonate diethyl ester	P capacity = 1.94mmol/g	3.4
XZ 01-032B	VBC 5% DVB MR	Calixarene	N. A.	0.0
XZ 01-067	VBC 5% DVB MR	Phosphorylated Calixarene	P capacity = 0.58mmol/g	37.2
LD 02-082	VBC 12% DVB MR	TEGME	N. A.	3.4
LD 02-081	VBC 12% DVB MR	Trihexylamine	N elemental = 0.38mmol/g	0.0
LD 02-088	VBC 12% DVB MR	Dimethylamine	N. D.	0.4
AP 01-042	VBC 12% DVB MR	TPGME	N. A.	16.5
AP 01-030	VBC 12% DVB MR	Phosphonate dibutyl ester	P capacity = 1.89mmol/g	9.3
AP 01-023	VBC 12% DVB MR	Dihexylamine	N capacity = 1.97mmol/g	0
AP 01-021B	VBC 12% DVB MR	Polyamine	N. D.	5.7
LD 02-097	VBC 12% DVB MR	Pb impregnated Phosphonic acid	N. D.	12.0
AP 01-018a	25:75 VBC:sty 5% DVB MR	Phosphonate dibutyl ester	N. D.	8.5

Table 4.1 (cont'd)

Resin code	**Matrix**	**Ligand**	**Characterization**	**Percent removal MTBE**[a]
AP 01-028	25:75 VBC:sty 12% DVB MR	Dihexylamine	N capacity = 1.022mmol/g	5.1
LD 02-086	25:75 VBC:sty 12% DVB MR	Trihexylamine	N capacity = 0.55mmol/g	16.3
AP 01-031	25:75 VBC:sty 12% DVB MR	Phosphonate dibutyl ester	P capacity = 1.075mmol/g	15.1
LD 02-092	PS 12% DVB MR	NO_2	N. D.	4.5
LD 02-098	PS 12% DVB MR	Br	Br elemental = 2 mmol/g	0
XAD-1	PS DVB Surface area = $100m^2/g$	None	N. A.	26.0
XAD-4	PS DVB Surface area = $780m^2/g$ Pore size = 50 Angstroms	None	N. A	86.5
GAC	Highly porous carbon	None	N. A.	93.3

[a] % MTBE removed = $\{([MTBE]_{initial} - [MTBE]_{experimental})/[MTBE]_{initial}\} \times 100$
N.A. = not applicable
N.D. = not determined

In a study comparing sorption of o-xylene, MTBE and TBA by several synthetic resins (Ambersorb 563, Dow Optipore L493, Amberlite XAD-4 and Amberlite XAD-7), o-xylene was preferred over MTBE and TBA.[29] Ambersorb 563 and 572 (Rohm and Haas Co., Philadelphia) was found to be efficient in the removal of MTBE from water that has been contaminated, relative to GAC.[30] It was concluded from the study that Ambersorb 563 and 572 were the most promising sorbents for MTBE removal. Other sorbents such as zeolites with high SiO_2/Al_2O_3 ratios retained 8-12 times more MTBE than activated carbons from solutions of 100µg/L MTBE.[33]

Solvent extraction experiments were conducted to determine for a series of complexants, which ones have an affinity for MTBE. In this way a better understanding of the nature of the molecular interactions between MTBE and groups with different functionalities can be obtained. Molecules which showed high affinity for MTBE would be possible choices of chemical groups for immobilization on polymer supports. Most solvents in Table 4-2 had comparable affinity for MTBE: p-cresol and 2-ethyl-1-hexanol, however, showed the greatest (percent MTBE removal was 100 %).

Trace quantities of an organic compound were added to MTBE solutions in order to determine whether any conclusions could be made with respect to selectivity. Benzene was chosen. Note that in the environment, it is common for MTBE to be accompanied by BTEX compounds.[32] A solution was prepared containing 150 ppm of MTBE and 150 ppm of benzene. It was found that the presence of benzene caused a reduction in percent MTBE removal, however, p-cresol retained its high affinity for MTBE (Table 4-3).

Table 4-2 The affinity of different solvents for MTBE

Solvent	**Percent removal MTBE**
4-chlorotoluene	90.3
m-cresol	97.7
p-cresol	99.9
cyclohexanol	92.4
2'- hydroxyacetophenone	79.1
methoxybenzylphenol	95.7
toluene	90.8
toluene & tributylphosphite	90.9
butylbenzene	95.7
p-xylene	92.6
mesitylene	91.4
chlorobenzene	94.6
m-nitrotoluene	83.0
isooctane	90.6
2-ethyl-1-hexanol	100.0

Table 4-3 The affinity of different solvents for MTBE in the presence of benzene

Solvent	**Percent removal MTBE**
4-chlorotoluene	90.0
p-cresol	100.0
cyclohexanol	64.6
toluene	92.7
butylbenzene	87.0
p-xylene	90.7
mesitylene	81.7
chlorobenzene	85.5
m-nitrotoluene	72.2
isooctane	79.5
2-ethyl-1-hexanol	91.4

Extraction chromatographic resins (EXC) are useful in metal ion separations.[35-39] These resins combine the advantages of high selectivity of solvent extraction and the simplicity and high efficiency of ion exchange while overcoming the pollution issues of conventional solvent extraction. There has been some evaluation of amino acid sorption on solvent impregnated resins.[39] P-cresol was chosen for impregnation in the resin based on results in Tables 4-2 and 4-3. Preparation of an EXC containing p-cresol was not successful. This was concluded by comparing IRs of XAD-4 before and after treatment with p-cresol which did not indicate any differences in their spectra such as presence of –OH stretch around 3200 cm^{-1}.

Investigations of a method to plug the micropores of some commercial resins were carried out. This was important as a means of improving the separations of metal ions in EXC resins by reducing tailing.[38] Secondly, the ability to successfully regenerate the resin may be impeded by the presence micropores within the bead. If these stagnant pores are removed, then the regeneration of the resin can be more efficient. Changes in surface area were used to determine the success of the pore-plugging experiments. It was observed (Table 4-4), that procedure II changed the pore surface area the most drastically. Additional measurements such as pore volumes and areas as well as sizes and distributions would be taken for further analysis. These properties of resins are important since the physical characteristics of the resin affect its performance in the sorption of MTBE.

Table 4-4 Results of different pore-plugging experiments and XAD-4

Method	**B.E.T (m^2/g)** **Treated (untreated)**
Procedure III	[a]534 (812)
Procedure I and XAD-4 Procedure I and PF-B100-A	695 (776) 90 (483)
Procedure II and XAD-4 Procedure II and PF-B100-A	80 (776) 54 (483)

[a] These results were obtained with a Micromeritics Gemini 2375 surface area analyzer.

Table 4-5 Prepared resins (not yet tested)

Resin code	Matrix	Ligand	Characterization
AP 01-201	Amberlite IR-120 Ion exchange resin, gel	Trimethydodecylammonium bromide	N capacity = 1.51mmol/g
AP 01-203	VBC 2% DVB gel	Phenol	Cl capacity = 0mmol/g
AP 01-208	Amberlyst 15 Ion exchange resin, MR	Trimethyldodecylammonium Bromide	N capacity = 1.035mmol/g
AP 01-209	VBC 2% DVB gel	Phenol and diphenylphosphate	P capacity = 1.465mmol/g
AP 01-070	4-VP 12% DVB MR	-	N capacity = 5.341mmol/g
AP 01-074	GMA, 8% DVB MR	Na salt of dodecanol	N. A.

4.4 Conclusions and Future Directions

A ligand showing significant recognition for MTBE has not been found. However, some ligand properties have been identified and confirmed such as hydrophobicity and polarity to be important in ligand design. The resin should be porous. Calixarenes can be potential ligands for MTBE sorption and this should be investigated further. Table 4-5 illustrates a further set of resins which have been synthesized for testing with MTBE solutions. The table contains some ionic resins which improves the hydrophilicity of the resin allowing for compatibility of MTBE and resin.

The liquid-liquid extraction studies were helpful in choosing appropriate solvents for preparation of extraction chromatographic resins and also in designing better ligands for immobilization on polymers. To quantify different solvents used in these studies, it would be better to change the detector in GC from FID to MS for accurate identification of compounds. Also, implementation of the method developed using the purge and trap will be useful for further work. Modification of the method for preparation of EXC resins would be necessary.

Preliminary work suggested that pore-plugging of resin was feasible. Investigations of the type of pores plugged and its effect on tailing would be required.

4.5 References

1. Suffet, I.; Shih, T.; Khan, E.; Wangpaichitr, M.; Rong, W.; Kong, J.; Sorption for removing methyl tertiary butyl ether (MTBE) from drinking water. Proceedings, Annual Conference, American Water Works Association, Denver, **1999**, 319-336.

2. Fiorenza, S.; Suarez, M. P.; Rifai, H. S. MTBE in groundwater: status and remediation *J. Environ. Eng.* **2002**, *128*, 773 - 781.

3. Squillace, P. J.; Zogorski, J. S.; Wilbur, W. G.; Price, C. V. Preliminary assessment of the occurrence and possible sources of MTBE in groundwater in the United States, 1993-1995. *Environ. Sci. Technol.* **1996**, *30*, 1721-1730.

4. Johnson, R.; Pandow, J. Bender, D.; Price, C.; Zogorski, J. MTBE To what extent will past releases contaminate community water supply wells? *Environ. Sci. Technol*. **2000**, *34*, 210A – 217A.

5. Shelly, S.; Fouhy, K. The drive for cleaner burning fuel. *Chem. Eng.* **1994**, *101*, 61-63.

6. New Hampshire Department of Health and Human Services Bureau of Health Risk Assessment. Health information summary Methyl t-Butyl Ether (MTBE) **2000.**

7. Ritter, S. K.; Alkylate Rising, *C & EN* **2001**, *79*, 63-67.

8. Squillace, P. J.; Pankow, J. P.; Korte, N. E. ; Zogorski, J. S. Review of the environmental behavior and fate of methyl *tert*-butyl ether. *Environ. Toxicol. Chem.* **1997**, *16*, 1836-1844.

9. Staudinger, J.; Roberts, P.V. A critical review of Henry's law constants for environmental applications. *Crit. Rev. Env. Sci. Technol.* **1996**, *26*, 205-297.

10. U.S. Environmental Protection Agency. Drinking water advisory: Customer acceptability advice and health effects analysis on Methyl tert-Butyl Ether (MTBE); EPA-822-F-97-008; Office of Water, U.S. EPA: Washington, DC. http://www.epa.gov/OST/Tools/MtBEaa.pdf.

11. Young, W. F.; Horth, H.; Crane, R.; Ogden, T.; Amott, M. Taste and odor threshold concentrations of potential potable water contaminants. *Water Res.* **1996**, *30*, 420-426.

12. Cater, S. R.; Dusset, B. W.; Megonnell, N. Reducing the threat of MTBE – contaminated groundwater. *Pollution Engineering*. **2000**, *32*, 36-39.

13. Mennear, J. H. Carcinogenicity studies on MTBE: Critical review and interpretation. *Risk Analysis*: an official publication of the Society for Risk Analysis. **1997**, *17*, 673-681.

14. Penske, N.; Sandler, S. I. Liquid-liquid equilibria of fuel oxygenate + water + hydrocarbon mixtures. 1. *J. Chem. Eng. Data* **1995**, *40*, 315-320.

15. Chang, P. B. L.; Young, T. M. Kinetics of Methyl tert-butyl ether degradation and by-product formation during UV / Hydrogen Peroxide Water Treatment. *Water Res.* **2000**, *34*, 2233-2240.

16. Effenberger, M.; Lobel, E.; Noack, T.; Schirmer, M. The gasoline additive Methyl-tert-Butyl Ether (MTBE) as challenge for groundwater. *Altlasten Spektrum* **2001**, *10*, 177-184.

17. Salanitro, J. P.; Diaz, L. A.; Williams, M. P.; Wisniewski, H. L. Isolation of a bacterial culture that degrades Methyl t-butyl ether. *Applied and Environmental Microbiology* **1994**, *60*, 2593-2596.

18. Deeb, R. A.; Scow, K. M.; Alvarez-Cohen, L. Aerobic MTBE biodegradation: an examination of past studies, current challenges and future research directions. *Biodegradation* **2000**, *11*, 171-186.

19. An, Y.-J.; Kampbell, D. H.; Cook, M. L. Co-occurrence of MTBE and benzene, toluene, ethylbenzene, and xylene compounds at marinas in large reservoir. *J. Environ. Eng.* **2002**, *128*, 902-906.

20. Wilhelm, M. J.; Adams, V. D.; Curtis, J. G.; Middlebrooks, E. J. Carbon adsorption and air-stripping removal of MTBE from river water. *J. Environ. Eng.* **2002**, *128*, 813-823.

21. Kawabata, N.; Sumiyama, Y.; Matsuura, N. Separation of alcohols from water by adsorption on cross-linked polymethacrylic ester containing a pyridinium group. *Ind. Eng. Chem. Res.* **1988**, *27*, 1882-1886.

22. MTBE Research Partnership. Evaluation of the Applicability of synthetic resin sorbents for MTBE removal from water. **1999**. Ed. Melin, G. National Water Research Institute.

23. Lin, S. H.; Wang, C. S.; Chang, C. H. Removal of Methyl *tert*-Butyl Ether from contaminated water by macroreticular resin. *Ind. Eng. Chem. Res.* **2002**, *41*, 4116-4121.

24. Rhodes, I. A. L.; Verstuyft, A. W. Selecting analytical methods for the determination of oxygenates in environmental samples and gasoline. *Environmental Testing & Analysis* **2001**.

25. Nouri, B.; Fouillet, B.; Toussaint, G.; Chambon, R. ; Chambon, P. Complementarity of purge-and-trap and head-space capillary gas chromatographic methods for determination of methyl-tert.-butyl ether in water. *J. Chromatogr. A* **1996**, *726*, 153-159.

26. Bauer, L. J.; Gutsche, D. Calixarenes. 15. The formation of complexes of calixarenes with neutral organic molecules in solution *J. Am. Chem. Soc.* **1985**, *107*, 6063-6069.

27. Kuhn, E. Water injection in gas chromatography part 1. *Sep. Times* **2001**, *14*, 10-11.

28. Kawabata, N.; Higuchi, I.; Yoshida, J. Removal and Recovery of Organic Pollutants from the Aquatic Environment. VII. Adsorption of phenol and carboxylic acids on crosslinked poly(4-vinylpyridine). *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3253-3258.

29. Malley, J. P. Jr.; Eliason, P. A.; Wagler, J. L. Point-of-entry treatment of petroleum contaminated ground water. *Water Environ. Res.* **1993**, *65*, 119-128.

30. McClure, A.; Megonnell, N. Activated carbon optimized to treat MTBE. *Water Technology* **2000**, 1-3.

31. Bi, E.; Haderlein S. B.; Schmidt, T. C.; Sorption of methyl *tert*-butyl ether (MTBE) and *tert*-butyl alcohol (TBA) to synthetic resins. *Water Res.* **2005**, *39*, 4164-4176.

32. Davis, S. W.; Powers, S. E. Alternative sorbents for removing MTBE from gasoline-contaminated groundwater. *J. Environ. Eng.* **2000**, *126*, 354-360.

33. Anderson, M. A. Removal of MTBE and other organic contaminants from water by sorption to high silica zeolites. *Environ. Sci. Technol.* **2000**, *34*, 725-727.

34. Wang, X.; Deshusses, M. A. Biotreatment of groundwater contaminated with MTBE: interaction of common environmental co-contaminants. *Biodegradation* **2007**, *18*, 37-50.

35. Yokoyama, T.; Makishima, A.; Nakamura, E. Separation of thorium and uranium from silicate rock samples using two commercial extraction chromatographic resins. *Anal. Chem.* **1999**, *71*, 135-141.

