SYNTHESE OF POLYMER-SUPPORTED AMIDE-TYPE LIGANDS AND COMPLEXATION OF LANTHANIDE IONS

by

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Abstract

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The complexation of lanthanide ions from acidic solutions was studied with cross-linked polystyrene modified with amide-type ligands: *N,N,N',N'*-tetramethylmalonamide (TMMA), monoamidated malonate and urea.

The TMMA resin showed preference towards Tb, Dy and Eu from highly acidic solutions. Ionic recognition is achieved through a mechanism in which two opposing processes—electrostatic attraction of $M(H_2O)_xCl_4^-$ or $M(H_2O)_x(NO_3)_4^-$ by the protonated ligand and (partial) loss of the waters of hydration—dominate at different points along the lanthanide series. The proposed complexation mechanism consists of protonation of one of the carbonyls, which is stabilized by hydrogen bonding to the neighboring carbonyl oxygen, formation of iminium site and ion exchange by exchanging the chloride ion with the lanthanide chloro or nitro complex.

The importance of the substituents at amide nitrogen was probed with immobilized malonate ligands monoamidated with diethylenetriamine (DETA-MAm) and immobilized diethylenetriamine ligands with one amine nitrogen converted to urea (Urea-3). The comparison of the lanthanides complexation by the TMMA, DETA-MAm and Urea-3, was carried out under conditions in which each resin has its best performance: 6 M HCl for TMMA and 8 M HCl for DETA-MAm and Urea-3. The protonated TMMA, with two electron-donating methyl groups at the iminium nitrogen to attenuate the (+) charge ($=NR_2(+)$), is the weakest ligand with ionic recognition properties towards the lanthanides in the middle of the series. The reduced ligand strength makes it more responsive towards changes between the electrostatic attraction and the enthalpy of dehydration. The protonated Urea-3 showed much higher lanthanide affinities than the TMMA and DETA-MAm, and its affinity trend paralleled the trend of lanthanides ionization potentials due to the absence of methyl group to attenuate the (+) charge ($=NH_2(+)$). The DETA-Mam is somewhere in between the TMMA and Urea-3 because its iminium has only one $-CH_2-$ moiety attenuating the (+) charge (=NHR(+)) and it is also a two-site interaction with the ammonium group probably contributing to the electrostatic stabilization of the chlorocomplex.

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1 Introduction

1.1 Purpose of the Study

The separation of lanthanides from their mixtures is challenging due to the similarity of their chemical properties derived from their same valence and similar ion radii.[1] On the other hand, their demand has been increasing in recent years in high-technology industry because of their unique electronic, optical and magnetic properties. Hence, the development of efficient separation technologies for lanthanide separation from water or wastewater is important from both the environmental and economic points of view.

Ion exchange with polymer-supported reagents, usually consisting of polystyrene or poly(glycidyl methacrylate) beads crosslinked with divinylbenzene (DVB) that have been modified with ligands designed to function as ion-selective complexants, is one of the most popular techniques for the separation of alkali, alkaline earth metals, transition metals, lanthanides and actinides[2]. Compared to solvent exchange, in which a compound capable of interacting with the target ion through ion exchange or other mechanism of complex formation is dissolved in an organic solvent and brings the metal ion into the organic phase as the interaction occurs, ion exchange with polymeric complexants can be used for dilute solutions and avoids the loss of extractant to the aqueous phase since the ligands are covalently incorporated to an insoluble polymer. In addition, ion exchange offers many other advantages including ease of operation, regeneration and reuse, and environmental compatibility[3].

In recent years, a great deal of research has been devoted to the subject of lanthanide separation using ion exchange and chelating resins.[4, 5, 6, 7, 8, 9, 10, 11, 12] Yet, there is no satisfactory solution for this problem and the need to understand the interaction of lanthanide and polymeric complexants and design ion-selective polymer-supported reagents for effective lanthanide separation remains.

Selectivity of a resin is of particular concern when it comes to designing polymer-supported reagents for separation. The main purpose of our work is an attempt to investigate lanthanide selectivities of polymer-supported complexants by looking into the interaction between lanthanides and polymer-supported amide-type ligands.

1.2 Objective of the Study

N,N-dialkylamides have drawn much attention for their adsorption properties of lanthanides as an alternative for organophosphorous extractants such as carbamoylmethyl phosphine oxide (CMPO). [13, 14, 15, 16, 17] They have also shown affinities towards lanthanides from highly acidic streams even after being bonded onto polymer supports[18]. For this reason, we will be focused on malonamide ligands by studying their complexation with lanthanides under acidic conditions after immobilizing them onto a polystyrene copolymer. The objective of this project is to understand the mechanism of metal ion complexation by polymer-supported reagents with, define the possible factors that affect the metal affinities of polymeric amide-type complexants, propose complexation modes, and explore how these factors influence metal ions affinities and selectivity.

1.3 Hypotheses

Malonamides are weak bases in which one of the carbonyl oxygens get protonated in acidic solution to form a six-membered ring with the neighboring carbonyl group. This ring structure is expected to stabilize the protonation and results in the formation of an iminium moiety. The iminium chloride will act as the site of ion exchange with the lanthanide chlorocomplex. It is postulated that substituent at the amide nitrogen is of great importance in determining the strength of the ligand by affecting the charge density at the iminium site. An electron-donating alkyl group weakens the positive charges at the iminium but hydrogen atom does not. In this work, we will test this hypothesis by comparing the malonamide resin with the monoamidated malonate and urea resin for their lanthanide affinities.