36. Gonzalez, M. P.; Saucedo, I.; Navarro, R.; Avila, M.; Guibal, E. Selective separation of Fe(III), Cd(II), and Ni(II) from dilute solutions using solvent-impregnated resins. *Ind. Eng. Chem. Res.* **2001**, *40*, 6004-6013.

37. Cortina, J. L.; Warshawsky, A. Developments in solid-liquid extraction by solvent-impregnated resins. *Ion Exch. Solvent Extr.* **1997***, 13*, 195-293.

38. Li, H.; Zhou, C.; Fu, B. Separation of platinum group metals by solvent-impregnated resins technique. *Guijinshu* **2001**, *22*, 49-53.

39. Kostova, A.; Bart, H.-J. Equilibrium study of amino acid reactive sorption with impregnated resins (Part I). *Solvent Extr. Ion Exch.* **2007**, *25*, 109-126.

40. Giddings, J. C. Kinetic origin of tailing in chromatography. *Anal. Chem.* **1963**, *35*, 1999-2002.

5 EXPERIMENTAL SECTION

5.1 Polymer preparation and Metal ion contact study procedures

5.1.1 Materials

Monomers, DVB (55.4% purity) and VBC (97% m-and p- isomers) were obtained from Sigma-Aldrich. All other chemicals were purchased from Fisher Scientific. All chemicals were used as received. Reagents for metal ion contact experiments and elemental analyses were of analytical grade purity. Ultrapure water (18 MΩcm^{-1}) used for synthesis and analysis was obtained from a Barnstead Nanopure unit, Barnstead USA. Precise temperature control of reactions was regulated by Therm-O-Watch devices.

5.1.2 Polymer syntheses

5.1.2.1 Copolymer synthesis (Preparation of VBC - 2 % DVB gel copolymer)

Vinylbenzyl chloride/divinylbenzene (VBC/DVB) beads were synthesized by suspension polymerization. The amounts indicated in the following procedure were for a typical preparation of 150 g of gel beads with a 2 % crosslink level. The organic phase consisted of dissolving 1.5 g BPO in 143 g VBC and 5.4 g of DVB with stirring. The organic phase was sparged for 5 min with nitrogen. The aqueous phase contained 28 g calcium chloride dihydrate and 1.28 g poly(vinylalcohol) (PVA) (tradename Gohsenol) in 250 mL water. The aqueous phase was heated to completely dissolve the PVA. Once dissolved, it was poured into a 500 mL 3-neck flask and sparged with nitrogen for 10 mins. The flask was equipped with an overhead stirrer, thermometer with a temperature controller, and a nitrogen gas inlet area.

The stir paddle was adjusted so that the top of the paddle was just above the aqueous phase in the flask. The organic phase was added and the nitrogen sweep turned on. The stir motor was turned on for 2 mins. The bead size was checked and the stir speed adjusted. This was repeated twice. The temperature was then increased at a rate of 7° C / 15 min to 80° C over 2 h. The beads were stirred at 80 °C for 10 h.

At the end of polymerization, 100 mL of water was added and the beads refluxed for 2 h. The beads were washed with 100 mL methanol and 100 mL water. They were Buchner dried and then purified by extraction with toluene in a soxhlet extraction apparatus for 17 h. The beads were placed in a drying dish under the fumehood and sieved using U. S. standard screens.

5.1.2.2 Synthesis of carboxylic acid resin[1]

In a 500 mL, three-neck round-bottomed flask, 30 g of sodium bicarbonate and 70 mL dimethyl sulfoxide were added and stirred for 2 hours. In a 100 mL beaker, 10 g of VBC beads were swelled in 80 mL dimethyl sulfoxide for 2 hours. The beads were added to the stirred bicarbonate / dimethyl sulfoxide mixture, using 40 mL of dimethyl sulfoxide to effect complete transfer of beads. The reaction was stirred at reflux for 20 hours. On completion of the reaction, the solution was removed and beads were washed with 100 mL methanol and then 100 mL water. The beads were next swollen in 60 mL of 70% aqueous dioxane for 1.5 hours. To the swollen beads, 130 mL of 3 N nitric acid solution was added and the mixture was heated at reflux for 24 hours. After this reaction, the beads were washed with 100 mL water (3 times) and separated from the nitric acid solution. The beads were swelled in 60 mL dioxane for 1.5 hours followed by the addition of 100 mL hydrogen peroxide (30 wt. %). The beads were heated to 80 degrees for 24 hours. Beads were recovered by filtration and washed with 100 mL water (3 times).

5.1.2.3 Synthesis of acid chloride resin

Five grams of vacuum dried (6 hours at 70 degrees) carboxylic acid resin were placed in a 250 mL three neck round-bottomed flask. To the beads, 50 mL thionyl chloride was added and the beads swelled for 1 hour. The mixture was refluxed for 48 h hours (17 h was a sufficient time for this reaction to obtain the same degree of functionalization). The beads were filtered and washed with 50 mL toluene (3 times).

5.1.2.4 Synthesis of carboxamide resin

Seven grams of acid chloride beads were swelled in 50 mL acetonitrile. After 1.5 hours, a solution of 60 mL diethylamine and 90 mL acetonitrile was added to beads and the reaction was carried out at 25 degrees for 17 hours. After the removal of the mixture, the beads were stirred in 50 mL methanol for 2 hours before washing with 50 mL water (2 times).

5.1.2.5 Synthesis of phosphonate ester resin[2]

Eight grams of VBC copolymer was placed in a flask to which 100 mL triethyl phosphite was added. After a contact time of 1 hour, the reaction mixture was heated to reflux for 17 hours. The beads were washed with 100 mL acetone (3 times).

5.1.2.6 Synthesis of 2-(2-aminoethoxy)ethanol resin

Four grams of VBC beads were swollen in 50 mL N-methyl pyrrolidone (NMP) for 1½ h. Fifty milliliters AEE and 50 mL NMP were mixed and then added to the flask containing the swollen beads. The temperature was slowly increased to 80 °C over 2h while stirring for 17 h. The reaction contents were filtered and the beads washed with 100 mL NMP and 100 mL water.

5.1.2.7 Synthesis of 2-(2-aminoethoxy)ethyl phosphate resin

In a flask containing 2.4 g (aminoethoxy)ethanol resin that was vacuum oven dried at 70 °C for 6 h, 50 mL NMP was added. The beads were swelled for 1 h, after which 5.5 mL DECP was introduced with stirring (or an amount equivalent to 5 times the mmol of N on resin). The beads were stirred at room temperature for 17 hours. The solution was removed and the beads were washed with 100 mL methanol and 100 mL water.

5.1.2.8 Synthesis of benzoylphosphonate diester

Five grams of acid chloride resin was swelled in 50 mL triethyl phosphite for 1 hour in a three neck round bottomed flask. The beads were refluxed for 17 hours under a nitrogen sweep. Upon removal of solvent with a gas dispersion tube, 50 mL methanol was added and the beads stirred for another 2 hours at room temperature. The beads were washed with 50 mL acetone (2 times) and then 50 mL water.

5.1.2.9 Synthesis of amidoethoxyethanol resins

Five grams of acid chloride resin were swelled in 100 mL acetonitrile for 1h. To the beads, a solution of 20 mL aminoethoxyethanol in 50 mL acetonitrile was added and the beads were heated to 60 degrees for 10 hours. After the reaction had finished, the solution was removed and 50 mL methanol was added. The beads were stirred for a further two hours at room temperature before washing with water.

5.1.2.10 Synthesis of other amidoalcohol resins

The synthesis of other amidoalcohol resins followed the same procedure as above. The solvent used was dioxane (there was no difference in appearance of reaction with dioxane compared to acetonitrile in the presence of aminoalcohols).

5.1.2.11 Synthesis of phosphorylated amidoalcohol resins

This resin was synthesized with 2.5 g of amidoalcohol resin swelled in 50 mL pyridine for 1 hour. Ten milliliters of DECP were added and the beads stirred at room temperature for 17 hours. The beads were washed with 50 mL methanol and 50 mL water.

5.1.2.12 Synthesis of methyl ester resins

These resins were synthesized by adding fifty milliliters of methanol to 2 g of acid chloride resin and stirring at room temperature for 2 hours. The reacting solvent was removed and the beads were washed with 50 mL water (twice).

5.1.2.13 Synthesis of glycol esters

Two grams of acid chloride resin was placed in a 3 neck flask. The beads were swelled in 50 mL dioxane for 1 hour. To the swollen beads, 15 mL ethylene glycol was added and the beads were refluxed for 17 hours. Upon removal of the reactants, the beads were washed with 50 mL methanol and 50 mL water.

5.1.3 Resin treatment & characterization procedures

5.1.3.1 Buchner dried resins

Resins were stored in water after conditioning and were vacuum filtered to remove excess moisture, before using for characterization e. g. acid capacity determinations and also metal ion contact studies. Wet resin was placed in a Buchner funnel and covered with a piece of latex, held in place with a rubber band. A vacuum of 710 mm Hg was applied for 5 minutes.

5.1.3.2 Percent solids determination

A 20 mL glass vial was heated in a 110°C oven for about 2 h. After cooling, the vial was accurately weighed. About 0.5 g of Buchner dried sample was weighed (to four decimal places) into the vial. The sample was dried for 17 h in the 110 °C oven and after cooling to room temperature in a dessicator, the sample was weighed. The solids % was then calculated using the formula,

$$\text{Percent solids} = (g_{\text{dry}}/g_{\text{buchner dry}}) \times 100$$

5.1.3.3 Acid capacity determination

About 0.5 g of Buchner dried resin (that was conditioned with 1L each of 4 wt. % NaOH – water – 4 wt. % HCl – water) was accurately weighed into a 250 mL Erlenmeyer flask. 50 mL of a standardized 0.1 N NaOH with 5 wt.% NaCl was added and the flask was covered with parafilm. The flask was shaken at a speed of 200 rpm for 17 h on a DS 500 Orbital Shaker. Ten milliliter aliquots were carefully pipetted out (care was taken not to remove any beads with the solution) and titrated with standardized 0.1 N HCl solution. The indicator used was phenolphthalein. A control titration using 10 mL of solution without bead contact was carried out. The acid capacity was calculated by the following equation.

$$\text{ACID CAPACITY} = \{(\text{vol. of HCl}_{\text{control}} - \text{vol. of HCl}_{\text{sample}}) \times 5 \times (\text{N HCl})\} / (\text{dry wt. of resin})$$

5.1.3.4 Nitrogen capacity determination [3,4]

About 0.2 g of dry resin was accurately weighed into a 500 mL 3-neck round-bottom flask. To this 0.25 g $CuSO_4$, 10 g K_2SO_4 and 25 mL 98% H_2SO_4 was added and some boiling chips. A long condenser (not attached to water supply) was connected to one of the openings and the other two openings were stoppered. The mixture was gently heated at first for about 1 h and then vigorously heated until the beads disappeared and the solution looked light blue in color (usually 6 h).

The condenser was then rinsed with minimal amounts of distilled water, and a magnetic stir bar added to the flask. About 100 mL of distilled water was added and the solution stirred. The condenser was replaced by a distillation apparatus and an addition funnel was placed on one end. The open end of the condenser was connected to a funnel, with the wide end of funnel immersed in 50 mL of a standardized 0.1 N HCl solution in a 600 mL beaker. The addition funnel was filled with 150 mL 6N NaOH. The NaOH solution was slowly added to the round-bottom flask, while the solution was being stirred. The solution should look dark-brown in color. The solution was heated so that the liquid can be distilled into the beaker containing standardized HCl. After about 35-45 minutes, the pH of the distillate was checked for neutrality using universal indicator litmus paper.

Once the solution was neutral, the solution was quantitatively transferred to a 250 mL volumetric flask and diluted to the mark with distilled water. Twenty five milliliter aliquots of solution was removed and titrated with bromocresol green indicator. The nitrogen capacity was calculated.

N CAPACITY = $\{(\text{vol. of NaOH}_{\text{control}} - (\text{vol. of NaOH}_{\text{sample}} \times 2)) \times 5 \times (\text{ N NaOH})\}/g_{\text{resin}}$

5.1.3.5 Phosphorus elemental analysis

All glassware was cleaned in an acid bath (solution containing Nochromix and concentrated sulfuric acid). Twenty milligrams of oven-dried resin was accurately weighed into a 125 mL Erlenmeyer flask. To this, 2 mL of 0.02 M $CuSO_4$ was added followed by 10 mL 98 % H_2SO_4. The mixture was heated for 2 h on a hot plate set at a medium-high setting. After cooling, 75 mL distilled water and 2.0 g of potassium persulfate were added and the mixture heated for another 2 h on a medium-low setting. A solution of 50 wt. % sodium hydroxide was added dropwise until the solution just turned brown. A 2 wt. % sulfuric acid solution was added until the pH became neutral. This solution is quantitatively transferred to a 100 mL volumetric flask. A 25 mL aliquot was transferred to a 50 mL volumetric flask followed by 10 mL of the indicating solution (vanadate-molybdate solution)*. A blank solution was prepared containing the 10 mL of the vanadate-molybdate solution. The solutions were diluted to the mark and allowed to develop for 15 min. A Spectronic 20D+ spectrophotometer (Thermo Electron Corporation), set at 470 nm was zeroed with the blank before determining the absorbance of the sample solution. Standard solutions of potassium dihydrogen phosphate were prepared and used to determine the slope and y-intercept of absorbance vs. concentration curve. The phosphorus capacity was determined from the following equations.

$$\text{mgL}^{-1}\ \text{P} = (\text{absorbance} - \text{intercept}) / \text{slope}$$

$$(\text{mgL}^{-1}\ \text{P} \times 50) / 1000 = \text{mg P}$$

$$\text{P cap.} = (\text{mg P} \times 4) / (30.974\text{mg/mmol} \times \text{g}_{\text{resin}})$$

*Preparation of vanadate-molybdate indicating solution

This solution is prepared by dissolving 25 g of ammonium heptamolybdate tetrahydrate in 300 mL water in a beaker. In another beaker, 1.28 g of ammonium metavanadate is dissolved in 300 mL water with heating, followed by 330 mL 12 N HCl. Both solutions were added to a 1 L volumetric flask and diluted to the mark with distilled water.

5.1.3.6 Chlorine elemental analysis

A Parr bomb calorimeter was used to burn the sample. The cylinder was rinsed with nanopure water and 5 mL of a 5 wt% Na_2CO_3 was added. About 0.1 g of oven-dried resin was accurately weighed into the metal capsule followed by 0.7 g mineral oil (the total weight should not exceed 1.0 g). The capsule was placed in the holder and a 10 cm long nickel alloy fuse wire was threaded through the bomb stem holes and positioned so that the wire sits above the oil, without touching the oil or sides of the capsule. The cylinder was capped and purged with oxygen gas (at least 2 times – about 30 atm of oxygen was added and released each time). On the third addition of oxygen, the gas was not released and the calorimeter was submerged in a water bath and connected to the bomb ignition unit. The bomb was ignited, and kept in the water bath for about 5 mins. The oxygen gas was released and upon opening the cap, the contents of the calorimeter were carefully washed into a 500 mL beaker and then transferred to a 250 mL volumetric flask.

Two 25 mL aliquots were removed and placed separately in two 125 mL Erlenmeyer flasks. To these solutions, 3 mL of 2 N HNO_3 were added followed by 10 mL of 0.05 N $AgNO_3$ solution. The solution was heated until boiling and then allowed to cool in a dark place. The boiled samples were filtered and then titrated with 0.05 N NH_4SCN using 3 mL of $FeNH_4(SO_4)_2$ as the indicating solution. A faint orange color denotes the end-point of the titration. A blank solution containing 10 mL $AgNO_3$ and indicating solution was titrated.

Chlorine capacity calculation:

$$\text{Cl CAPACITY} = \{(\text{vol. of } NH_4SCN_{\text{control}} - \text{vol. of } NH_4SCN_{\text{sample}}) \times 10 \times (\text{N } NH_4SCN)\}/g_{\text{resin}}$$

5.1.3.7 Infrared spectroscopy

FTIR spectra (4000-500 cm^{-1}) of resins using the KBr pellet method were taken on a Bomem FTIR spectrophotometer (Hartmann and Braun). About 10 mg of resin was ground with 100 mg KBr and compressed using a press until a clear disc forms.[5]

5.1.4 Contact study procedures for metal ions

5.1.4.1 Metal ion solution preparation

Each metal ion solution was prepared in concentrations of 10^{-2} N using nanopure water and reagent grade metal nitrates and acids in a 100 mL volumetric flask. Contact solutions were prepared by subsequent dilutions of the stock metal ion solution in volumetric flasks. All solutions had a concentration of 10^{-4} N.

5.1.4.2 Metal ion contact study experiments

A mass of resin corresponding to 0.28 - 0.34 mmol functional group was weighed out into a 20 mL PTFE scintillation vial. The resin was solvent exchanged three times with 5 mL of the background solution. This was done by placing the resin with solution on an orbital shaker for 15 mins, removing the solution from the beads with a Pasteur pipet ensuring that beads were not lost in the process. After the removal of the last exchange solution, the contact solution (5 mL) was added and the beads placed on the shaker (VWR DS500 Orbital Shaker) for 17 h. The contact solution was removed with a Pasteur pipet and placed in a clean polyethylene terephthalate scintillation vial for analysis. The results of the contact study were expressed as percent metal ion (% M^{n+}) complexed and distribution coefficient values (D), defined below:

$$\% \, M^{n+} \text{ complexed} = \{([M^{n+}{}_{(aq)}]_{\text{initial}} - [M^{n+}{}_{(aq)}]_{\text{equilibrium}}) / [M^{n+}{}_{(aq)}]_{\text{initial}}\} \times 100$$

$$D = (\text{mmol } M^{n+}]_{\text{resin}}/g_{\text{resin}})/(\text{mmol } M^{n+}]_{\text{soln}}/\text{mL}_{\text{soln}})$$

5.1.4.3 Metal ion determination by Inductively coupled plasma – atomic emission spectroscopy (ICP-AES)

The contact solutions were analyzed by ICP-AES (Spectra Analytical Instruments, Spectroflame M120E). Each analyte was determined at a specific wavelength listed in Table 5-1.

Table 5-1 Selected wavelengths for metal ions analyzed.

Metal ion	**Wavelength (nm)**
Pb(II)	220.353
Cd(II)	228.802
Cu(II)	224.700
Ni(II)	221.647
Zn(II)	213.856
Al(III)	167.083
Fe(III)	259.940
Eu(III)	381.970

5.2 Polymer preparation & MTBE contact study procedures

5.2.1 *Materials*

MTBE used was 99% pure (Fisher Scientific). Water for dilutions was obtained from a Barnstead Nanopure unit, Barnstead USA. Stock solutions were prepared in glass flasks and stored in a refrigerator kept at 4 °C.

5.2.2 *Synthesis of polymers and modification procedures*

5.2.2.1 Copolymer synthesis – Preparation of 25% VBC / 75% Sty - 12 % DVB MR copolymer

These beads were synthesized in a manner similar to gel resins but in the presence of 4-methyl-2-pentanol (4M2P). The amounts indicated in the following procedure were for a typical preparation of 150 g of VBC/styrene MR beads with a 12 % crosslink level. The organic phase consisted of dissolving 1.50 g BPO in 37.34 g VBC, 79.13 g styrene and 34.44 g DVB with stirring. 150.49 g 4M2P was added to this mixture. The organic phase was sparged for 5 min with nitrogen. The aqueous phase contained 60.6 g calcium chloride dihydrate and 3.6 g poly(vinylalcohol) (PVA, tradename Gohsenol) in 476 mL water. The aqueous phase was heated to completely dissolve the PVA. Once dissolved, it was poured into a 500 mL 3-neck flask and sparged with nitrogen for 10 mins. The flask was equipped with an overhead stirrer, thermometer and a temperature controller, and a nitrogen gas inlet area.

The stir paddle was adjusted so that the top of the paddle was just above the aqueous phase in the flask. The organic phase was added and the nitrogen sweep turned on. The stir motor was turned on for 2 mins. The bead size was checked and the stir speed adjusted. This was repeated twice. The temperature was then increased at a rate of 7° C / 15 min to 80° C over 2 h. The beads were stirred at 80 °C for 10 h.

At the end of polymerization, 100 mL of water was added to the beads. A Dean Stark trap was fitted and the condenser reattached. The mixture was heated for 6 h and the 4M2P distilled off. The remaining solution was removed with a gas dispersion tube. The beads were then purified by extraction with toluene in a soxhlet extraction apparatus for 17 h. The beads were placed in a drying dish under the fumehood and sieved using U.S. standard screens.

5.2.2.2 Preparation of VBC - 12 % DVB MR copolymer

These beads were prepared as above with the following changes to the amounts of the components of the aqueous phase and organic phase -

Aqueous phase – 2.69 g PVA, 60.5 g $CaCl_2 \cdot 2H_2O$, 475.27 g H_2O

Organic phase – 1.57 g BPO, 115.95 g VBC, 32.65 g DVB, 149.76 g 4M2P

5.2.2.3 Preparation of poly(acetoxystyrene) - 12 % DVB

These beads were prepared as above with the following changes to the amounts of the components of the aqueous phase and organic phase -

Aqueous phase – 0.54 g PVA, 12 g $CaCl_2 \cdot 2H_2O$, 96 g H_2O

Organic phase – 0.32 g BPO, 24.7 g AcSty, 6.93 g DVB, 32 g 4M2P

Polymerization conditions changed: the mixture was stirred for 18 h at 75 °C.

5.2.2.4 Synthesis of poly(butylacrylate) resin

In this polymerization, the aqueous phase contained 0.84 g PVA, 19 g $CaCl_2 \cdot 2H_2O$, 150 g H_2O and the organic phase, 0.50 g BPO, 38.7 g butyl acrylate, 10.8 g

DVB, 50 g 4M2P for 50 g beads. Note that initially beads were seen forming but at the end of reaction the beads coalesced and a mortar and pestle was used to break up the polymer.

5.2.2.5 Immobilization of polyamine on VBC/Sty polymer

2 g of polymer was swelled in 30 mL dioxane. 8 mL triethylenetetramine was added and the beads refluxed for 17h. Beads were washed with 50 % dioxane, water, methanol and acetone.

5.2.2.6 Immobilization of dihexylamine on VBC/Sty polymer

2.5 g of polymer was swelled in 300 mL dioxane. 24.7 g of dihexylamine was added and the mixture refluxed for 17h.

5.2.2.7 Immobilization of TPGME on VBC polymer

In a 250 mL flask, 100mL dioxane, 6.85g TPGME and 1.39 g sodium hydride was stirred for 5 h under a nitrogen sweep. In another flask, 2.6 g of VBC polymer was swelled in 100 mL dioxane. The TPGME mixture was added to the flask containing the polymer and the mixture heated under reflux conditions with a nitrogen sweep.

5.2.2.8 Preparation of EXC resin with p-cresol

About 1 g of vacuum oven dried XAD-4 was stirred overnight in a mixture of 100 mL toluene and 20 mL p-cresol. The toluene and p-cresol was removed and the resin was washed with water (3 times). The resin was dried for 5 h in the air and then transferred to an oven and kept at 110 °C for 17 h.

5.2.3 Contact study procedures for MTBE

5.2.3.1 MTBE solution preparation and contact study procedures

Twenty milliliters of 150 ppm MTBE solution containing 250 mg of resin were shaken for 17 h with 20 mL of solution in a 20 mL screw capped vial using a Burrell Wrist Action shaker. The time of shaking was determined by equilibrium studies. At the end of this time, 1 microliter of solution was analyzed. Controls of Amberlite XAD-4 (Supelco) and activated carbon (Fisher Scientific) were used and a blank solution was prepared each time a batch of resins was tested.

5.2.3.2 GC-FID Analysis procedures

Operating conditions of GC/FID

A gas chromatograph equipped with a flame ionization detector (Agilent 6850) was used to analyze the performance of the resins. A capillary column (HP-1 methyl siloxane), 30 m long with an internal diameter of 320 μm was used. The temperature at the inlet was set at 200 °C. The GC was operated in split mode (50:1), with a column flow of 2 mL / min. The oven temperature was programmed as follows: kept at 30 °C for 5 min, then heat from 30°C to 90 °C at 10 °C / min. and hold for 3 min. at 90 °C, heat to 200 °C at 10 °C / min. and hold for 11.25 min.

The temperature of the detector was kept at 250 °C and operated with a hydrogen flow rate of 60 mL/min and an air flow rate of 450 mL/min. The carrier gas make-up flow was 28 mL/min.

1 microliter aliquots of aqueous MTBE solution was injected into the GC/FID system. MTBE was observed at a retention time of 2.24 min. Calibration curves were generated between 59.24 ppm and 236.8 ppm inclusive, i. e. 59.24 ppm, 118.4 ppm, 177.6 ppm, 236.8 ppm, from a stock solution of 5924 ppm. Linearity $\geq$ 0.99 was achieved. Calibration curves were generated prior to analyses of any set of samples and linearity measured before making any conclusions with respect to the sample involved. The results were expressed as percent MTBE (% MTBE) removed, given below:

$$\% \text{ MTBE removed} = \{([\text{MTBE}]_{\text{initial}} - [\text{MTBE}]_{\text{experimental}})/[\text{MTBE}]_{\text{initial}}\} \times 100$$

5.2.3.3 Method development - MTBE solution preparation and contact study procedures when a purge and trap is introduced in analytical method

25 mg of resin was contacted with 40 mL of 1.48 ppm solution in 40 mL vials. After a 17 h shake, 15 mL of solution was removed with a disposable syringe and an aliquot (10 mL) was accurately pipetted out and diluted by a factor of 2.5. Five milliliters of this solution was transferred with a 5 mL Luer lock syringe to the sparger of the purge and trap (Tekmar LSC 2000) for purging.

Purge and Trap parameters operating conditions

Sample volume = 5 mL

Purge flow = 20 mL/min

Purge time = 10 min

Purge temperature = 40 °C

Dry purge = 90 s

Desorb temperature = 125 °C

Desorb time = 90s

Bake time = 5 min

Bake temperature = 260 °C

The trap used was a Supelco Vocarb K 3000 (Carbopack B, Carboxen 1000, Carboxen 1001). A ten min bake time followed by 2 washes of the sparger with nanopure water (conductivity = 18.2 Scm^{-1}) was sufficient to prevent cross contamination.

GC / FID parameters with purge and trap

Analyses were made in the splitless mode with a column flow of 1mL / min through a column (HP-1, 15 m × 320 μm I.D. × 0.25 μm). Isothermal temperature was employed at 50 °C. The instrument was operated under the constant flow mode with helium gas as the carrier gas.

FID parameters were also adjusted,

Hydrogen = 40 mL / min

Air = 450 mL / min

Carrier gas = 45 mL / min

Temperature = 250 °C

See Appendix - Section V for a sample chromatogram.

5.2.3.4 Porosity determination.

A surface area analyzer (Micromeritics TriStar 3000) was used. The sample was vacuum oven dried at 70 °C for 6 h. before weighing out approximately 0.5 g of the dried material. It was then degassed at 50 °C for 2 h. under a nitrogen stream. After cooling under the stream of nitrogen, the sample was reweighed to determine the actual mass of sample used. The following mathematical models were applied for data reduction Brunner-Emmett-Teller (BET), Dubinin-Astakov and t-plots for surface area treatment, pore size distributions and pore volumes.[6]

5.3 References

1. Alexandratos, S. D.; Hussain, L. A. Synthesis of α-, β- and γ- ketophosphonate polymer-supported reagents: The role of intra-ligand cooperation in the complexation of metal ions. *Macromolecules* **1998**, *31*, 3235-3238.

2. Alexandratos, S. D.; Zhu, X. Bifunctional coordinating polymers: Auxillary groups as a means of tuning the ionic affinity of immobilized phosphate ligands. *Macromolecules* **2005**, *38*, 5981-5986.

3. Bradstreet, R. B. Kjeldahl method for organic nitrogen. *Anal. Chem*. **1954**, *26*, 185-187.

4. Kirk, P. L. Kjeldahl method for total nitrogen. *Anal. Chem.* **1950**, *22*, 354-358.

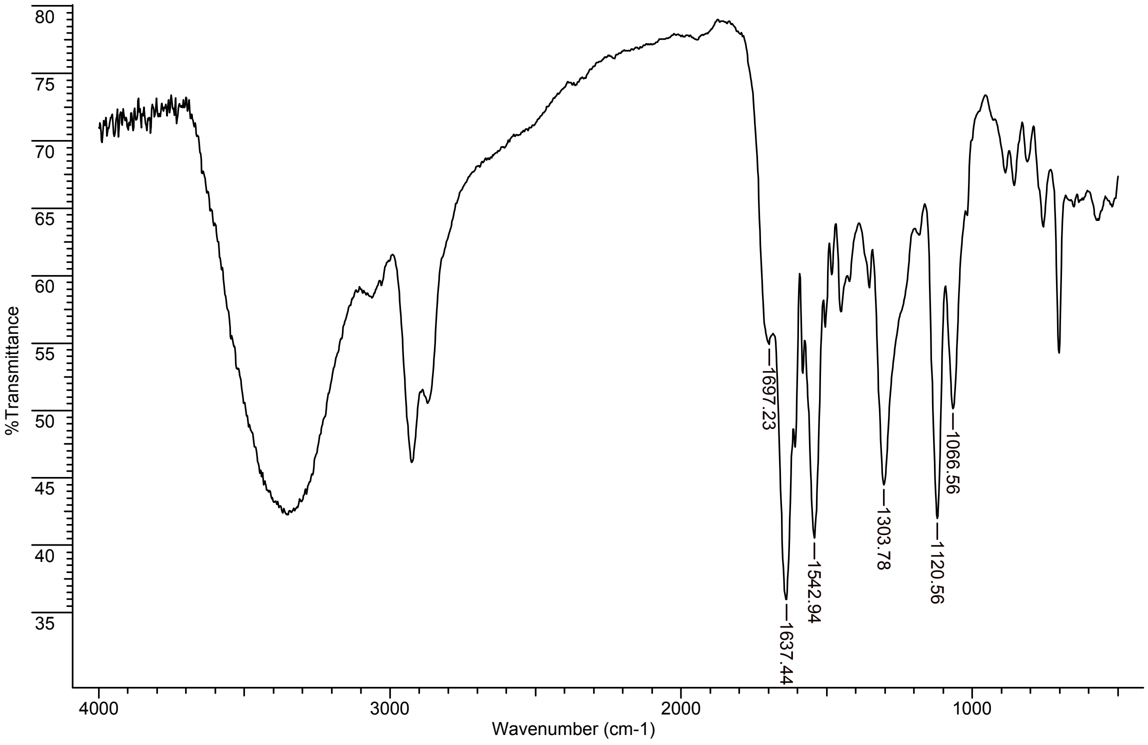
5. Alexandratos, S. D.; Zhu, X. Amination of poly(vinylbenzyl chloride) with N, N-dimethylformamide. *Macromolecules* **2003**, *36*, 3436-3439.

6. Webb, P. A.; Orr, C. Analytical methods in fine particle technology, 1st ed.; Micromeritics Instrument, **1997**; Chapter 3.

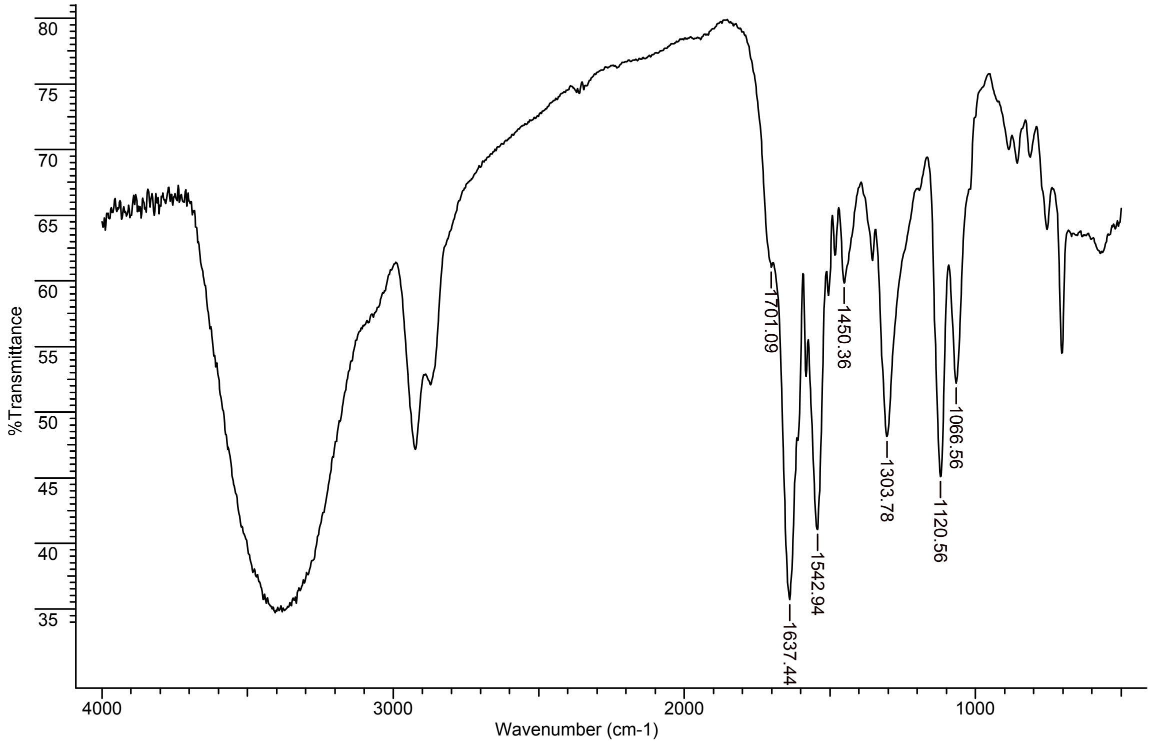
APPENDIX (SECTIONS I – V)

Section I – IR spectra of amidoalcohol prepared in different solvents

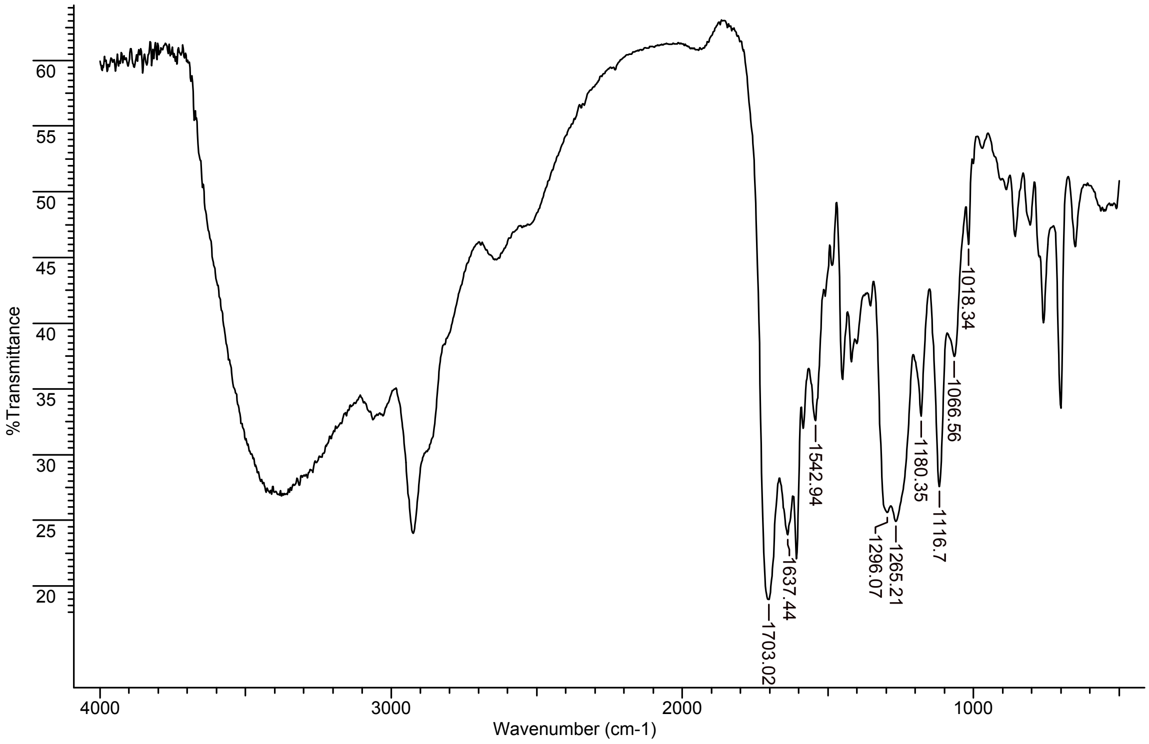
DIGLYME (4-108)



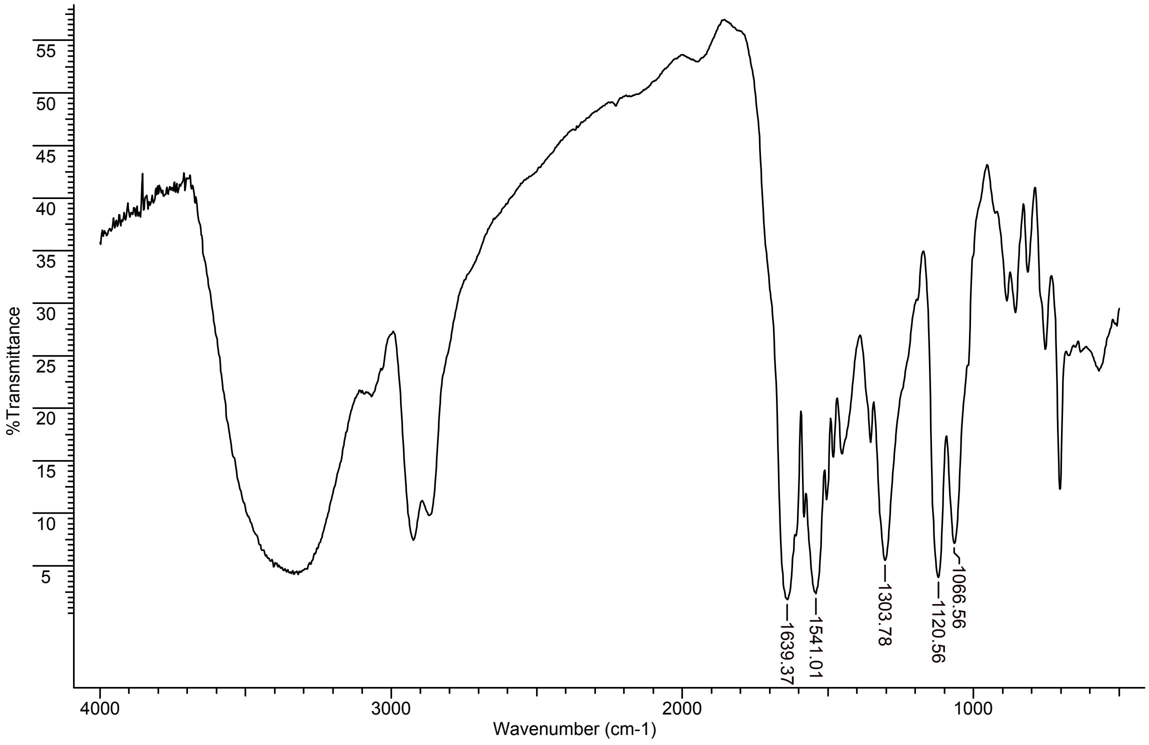
Acetonitrile



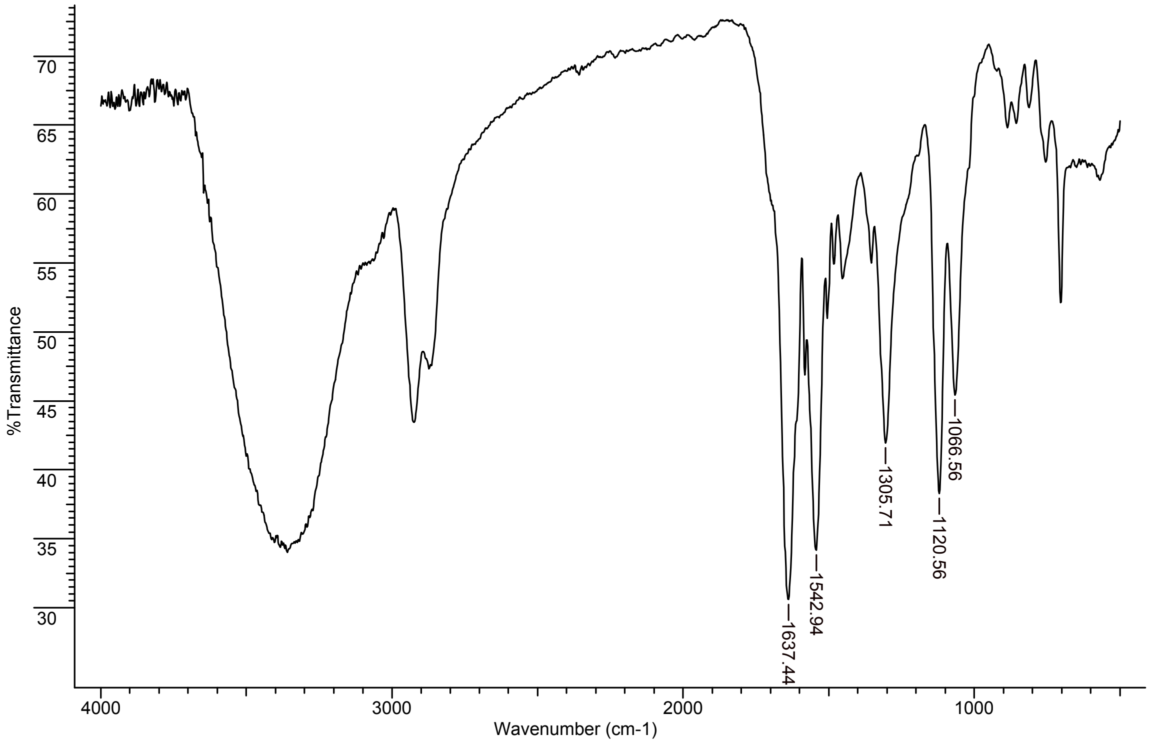
DMF(4-109)



THF(4-40)



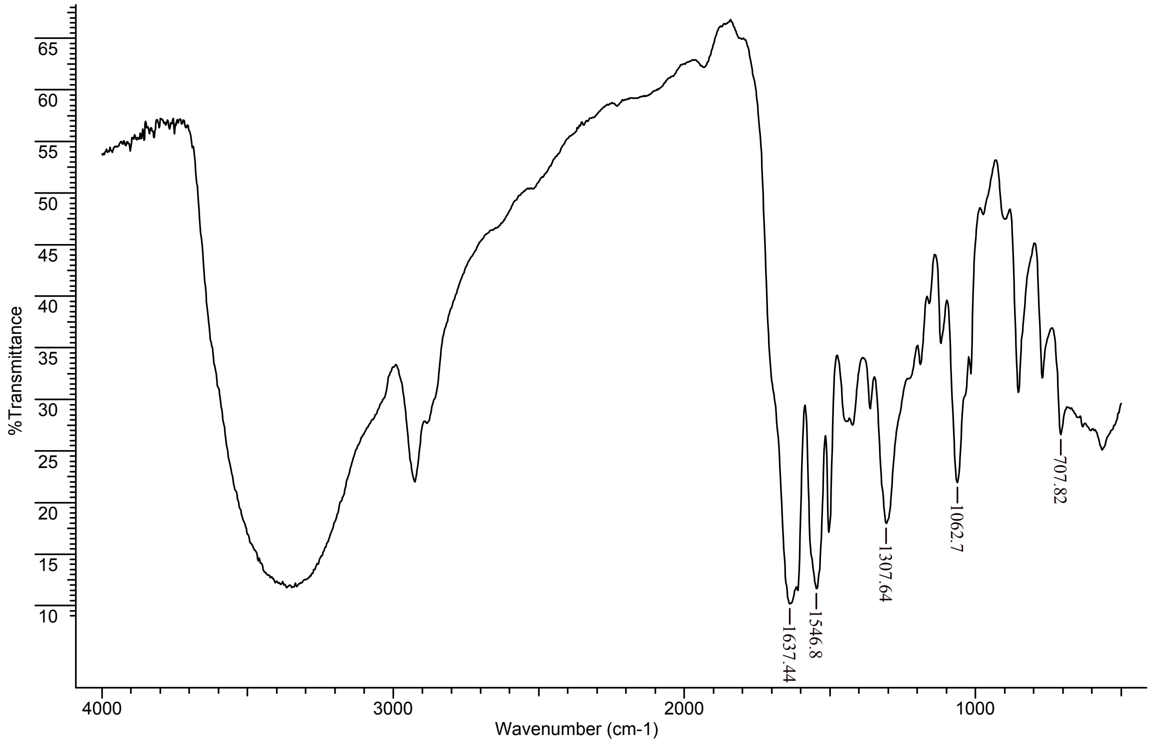
Dioxane (4-97)



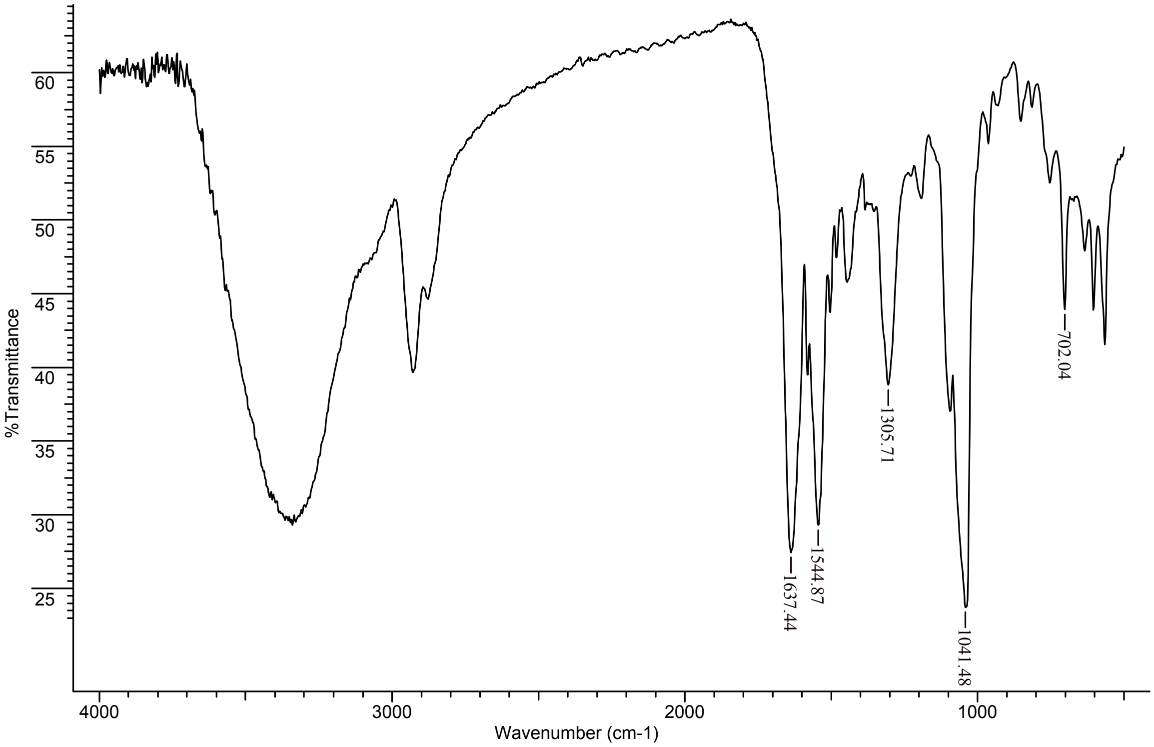
%Transmittance
70
65
60
55
50
45
40
35
30
4000
3000
2000
1000
Wavenumber (cm-1)
1637.44
1542.94
1305.71
1120.56
1066.56

Section II – IR spectra of Amidoalcohol resins

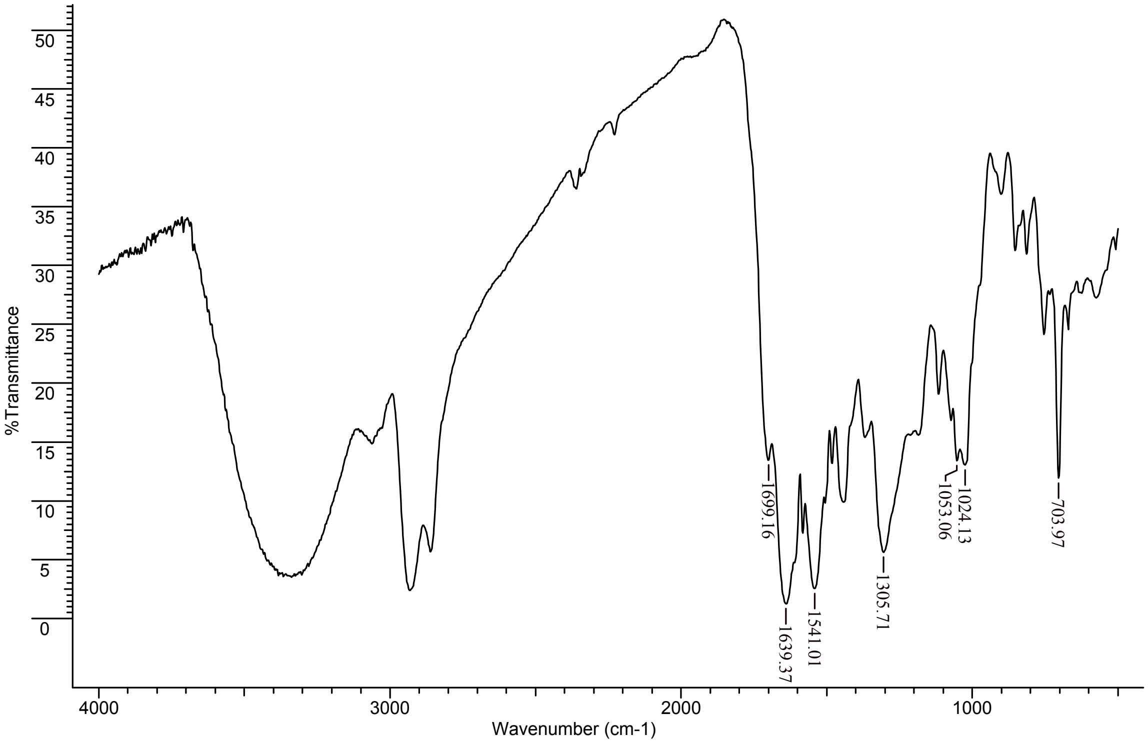
Amidoethanol resin



Amidopropanol resin

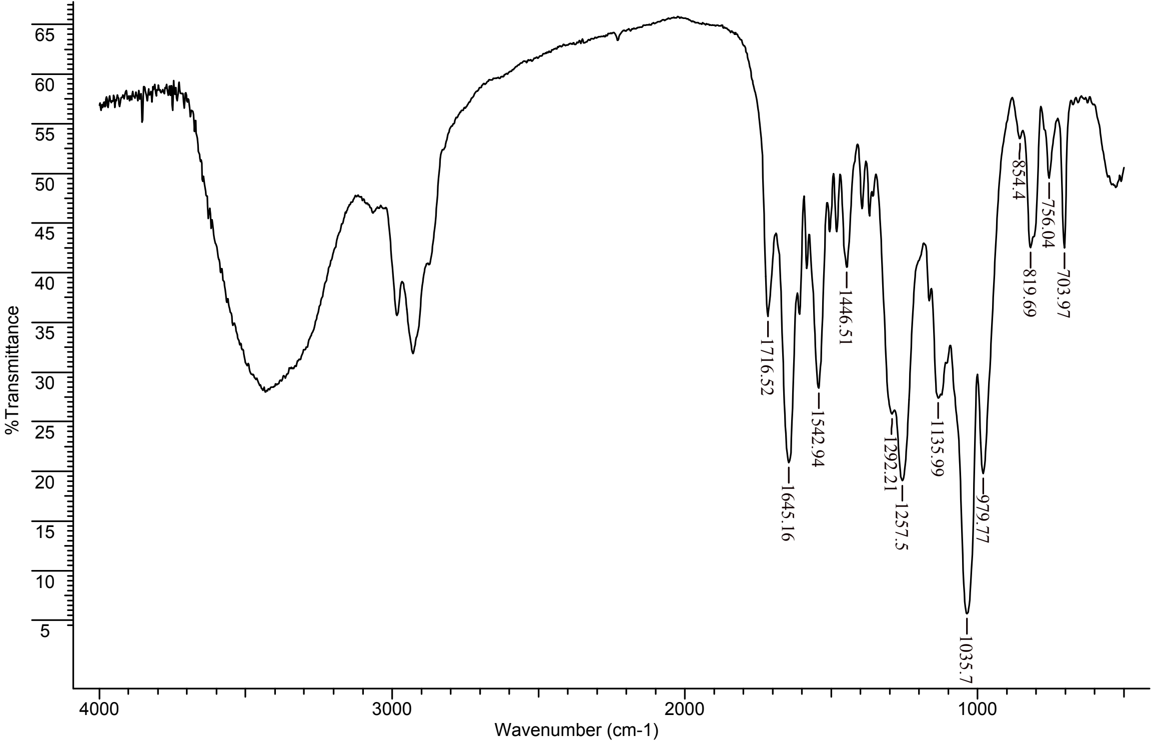


Amidopentanol resin

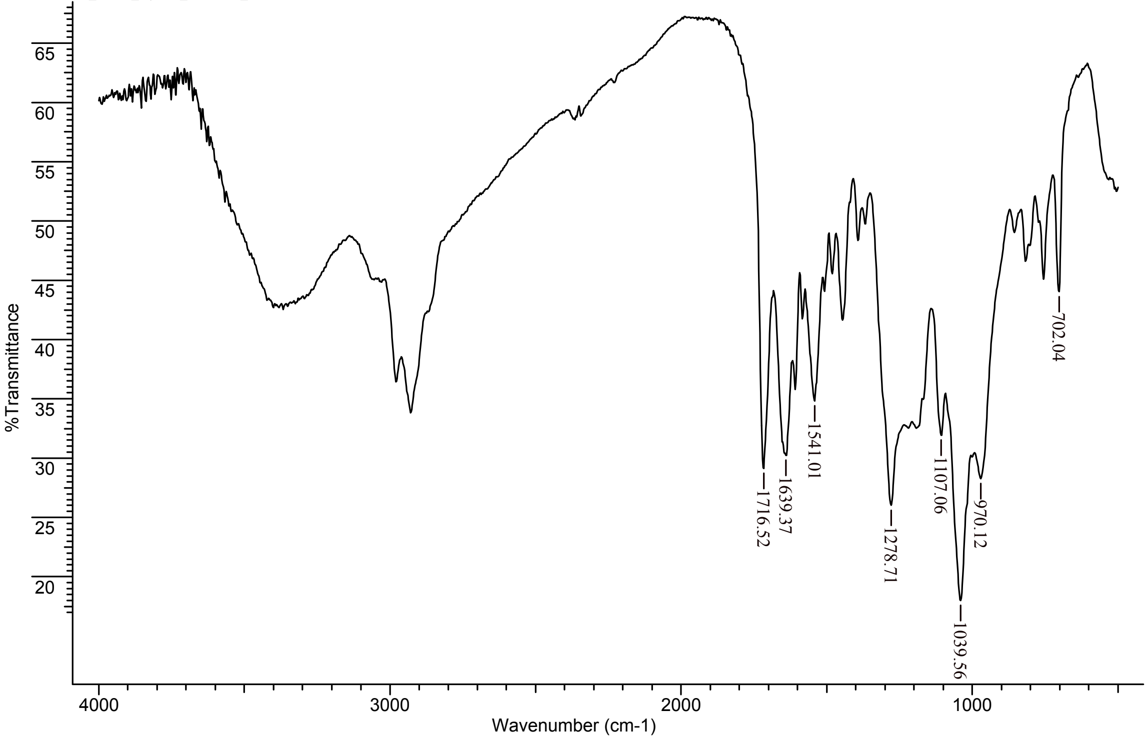


Section III – Phosphorylated amidoalcohol resins

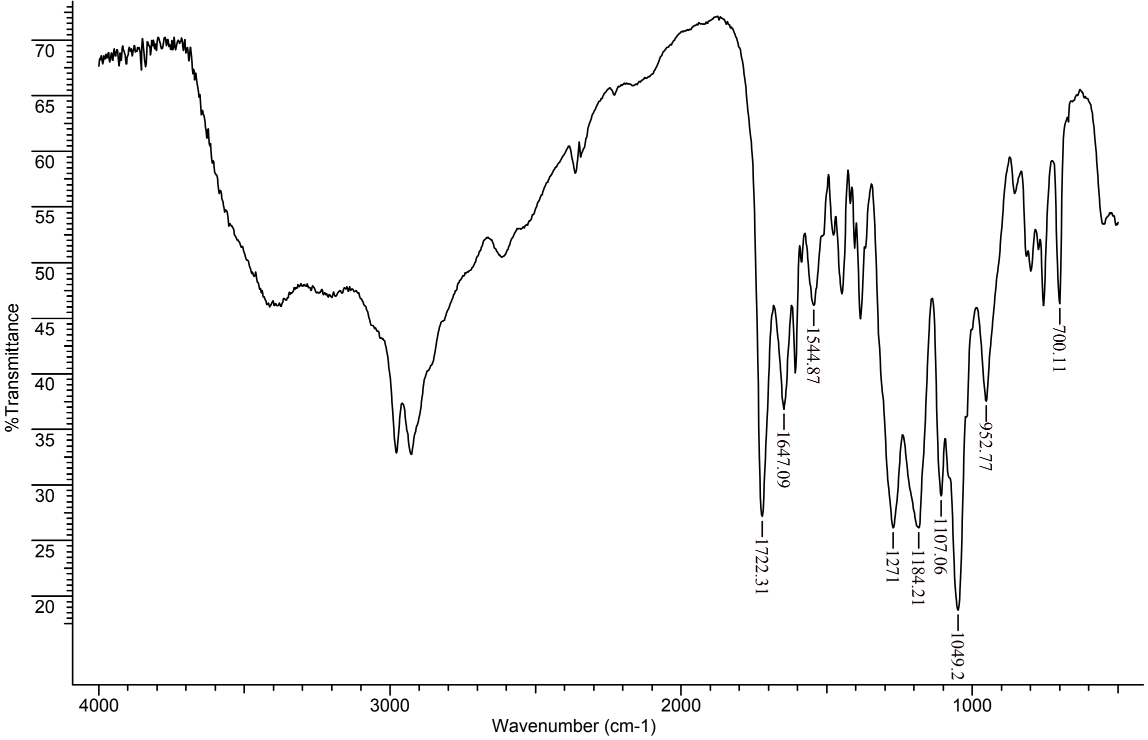
2-(2-amidoethoxy)ethyl phosphate ester resin



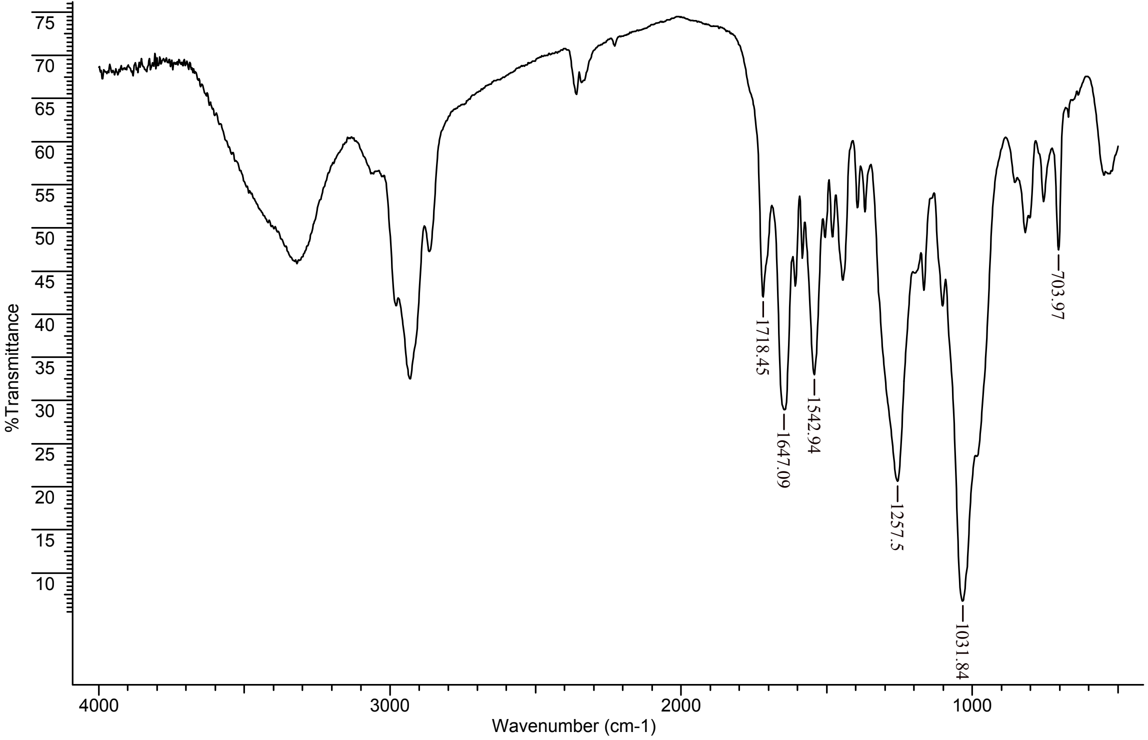
Amidopropyl phosphate



2-amido-2-methylpropyl phosphate ester resin

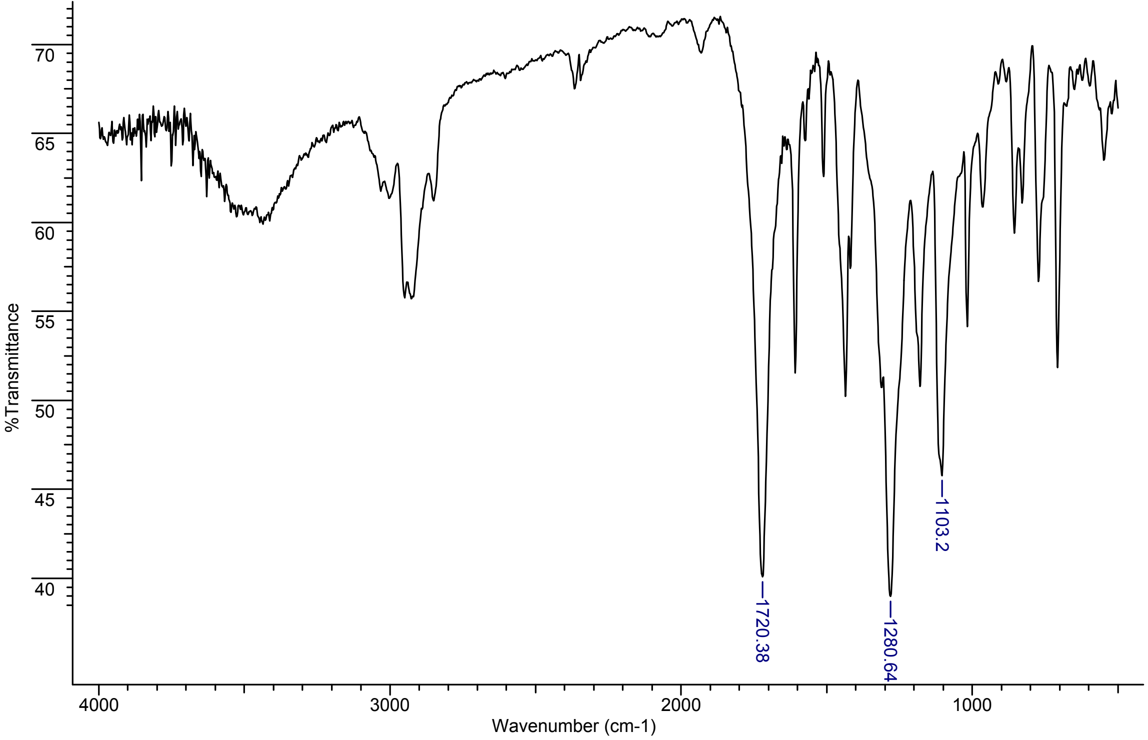


Amidopentyl phosphate ester resin

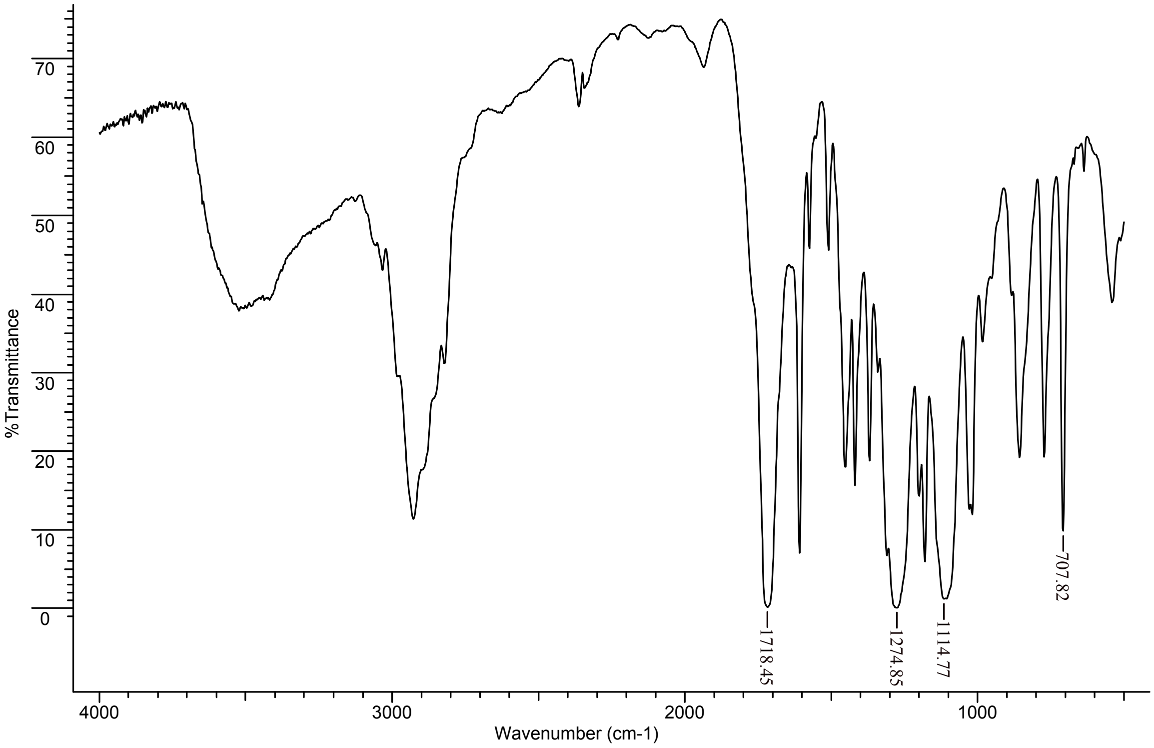


Section IV – IR spectra of other resins

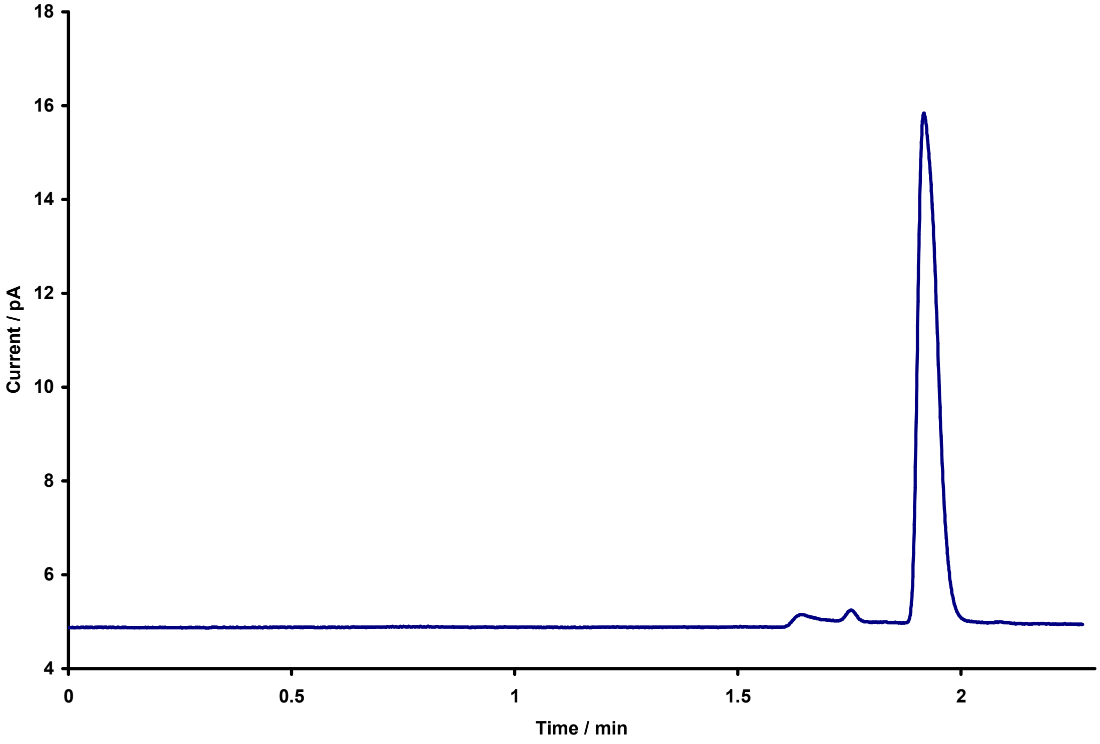
Methyl ester resin



Methoxyethyl ester



Section V - Chromatogram of MTBE sample (74 ppb) analyzed with a GC/FID with prior sample treatment using a purge and trap



BIBLIOGRAPHY

Chapter 1

1. Hudson, M. J. Some new strategies for the chemical separation of actinides and lanthanides. *Czech J. Phys.* **2003**, *53* (Suppl. A, Pt. 1), A305-A311.

2. Kaliyappan, T.; Kannan, P. Co-ordination polymers**.** *Prog. Polym. Sci.* **2000**, *25*, 343-370.

3. Pennington, L. D.; Williams, M. B. Chelating ion-exchange resins**.** *Ind. Eng. Chem*. **1959**, *51*, 759-762.

4. Sahni, S. K.; Reedijk, J. Coordination chemistry of chelating resins and ion exchangers. *Coord. Chem. Rev*. **1984**, *59*, 1-139.

5. Yuchi, A.; Sato, T.; Morimoto, Y.; Mizuno, H.; Wada, H. Adsorption mechanism of trivalent metal ions on chelating resins containing iminodiacetic acid groups with reference to selectivity. *Anal. Chem.* **1997**, *69*, 2941-2944.

6. Pesavento, M.; Biesuz, R.; Riva, F. D.; Alberti, G. Investigation of the complexation properties of a natural water towards copper(II), manganese(II) and aluminum(III), based on sorption of metal ions on a complexing resin. *Polyhedron* **2002**, *21*, 1343-1350.

7. Rahman, M. Z. Ab; Rahman, L.; Silong, S.; Yunus, W. M. Z. W.; Ahmad, M.; Haron, M. J. Poly(amidoxime) chelating resin used for separation of metal ions in aqueous media. *Orient. J. Chem.* **2001**, *17*, 205-208.

8. Zhu, X.; Alexandratos, S. D. Affinity and Selectivity of Immobilized N-Methyl-D-glucamine for mercury(II) ions. *Ind. Eng. Chem. Res*. **2005**, *44*, 7490-7495.

9. Dambies, L. Salinaro, R.; Alexandratos, S. D.; Immobilized N-methyl-D-glucamine as an arsenate-selective resin. *Environ. Sci.Technol*. **2004**, *38*, 6139-6146.

10. Denizli, A.; Garipcan, B.; Karabakan, A.; Say, R.; Emir, S.; Patir, S. Metal-complexing ligand methacryloylamidocysteine containing polymer beads for Cd(II) removal. *Sep. Purif. Technol*. **2003**, *30*, 3-10.

11. Hay, B. P.; Zhang, D.; Rustad, J. R. Structural criteria for the rational design of selective ligands. 2. Effect of Alkyl substitution on metal ion complex stability with ligands bearing ethylene-bridged ether donors. *Inorg. Chem.* **1996**, *35*, 2650-2658.

12. George, B.; Mathew, B.; Effect of the degree of crosslinking on the metal ion specificity of polyacrylamide-supported glycines. *J. Macromol. Sci., Pure Appl. Chem.* **2001**, A*38*, 429-449.

13. Czerwinski, K. R.; Draye, M. Favre-Reguillon, A.; Foos, J.; Guy, A.; Lemaire, M. Ion selective resins: development and applications for nuclear waste management. *Materials Research Society Symposium Proceedings*, **1999**, *556*, 1277-1284.

14. Bilba, D.; Bejan, D.; Tofan L. Chelating sorbents in inorganic chemical analysis, *Croat. Chem. Acta* **1998**, *71*, 155-178.

15. Irving, H. M.; Williams, R. J. P. The stability of transition-metal complexes. *J. Chem. Soc*. **1953**, *637*, 3192-3210.

16. Williams, S. M.; Brodbelt, J. S.; Marchand, A. P.; Cal, D.; Mlinaric-Majerski, K. Metal complexation of thiacrown ether macrocycles by electrospray ionization mass spectrometry. *Anal. Chem*. **2002**, *74*, 4423-4433.

17. Blakemore, J. D.; Chitta, R.; D'Souza, F. Synthesis and study of crown ether-appended boron dipyrrin chemosensors for cation detection. *Tetrahedron Lett*. **2007**, *48*, 1977-1982.

18. Hancock, R. D.; Maumela, H.; de Sousa, A. S. Macrocyclic ligands with pendent amide and alcoholic oxygen donor groups. *Coord. Chem. Rev*. **1996**, *148*, 315-347.

19. Zhang, X. X.; Izatt, R. M.; Bradshaw, J. S.; Krakowiak, K. E. Approaches to improvement of metal ion selectivity by cryptands. *Coord. Chem. Rev*. **1998**, *174*, 179-189.

20. Hancock, D. Chelate ring size and metal ion selection: the basis of selectivity for metal ions in open-chain ligands and macrocycles. *J. Chem. Educ*. **1992**, *69*, 615-621.

21. Voss, D. A. Jr.; Farquhar, E. R.; Horrocks, W. D. Jr.; Morrow, J. R. Lanthanide(III) complexes of amide derivatives of DOTA exhibit an unusual variation in stability across the lanthanide series. *Inorg. Chim. Acta* **2004**, *357*, 859-863.

22. Ohto, K.; Fujimoto, Y.; Inoue, K. Stepwise extraction of two lead ions with a single molecule of calix[4]arene tetracarboxylic acid. *Anal. Chim. Acta* **1999**, *387*, 61-69.

23. Ohto, K.; Tanaka, Y.; Yano, M.; Shinohara, T.; Murakami, E.; Inoue, K. Selective adsorption of lead ion on calix[4]arene carboxylate resin supported by polyallylamine. *Solvent Extr. Ion Exch*. **2001**, *19*, 725-741.

24. Chen, H.; Olmstead, M. M.; Albright, R. L.; Devenyi, J.; Fish, R. H. Metal-ion-templated polymers: synthesis and structure of N-(4-vinylbenzyl)-1,4,7-triazacyclononanezinc(II) complexes, their copolymerization with divinylbenzene, and metal-ion selectivity studies of the demetalated resins-

evidence for a sandwich complex in the polymer matrix. *Angew. Chem. Int. Ed.* **1997**, *36*, 642-645.

25. Lo, H. C.; Chen, H. Fish, R. H. Metal-ion-templated polymers, 3. Synthesis of a [{mono-N-(4-vinylbenzyl)-1,4,7-triazacyclononane}2Hg](OTf)$_2$ sandwich complex, polymerization of this monomer with divinylbenzene, and Hg^{2+} ion selectivity studies with the demetallated resin. *Eur. J. Inorg. Chem.* **2001**, *9*, 2217-2220.

26. Kimaro, A.; Kelly, L. A.; Murray, G. M. Synthesis and characterization of molecularly imprinted uranyl ion exchange resins. *Sep. Sci Technol.* **2005**, *40*, 2035-2052.

27. Van de Water, L. G. A.; Driessen, W. L.; Reedijk, J.; Sherrington, D. C. Metal-ion extraction by immobilized aza crown ethers. *Eur. J. Inorg. Chem.* **2002**, 221-229.

28. Ahrland, S.; Chatt, J.; Davis, N. R. The relative affinities of ligand atoms for acceptor molecules and ions. *Quart. Rev.* **1958**, *12*, 265-276.

.

29. Pearson, R. G. Hard and soft acids and bases *J. Am. Chem. Soc.* **1963**, *85*, 3533-3539.

30. Klopman, G. Chemical reactivity and the concept of charge- and frontier-controlled reactions. *J. Am. Chem. Soc.* **1968**, *90*, 223-234.

31. Parr, R. G.; Pearson, R. G. Absolute hardness: Companion parameter to absolute electronegativity. *J. Am. Chem. Soc.* **1983**, *105*, 7512-7516.

32. Van de Water, L. G. A.; Driessen, W. L.; Glenny, M. W.; Reedijk, J.; Schroder, M. Selective and reversible extraction of heavy metal-ions by mixed-donor crown ether-modified oxirane and thiirane resins. *React. Funct. Polym.* **2002**, *51*, 33-47.

33. Van de Water, L. G. A.; Ten Hoote, F.; Driessen, W. L.; Reedijk, J.; Sherrington, D. C. Selective extraction of metal ions by azathiacrown ether-modified polar polymers. *Inorg. Chim. Acta* **2000**, *303*, 77-85.

34. Adam, K. R.; Baldwin, D. S.; Duckworth, P. A.; Lindoy, L. F.; McPartlin, M.; Bashall, A.; Powell, H. R.; Tasker, P. A. Macrocyclic ligand design. Effect of donor-set and ring-size variation on silver(I) / lead(II) discrimination within an extended series of dibenzo substituted rings. *J. Chem. Soc. Dalton Trans*. **1995**, *7*, 1127-1131.

35. Bakir, J. A. Jeragh, Abdel-Zaher A. Elassar, Ali El-Dissouky. Ligating behavior and metal uptake of N-sulphonylpolyamine chelating resins anchored on polystyrene-divinylbenzene beads. *J. Appl. Polym. Sci.* **2005,** *96*, 1839-1846.

36. Sun, C.; Qu, R.; Ji C.; Wang, Q.; Wang, C.; Sun, Y. Cheng, G. A chelating resin containing S, N and O atoms: synthesis and adsorption properties for Hg(II). *Eur. Polym. J.* **2006**, *42*, 188-194.

37. Anpilogova, G. R.; Vorob'eva, A. I.; Onina, S. A.; Khisamutdinov, R. A.; Murinov, Y. I.; Monakov, Y. B. Vinyl 2-hydroxyethyl sulfide polymers and their sorption properties with respect to transition metals. *Russ. J. Appl. Chem.* **2006**, *79*, 1593-1599.

38. Yanagida, S.; Takahashi, K.; Okahara, M. Metal-ion complexation of noncyclic poly(oxyethylene) derivatives. III. Complexation in aprotic solvent and isolation of their solid complexes. *Bull. Chem. Soc. Jpn*. **1978**, *51*, 3111-3120.

39. McCall, K. A.; Fierke, C. A. Probing determinants of metal ion selectivity in carbonic anydrase using mutagenesis. *Biochemistry* **2004**, *43*, 3979-3986.

40. Pesonen, H.; Sillanpaeae, A.; Aksela, R.; Laasonen, K. Density functional complexation study of metal ions with poly(carboxylic acid) ligands. Part 2. Poly(acrylic acid - co - maleic acid), poly(methyl vinyl ether - co - maleic acid), and poly(epoxy succinic acid). *Polymer* **2005**, *46*, 12653-12661.

41. Shea, K. J. Molecular imprinting of synthetic network polymers: the de novo synthesis of macromolecular binding and catalytic sites. *Trends in Polymer. Science* **1994**, 2, 166-173.

42. Rao, T. P.; Kala, R.; Daniel, S. Metal ion-imprinted polymers – Novel materials for selective recognition of inorganics. *Anal. Chim. Acta* **2006**, *578*, 105-116.

43. Maeda, M.; Murata, M. Template dependent metal absorptivity of dialkyl phosphate type resins prepared by surface template polymerization technique. *Anal. Sci.* **1994**, *10*, 113-115.

44. Say, R.; Birlik, E.; Ersoz, A.; Yilmaz, F.; Gedikbey, T.; Denizli, A. Preconcentration of copper on ion-selective imprinted polymer microbeads. *Anal. Chim. Acta* **2003**, *480*, 251-258.

45. Singh, A.; Puranik, D.; Guo, Y.; Chang, E.L. Towards achieving selectivity in metal ion binding by fixing ligand-chelator complex geometry in polymers. *React. Funct. Polym.* **2000**, *44*, 79-89.

46. Huang, S-P.; Li, W.; Franz K. J.; Albright, R. L.; Fish, R. H. Polymer pendant ligand chemistry. 3. A biomimetic approach to selective metal ion removal and recovery from aqueous solution with polymer-supported sulfonated catechol and linear catechol amide ligands. *Inorg. Chem.* **1995**, *34*, 2813-2819.

47. Melby, L. R. Polymers for Selective Chelation of Transition Metal Ions. *J. Am. Chem. Soc*. **1975**, *97*(14), 4044-4051.

48. Ozawa, M.; Sano, Y.; Tanaka, Y. CMPO-TRUEX process and its application in the separation of actinides from high-level liquid wastes. *Miner. Process. Extr. Metall. Rev.* **2000**, *21*, 249-275

49. Boerrigter, H.; Verboom, W.; Reinhoudt, D. N. Novel Resorcinarene cavitand-based CMP(O) cation ligands: synthesis and extraction properties. *J. Org. Chem.* **1997**, *62*, 7148-7155.

50. Arnaud-Neu, F.; Boehmer, V.; Dozol, J.-F.; Gruettner, C.; Jakobi, R. A.; Kraft, D.; Mauprivez, O.; Rouquette, H.; Schwing-Weill, M.-J.; Simon, N.; Vogt, W. Calixarenes with diphenylphosphorylacetamide functions at the upper rim. A new class of highly efficient extractants for lanthanides and actinides. *J. Chem. Soc. Perkin Trans. 2* **1996**, *6*, 1175-1182.

51. Kulkarni, P. G.; Gupta, K. K.; Gurba, P. B.; Janardan, P.; Changrani, R. D.; Dey, P. K.; Manchanda, V. K. Solvent extraction behaviour of some fission product elements with N,N-dihexyl octanamide and tri-n-butyl phosphate under simulated PUREX process conditions**.** *Radiochim. Acta* **2006**, *94*, 325-329.

52. Obaseki, O. O.; Ipinmoroti, K. O.; Ajayi, O. O. Separation of copper and zinc cations from each other in aqueous acid sulfate solution using tri-n-butyl phosphate (TBP). *Global J. Pure Appl. Sci.* **2006**, *12*, 93-97.

53. Alexandratos, S. D.; Hussain, L. A. Synthesis of α-, β- and γ-ketophosphonate polymer supported reagents: the role of intraligand cooperation in the complexation of metal ions. *Macromolecules* **1998**, *31*, 3235-3238.

54. Alexandratos, S. D.; Trochimczuk, A. W.; Crick, D. W.; Horwitz, E. P.; Gatrone, R. C.; Chiarizia, R. Synthesis and Ion-Complexing Properties of a Novel Polymer-Supported Reagent with Diphosphonate Ligands. *Macromolecules* **1996**, *29*, 1021-1026.

55. Alexandratos, S.D.; Trochimczuk, A. W.; Horwitz, E. P.; Gatrone, R. G. Synthesis and characterization of a bifunctional ion exchange resin with polystyrene-immobilized diphosphonic acid ligands. *J. Appl. Polym. Sci.* **1996**, *61*, 273-278.

56. Yamabe, K; Ihara, T. Jyo, A. Metal ion selectivity of macroreticular chelating cation exchange resins with phosphonic acid groups attached to phenyl groups of a styrene-divinylbenzene copolymer matrix. *Sep. Sci. Technol.* **2001**, *36*, 3511-3528.

57. Egawa, H.; Yamabe, K.; Jyo, A. Studies on selective adsorption resins. XXXIII. Behavior of macroreticular chelating resins containing phosphinic or phosphonic acid groups in the adsorption of trivalent lanthanides. *J. Appl. Polym. Sci.* **1994**, *52*, 1153-1164.

58. Alexandratos S. D.; Zhu, X.; Bifunctional Coordinating Polymers: Auxiliary Groups as a Means of Tuning the Ionic Affinity of Immobilized Phosphate Ligands. *Macromolecules* **2005**, *38*, 5981-5986.
59. Rao, L.; Tian, G. LBNL-5924, **2006**.
60. Alexandratos, S. D.; Hong, M.-J**.** Enhanced metal ion affinities by supported ligand synergistic interaction in bifunctional polymer-supported aminomethylphosphonates. *Sep. Sci. Technol.* **2002**, *37*, 2587-2605.

Chapter 2

1. Ivanova, E.; Todorova, O. Immobilized organic reagents and their use in analytical chemistry. *Izvestiya po Khimiya* **1989**, *22*, 78-93.
2. Sherrington, D. C. Polymer-supported reagents, catalysts, and sorbents: evolution and exploitation-a personalized view**.** *J. Polym. Sci., Part A: Polym. Chem*. **2001**, *39*, 2364-2377.
3. Alexandratos, S. D. New polymer-supported ion-complexing agents: Design, preparation and metal ion affinities of immobilized ligand**s.** *J. Hazard. Mater.* **2007**, *139*, 467-470.
4. Taylor, P. Removal of trace concentrations of heavy metals using complexing ion-exchange resins. *Sep. Sci. Technol*. **2006**, *41*(11), 2575-2579.
5. Merdivan, M.; Buchmeiser, M. R.; Bonn, G. Phosphonate-based resins for the selective enrichment of uranium (VI). *Anal. Chim. Acta* **1999**, *402*, 91-97.
6. Zhao, J.; Bai, Y. Li, D.; Li, W. Extraction of rare earths(III) from nitrate medium with di-(2-ethylhexyl)-2-ethylhexyl phosphonate and synergistic extraction combined with 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5. *Sep. Sci. Technol.* **2006**, *41*, 3047-3063.
7. Berthon, C.; Chachty, C. NMR and IR spectrometric studies of monoamide complexes with plutonium(IV) and lanthanide(III) nitrates. *Solvent. Extr. Ion Exch*. **1995**, *13*, 781-812.
8. Stine, C. L. Ph.D. Dissertation, University of Tennessee. Knoxville **2002.**
9. Alexandratos, S. D.; Hussain, L. A. Synthesis of α-, β- and γ-ketophosphonate polymer supported reagents: the role of intraligand cooperation in the complexation of metal ions. *Macromolecules* **1998**, *31*, 3235-3238.
10. Chattopadhyay, S. Assignments of the vibrational frequencies of some benzyl compounds. *Indian Journal of Physics* **1967**, *41*, 759-770.

11. Bird, C. W.; Carbon-halogen stretching frequencies of some benzyl chlorides and bromides. *Spectrochim. Acta, Part A: Molecular and Biomolecular Spectroscopy* **1968**, *24*, 1666-1667.

12. Mannion, J.; Wang, T. S. An infrared study of the CH_2Cl group in benzyl chloride and derivatives. *Spectrochim. Acta* **1964**, *20*, 45-49.

13. Condit, D. A.; Craven, S. M.; Katon, J. E.; Vibrational spectra of some benzoyl halides. Benzoyl chloride, benzoyl-d5 chloride and benzoyl bromide, *Appl. Spectrosc*. **1974**, *28*, 420-426.

14. Wilhelm, C.; Gardette, J. L. Infrared identification of carboxylic acids formed in polymer photooxidation. *J. Appl. Polym. Sci*. **1994**, *51*, 1411-1420.

15. Lee, W. S.; Park, K. H.; Yoon, Y.-J. N, N-dimethylamination of acid chloride with DMF. *Synth. Commun*. **2000**, *30*, 4241-4245.

16. Alexandratos, S. D.; Zhu, X.; High-affinity ion-complexing polymer-supported reagents: Immobilized phosphate ligands and their affinity for the uranyl ion. *React. Funct. Polym*. **2007**, *67*, 375-382.

17. Boehme, C.; Wipff, G. Carbamoylphosphine oxide complexes of trivalent lanthanide cations: role of counterions, ligand binding mode, and protonation investigated by quantum mechanical calculations. *Inorg. Chem*. **2002**, *41*, 727-737.

18. Schurhammer, R.; Erhart, V.; Troxler, L.; Wipff, G. Interaction of M^{3+}cations with phosphoryl containing $(alkyl)_3P{=}O$ versus $(alkyl\text{-}O)_3P{=}O$ ligands: steric effects are more important than basicity effects. *J. Chem. Soc., Perkin Trans 2* **1999**, 2423-2431.

19. Miyaza, A.; Barnes, R. M. Complexation of some transition metals, rare earth elements, and thorium with a poly(dithiocarbamate) chelating resin. *Anal. Chem*. **1981**, *53*, 299-304.

Chapter 3

1. Sano, Y.; Karino, J.; Koyama, T.; Funasaka, H. NMR study of lanthanide(III) nitrate complexes in CMPO/TBP systems. *J. Alloys Compd.* **2000**, *303-304*, 151-156.

2. Someda, H. H.; El-Zahhar, A. A.; Shehata, M. K.; El-Naggar, H. A. Extraction studies of UO_2^{2+} by dihexyl-N,N-diethyl carbamoyl methyl phosphonate (DHDECMP). *J. Radioanal. Nucl. Chem.* **1998**, *228*, 37-41.

3. Rao, L. Tian, G. Complexation of actinides with derivatives of oxydiacetic acid. LBNL-59274, **2006.**

4. Iveson, P. B.; Drew, M. G. B.; Hudson, M. J.; Madic, C. Structural studies of lanthanide complexes with new hydrophobic malonamide solvent extraction agents. *J. Chem. Soc. Dalton Trans: Inorganic. Chemistry* **1999**, *20*, 3605-3610.

5. Gannaz, B.; Chiarizia, R.; Antonio, M. R.; Hill, C.; Cote, G.; Extraction of Lanthanides (III) and Am (III) by mixtures of malonamide and dialkylphosphoric acid. *Solvent Extr. Ion Exch.* **2007**, *25*, 313-337.

6. Manchanda, V. K.; Pathak, P. N. Amides and diamides as promising extractants in the back end of the nuclear fuel cycle: an overview. *Sep. Purif. Technol.* **2004**, *35*, 85-103.

7. Boerrigter, H.; Verboom, W.; Reinhoudt, D. N. Novel Resorcinarene Cavitand-Based CMP(O) Cation Ligands: Synthesis and Extraction Properties. *J. Org. Chem.* **1997**, *62*, 7148-7155

8. Arnaud-Neu, F.; Bohmer, V.; Dozol, J-F.; Gruttner, G.; Jakobi, R. A.; Kraft, D.; Mauprivez, O.; Rouquette, H.; Schwing-Weill, M.-J.; Simon, N.; Vogt, W. Calixarenes with diphenylphosphorylacetamide functions at the upper rim. A new class of highly efficient extractants for lanthanides and actinides. *J. Chem. Soc. Perkin Trans 2* **1996**, *6*, 1175-1182.

9. Arduini, A.; Bohmer, V.; Delmau, L.; Desreux, J- F.; Dozol, J-F.; Carrera, M. A. G.; Lambert, B.; Musigmann, C.; Pochini, A.; Shivanyuk, A.; Ugozzoli, F. Rigidified calixarenes bearing four carbamoylmethylphosphine oxide or carbamoylmethylphosphoryl functions at the wide rim. *Chem. Eur. J.* **2000**, *6*, 2135-2144.

10. Trochimczuk, A. W.; Jezierska, J. New amphoteric chelating/ion exchange resins with substituted carbamylethylenephosphonates; synthesis and EPR studies of Cu(II) complexes. *Polymer* **2000**, *41*, 3463-3470.

11. Alexandratos, S. D.; Hussain, L. A. Synthesis of α-, β- and γ-ketophosphonate polymer supported reagents: the role of intraligand cooperation in the complexation of metal ions. *Macromolecules* **1998**, *31*, 3235-3238.

12. Berlin, K. D.; Hellwege, D. M.; Nagabhushanam, M. Dialkyl esters of acylphosphonic acids. *J. Org. Chem.* **1965**, *30*, 1265-1267.

13. Kawabe, H.; Yanagita, M. Group interactions in polyelectrolytes. I. Amination kinetics of chloromethylated polystyrene. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1518-1524.

14. Alexandratos S. D; Zhu X. Immobilized tris(hydroxymethyl)aminomethane as a scaffold for ion-selective ligands: the auxiliary group effect on metal ion binding at the phosphate ligand. *Inorg. Chem*. **2007**, *46*, 2139-47.

15. Vaidya, S. V.; Bapat, S. S.; Kale, A. S.; Mokashi, S. V. Weak base anion-exchange resin: simplification of amination process and control on SBC. *Ion Exch. Adv. Proc. IEX* **1992**, 112-119.

16. Seliger, H. New synthesis of polystyrene and styrene copolymers with primary aromatic amino groups. *Makromolekulare Chemie.* **1973**, *169*, 83-93.

17. Shabanov, A. L. ; Azizov, A. M. ; Sultanzade, S. S. ; Azizova, N. A.; Alieva, N. T. Alkylation of 2-aminoethanol to the corresponding tertiary amino alcohols. *Azerbaidzhanskii Khimicheskii Zhurnal* **1988,** 67-70.

18. Kawabe, H. Group interactions in polyelectrolytes. XIV. Amination of chloromethylated polystyrene with amino alcohols. *Hiroshi. Bull. Chem. Soc. Jpn.* **1981**, *54*, 2886-2892.

19. Kirzecky, N. D.; Thomson, L. M.; Wayne, R. S. Acid chloride to ester formation: mechanism of sulfur dioxide-amine interference. *J. Org. Chem.* **1987**, *52*, 3452-3455.

20. Hubbard, P.; Brittain, W. J. Mechanism of Amine-Catalyzed Ester Formation from an Acid Chloride and Alcohol. *J. Org. Chem.* **1998**, *63*, 677-683.

21. Cohen, H.; Mier, J. D. Esterification of carboxylic acids with triethyl orthoformate. *Chem. Ind*. **1965**, *8,* 349-350.

22. Wade, L. G. Jr. Organic Chemistry, 3rd ed. Prentice-Hall: New Jersey, **1995**, p. 264.

23. Yadav, L. D. S. Organic Spectroscopy, Kluwer Academic: The Netherlands, Anamaya: New Delhi, **2005**; Chapter 3.

24. Diem, M. Introduction to Modern Vibrational Spectroscopy, John Wiley & Sons: New York, **1993**; pp 208–210.

25. Avram, M.; Mateescu, Gh. D. Infrared Spectroscopy: applications in organic chemistry, Wiley-Interscience: New York, **1972**; pp. 444–449.

26. Alexandratos, S. D.; Hong, Min-Jeong**.** Enhanced metal ion affinities by supported ligand synergistic interaction in bifunctional polymer-supported aminomethylphosphonates. *Sep. Sci. Technol*. **2002**, *37*, 2587-2605.

27. Alexandratos, S. D.; Smith, S. D. Intraligand cooperation in metal-ion binding by immobilized ligands: the effect of bifunctionality. *J. Appl. Polym. Sci.* **2004**, *91*, 463-468.

28. Shriver, D. F.; Atkins, P. W. Inorganic Chemistry, 3rd ed. W. H. Freeman: New York **2003**, pp. 167-169

29. Alexandratos, S. D.; Zhu, X. Bifunctional coordinating polymers: Auxillary groups as a means of tuning the ionic affinity of Immobilized phosphate ligands *Macromolecules* **2005**, *38*, 5981-5986.

30. Yantasee, W.; Lin, Y.; Fryxell, G. E.; Busche, B. J.; Birmbaum, J. C. Removal of heavy metals from aqueous solution using novel nanoengineered sorbents: self-assembled carbamoylphosphonic acids on mesoporous silica. *Sep. Sci. Technol.* **2003**, *38*, 3809-3825.

31. Yamada, M.; Kishii, N.; Araki, K.; Shiraishi, S. Extraction and release of divalent metal ions by 6,6'-diamino-2,2'-bipyridine supported on polymer beads. *Nippon Kagaku Kaishi* **1989**, *6*, 988-992.

32. Qu, R.; Sun, C.; Ji, C.; Wang, C.; Zhao, Z.; Yu, D. Synthesis and adsorption properties of macroporous cross-linked polystyrene that contains an immobilizing 2,5-dimercapto-1,3,4-thiodiazole with tetraethylene glycol spacers. *Polym. Eng. Sci.* **2005**, *45*, 1515-1521.

33. Hojjatie, M.; Valiente, M.; Ribas, X.; Freiser, H. "Spacer" modified polymer bonded metal chelating ligands. Iranian *Journal of Polymer Science & Technology* **1994**, *3*, 105-14.

34. Sugii, A.; Ogawa, N.; Harada, K.; Nishimura, K. Metal sorption of macroreticular poly(4-vinylpyridine) resins cross-linked with oligo(ethylene glycol dimethacrylates). *Anal. Sci.* **1988**. *4*, 399-402.

35. Salem, N. M.; Ebraheem, K. A. K.; Mubarak, S. M. The effects of spacer groups on the chelation characteristics of some Mannich polymers containing 8-hydroxyquinoline. *React. Funct. Polym.* **2004**, *59*, 63-69.

36. Nishide, H.; Shimidzu, N.; Tsuchida, E. Chelating resin: Pyridine derivatives attached to poly(styrene) beads with spacer group. *J. Appl. Polym. Sci.* **1982**, *27*, 4161-4169.

37. Kumagai, H.; Inoue, Y.; Yokoyama, T.; Suzuki, T. M.; Suzuki, T. Chromatographic selectivity of rare earth elements on Iminodiacetate-type chelating resins having spacer arms of different lengths: Importance of steric flexibility of functional group in a polymer chelating resin. *Anal. Chem.* **1998**, *70*, 4070-4073.

38. Marcus, Y. Solvent Extraction of Inorganic Species. *Chem. Rev.* **1963**, *63*, 139-170.

39. Topp, K.-D.; Grote, M. Synthesis and characterization of a 1,2,4,5-tetrazine-modified ion-exchange resin. *React. Funct. Polym*. **1996**, *31*,117-136.

40. Sanchez, J. M.; Hidalgo, M.; Salvado, V. The gold (III) and palladium (II) on new phosphine sulphide-type chelating polymers bearing different spacer arms. Equilibrium and kinetic characterisation. *React. Func. Polym.* **2001**, *46*, 283-291.

41. Lauth, M.; Frere, Y.; Prevost, M. Gramain, PH. Complexation properties of a homologous series of linear polythioethers grafted onto macroporous polystyrene matrices. Selective binding of mercury(II) and silver(I). *React. Polym*. **1990**, *13*, 73-81.

42. Lauth, M.; Frere, Y.; Meurer, B.; Gramain, PH.; Prevost, M. Poly(ethylene oxide) grafted onto Polystyrene-divinylbenzene macroporous resins. Covalent binding of mercuric chloride. *React. Polym*. **1990**, *12*, 155-166.

43. Li, H.; Tian, D.; Xiong, D.; Gao, Z. Synthesis of calix[4]crown-4 oligomers containing hard and soft binding sites. *J. Appl. Polym. Sci*. **2007**, *104*, 3201-3205.

44. Alexandratos, S. D.; Zhu, X. Immobilized phosphate ligands with enhanced ionic affinity through supported ligand synergistic interaction. *Sep. Sci. Technol.* **Feb. 2008** (submitted)

45. Efendiev, A. A.; Orujev, D. D.; Sidorchuk, I. I. Selective polymer sorbents on the basis of copolymers of dialkyl esters of vinylphosphonic acid and acrylic acid. *React. Polym*. **1983**, *1*, 295-300.

46. Coupez, B.; Boehme, C.; Wipff G. Interaction of bifunctional carbonyl and phosphoryl ligands with M3+ lanthanide cations: how strong is the bidentate effect? The role of ligand size and counterions investigated by quantum mechanics. *Phys. Chem. Chem. Phys*. **2002**, *4*, 5716-5729.

Chapter 4

1. Suffet, I.; Shih, T.; Khan, E.; Wangpaichitr, M.; Rong, W.; Kong, J.; Sorption for removing methyl tertiary butyl ether (MTBE) from drinking water. Proceedings, Annual Conference, American Water Works Association, Denver, **1999**, 319-336.

2. Fiorenza, S.; Suarez, M. P.; Rifai, H. S. MTBE in groundwater: status and remediation *J. Environ. Eng.* **2002**, *128*, 773 - 781.

3. Squillace, P. J.; Zogorski, J. S.; Wilbur, W. G.; Price, C. V. Preliminary assessment of the occurrence and possible sources of MTBE in groundwater in the United States, 1993-1995. *Environ. Sci. Technol.* **1996**, *30*, 1721-1730.

4. Johnson, R.; Pandow, J. Bender, D.; Price, C.; Zogorski, J. MTBE To what extent will past releases contaminate community water supply wells? *Environ. Sci. Technol*. **2000**, *34*, 210A – 217A.

5. Shelly, S.; Fouhy, K. The drive for cleaner burning fuel. *Chem. Eng.* **1994**, *101*, 61-63.

6. New Hampshire Department of Health and Human Services Bureau of Health Risk Assessment. Health information summary Methyl t-Butyl Ether (MTBE) **2000.**

7. Ritter, S. K.; Alkylate Rising, *C & EN* **2001**, *79*, 63-67.

8. Squillace, P. J.; Pankow, J. P.; Korte, N. E. ; Zogorski, J. S. Review of the environmental behavior and fate of methyl *tert*-butyl ether. *Environ. Toxicol. Chem.* **1997**, *16*, 1836-1844.

9. Staudinger, J.; Roberts, P.V. A critical review of Henry's law constants for environmental applications. *Crit. Rev. Env. Sci. Technol*. **1996**, *26*, 205-297.

10. U.S. Environmental Protection Agency. Drinking water advisory: Customer acceptability advice and health effects analysis on Methyl tert-Butyl Ether (MTBE); EPA-822-F-97-008; Office of Water, U.S. EPA: Washington, DC. http://www.epa.gov/OST/Tools/MtBEaa.pdf.

11. Young, W. F.; Horth, H.; Crane, R.; Ogden, T.; Amott, M. Taste and odor threshold concentrations of potential potable water contaminants. *Water Res.* **1996**, *30*, 420-426.

12. Cater, S. R.; Dusset, B. W.; Megonnell, N. Reducing the threat of MTBE – contaminated groundwater. *Pollution Engineering*. **2000**, *32*, 36-39.

13. Mennear, J. H. Carcinogenicity studies on MTBE: Critical review and interpretation. *Risk Analysis*: an official publication of the Society for Risk Analysis. **1997**, *17*, 673-681.

14. Penske, N.; Sandler, S. I. Liquid-liquid equilibria of fuel oxygenate + water + hydrocarbon mixtures. 1. *J. Chem. Eng. Data* **1995**, *40*, 315-320.

15. Chang, P. B. L.; Young, T. M. Kinetics of Methyl tert-butyl ether degradation and by-product formation during UV / Hydrogen Peroxide Water Treatment. *Water Res.* **2000**, *34*, 2233-2240.

16. Effenberger, M.; Lobel, E.; Noack, T.; Schirmer, M. The gasoline additive Methyl-tert-Butyl Ether (MTBE) as challenge for groundwater. *Altlasten Spektrum* **2001**, *10*, 177-184.

17. Salanitro, J. P.; Diaz, L. A.; Williams, M. P.; Wisniewski, H. L. Isolation of a bacterial culture that degrades Methyl t-butyl ether. *Applied and Environmental Microbiology* **1994**, *60*, 2593 – 2596.

18. Deeb, R. A.; Scow, K. M.; Alvarez-Cohen, L. Aerobic MTBE biodegradation: an examination of past studies, current challenges and future research directions. *Biodegradation* **2000**, *11*, 171-186.

19. An, Y.-J.; Kampbell, D. H.; Cook, M. L. Co-occurrence of MTBE and benzene, toluene, ethylbenzene, and xylene compounds at marinas in large reservoir. *J. Environ. Eng.* **2002**, *128*, 902-906.

20. Wilhelm, M. J.; Adams, V. D.; Curtis, J. G.; Middlebrooks, E. J. Carbon adsorption and air-stripping removal of MTBE from river water. *J. Environ. Eng.* **2002**, *128*, 813-823.

21. Kawabata, N.; Sumiyama, Y.; Matsuura, N. Separation of alcohols from water by adsorption on cross-linked polymethacrylic ester containing a pyridinium group. *Ind. Eng. Chem. Res.* **1988**, *27*, 1882-1886.

22. MTBE Research Partnership. Evaluation of the Applicability of synthetic resin sorbents for MTBE removal from water. **1999**. Ed. Melin, G. National Water Research Institute.

23. Lin, S. H.; Wang, C. S.; Chang, C. H. Removal of Methyl *tert*-Butyl Ether from contaminated water by macroreticular resin. *Ind. Eng. Chem. Res.* **2002**, *41*, 4116-4121.

24. Rhodes, I. A. L.; Verstuyft, A. W. Selecting analytical methods for the determination of oxygenates in environmental samples and gasoline. *Environmental Testing & Analysis* **2001**.

25. Nouri, B.; Fouillet, B.; Toussaint, G.; Chambon, R. ; Chambon, P. Complementarity of purge-and-trap and head-space capillary gas chromatographic methods for determination of methyl-tert.-butyl ether in water. *J. Chromatogr. A* **1996**, *726*, 153-159.

26. Bauer, L. J.; Gutsche, D. Calixarenes. 15. The formation of complexes of calixarenes with neutral organic molecules in solution *J. Am. Chem. Soc.* **1985**, *107*, 6063-6069.

27. Kuhn, E. Water injection in gas chromatography part 1. *Sep. Times* **2001**, *14*, 10-11.

28. Kawabata, N.; Higuchi, I.; Yoshida, J. Removal and Recovery of Organic Pollutants from the Aquatic Environment. VII. Adsorption of phenol and carboxylic acids on crosslinked poly(4-vinylpyridine). *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3253-3258.

29. Malley, J. P. Jr.; Eliason, P. A.; Wagler, J. L. Point-of-entry treatment of petroleum contaminated ground water. *Water Environ. Res.* **1993**, *65*, 119-128.

30. McClure, A.; Megonnell, N. Activated carbon optimized to treat MTBE. *Water Technology* **2000**, 1-3.

31. Bi, E.; Haderlein S. B.; Schmidt, T. C.; Sorption of methyl *tert*-butyl ether (MTBE) and *tert*-butyl alcohol (TBA) to synthetic resins. *Water Res.* **2005**, *39*, 4164-4176.

32. Davis, S. W.; Powers, S. E. Alternative sorbents for removing MTBE from gasoline-contaminated groundwater. *J. Environ. Eng.* **2000**, *126*, 354-360.

33. Anderson, M. A. Removal of MTBE and other organic contaminants from water by sorption to high silica zeolites. *Environ. Sci. Technol.* **2000**, *34*, 725-727.

34. Wang, X.; Deshusses, M. A. Biotreatment of groundwater contaminated with MTBE: interaction of common environmental co-contaminants. *Biodegradation* **2007**, *18*, 37-50.

35. Yokoyama, T.; Makishima, A.; Nakamura, E. Separation of thorium and uranium from silicate rock samples using two commercial extraction chromatographic resins. *Anal. Chem.* **1999**, *71*, 135-141.

36. Gonzalez, M. P.; Saucedo, I.; Navarro, R.; Avila, M.; Guibal, E. Selective separation of Fe(III), Cd(II), and Ni(II) from dilute solutions using solvent-impregnated resins. *Ind. Eng. Chem. Res.* **2001**, *40*, 6004-6013.

37. Cortina, J. L.; Warshawsky, A. Developments in solid-liquid extraction by solvent-impregnated resins. *Ion Exch. Solvent Extr.* **1997***, 13*, 195-293.

38. Li, H.; Zhou, C.; Fu, B. Separation of platinum group metals by solvent-impregnated resins technique. *Guijinshu* **2001**, *22*, 49-53.

39. Kostova, A.; Bart, H.-J. Equilibrium study of amino acid reactive sorption with impregnated resins (Part I). *Solvent Extr. Ion Exch.* **2007**, *25*, 109-126.

40. Giddings, J. C. Kinetic origin of tailing in chromatography. *Anal. Chem.* **1963**, *35*, 1999-2002.

Chapter 5

1. Alexandratos, S. D.; Hussain, L. A. Synthesis of α-, β- and γ- ketophosphonate polymer-supported reagents: The role of intra-ligand cooperation in the complexation of metal ions. *Macromolecules* **1998**, *31*, 3235-3238.

2. Alexandratos, S. D.; Zhu, X. Bifunctional coordinating polymers: Auxillary groups as a means of tuning the ionic affinity of immobilized phosphate ligands. *Macromolecules* **2005**, *38*, 5981-5986.

3. Bradstreet, R. B. Kjeldahl method for organic nitrogen. *Anal. Chem*. **1954**, *26*, 185-187.

4. Kirk, P. L. Kjeldahl method for total nitrogen. *Anal. Chem*. **1950**, *22*, 354-358.

5. Alexandratos, S. D.; Zhu, X. Amination of poly(vinylbenzyl chloride) with N, N-dimethylformamide. *Macromolecules* **2003**, *36*, 3436-3439.

6. Webb, P. A.; Orr, C. Analytical methods in fine particle technology, 1st ed.; Micromeritics Instrument, **1997**; Chapter 3.