1.4 Scope and Organization

The main body of this dissertation begins with a literature review (Chapter II) in which a brief summary about all the aspects of the polymer-supported reagents that have been used for separation and important chemical properties of lanthanides in solution is followed by a detailed literature survey of polymer-supported reagents used for lanthanide separation. Studies with actinides are included when they help clarify the mechanisms of the lanthanide complexation reactions. A variety of polymeric ligands are grouped into four categories according to the polarizability of their donor atoms. The details of various mechanisms responsible for the extraction of ion exchange and chelating resin are to be discussed in view of a relationship among the donor atoms, hydration of the lanthanides, solvation of the metal with counterions and protonation of the immobilized ligand.

The subsequent chapters are focused on the preparation and characterization of immobilized amide-type ligands, including *N, N, N', N'*-tetramethylmalonamide (Chapter III), monoamidated malonate (Chapter IV) and urea (Chapter V), The complexation behavior of these resins with lanthanides under acidic conditions is investigated in depth. Particular emphasis is placed on the mechanism of the ionic recognition exhibited by the TMMA resin.

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2 Literature Review

2.1 Introduction

The selective complexation of lanthanide ions from aqueous solutions is important to applications in nuclear waste management,[1, 2, 3] luminescent probes in medicine and biology,[4] and catalysis in organic synthesis.[5] Extensive research has been done with organophosphorus extractants for the separation of lanthanides and actinides. The compounds studied include tributyl phosphate (TBP), trioctylphosphine oxide (TOPO) and the carbamoylmethylphosphine oxides.[6, 7, 8, 9] In general, these compounds extract the lanthanides more efficiently from acidic solutions.

The practical applications of soluble and immobilized lanthanide and actinide complexants is evident through the patent literature: bis-diglycolamides can be used to treat acidic high-level radioactive waste;[10] lanthanide-doped polymers can be applied in laser and optical amplifiers;[11] cascade polymers bearing lanthanide-selective ligands can be used in medical diagnostics;[12] lanthanide-based complexes can be used as catalysts for olefin polymerization;[13, 14] and resins can be used in the recovery of hafnium from irradiated tantalum solutions.[15]

The separation of lanthanides is complicated by their similar properties, including their trivalent oxidation state and low polarizability, and the solution variables, including the acidity, counterions, and presence of soluble complexants: pH affects speciation[16, 17, 18, 19] and the complexation mechanism;[1] counterions such as chloride and nitrate coordinate to metal ions differently and this influences their interaction with the ligands;

and soluble complexants alter the ion's hydrophilicity which then affects its extractability.[20, 21]

Solvent extraction and ion-exchange resins are the most common technologies for lanthanide separations. Solvent extraction separates complexes based on solubility differences between two immiscible liquids, usually water and an organic solvent, in contact with each other. The extraction is from an aqueous phase into an organic phase. The extractants solvate, exchange or chelate the metal ion.[22] Although solvent extraction has long been used to remove ions from water, the finite aqueous solubility of the extractants, solvents and modifiers, and their loss through phase disengagement remain important problems.[23] Additionally, solvent extraction cannot be applied to dilute metal ion solutions due to the large volume of organic phase that would be needed.

Cross-linked polymers with functional groups capable of binding metal ions operate on the same principle as solvent extraction but may have advantages compared to soluble extractants. The ligand is covalently bound to the polymer support so that no loss of extractant occurs. Stripping of the metal ions from the complexant is important to both solvent extraction and polymer-based processes; regeneration and reuse of the polymers is particularly important to the economics of their application.

Because no organic solvent is required, this process is environmentally compatible.[24, 25, 26] Alternatively, the chelant can be physically sorbed into a polymer support. Though some solubility loss of the chelant is possible, this method is simpler and more versatile than one involving covalent modification of the support. While polymer-supported reagents can have slow rates of equilibration, this can be circumvented by macroporosity[25] and bifunctionality.[27]

This review is part of a study aimed at understanding the principles behind the selectivity of immobilized ligands. The emphasis here is on lanthanide separations, but studies with actinides are included when they help clarify the mechanisms of the lanthanide complexation reactions. The lanthanides form a unique series for studying the influence of charge density on complexation reactions. Lanthanides are also important as models for trivalent actinides which are less amenable to experimental investigations.

2.2 Polymer Support

The design of polymer-supported reagents for a targeted metal ion consists of two components: the choice of polymer support and its subsequent functionalization. The polymer support should be chemically and physically stable, and of sufficient porosity to allow access of reagents for the functionalization reaction and of the metal ions to the ligand.[28]

Copolymers of styrene-divinylbenzene are widely available supports and are used to prepare many commercially available resins, including the Amberlite, Dowex and Purolite product lines.[29] Vinylbenzyl chloride and glycidyl methacrylate are utilized to synthesize resins via nucleophilic reactions.[28] The cross-linked polymers are prepared as beads with high mechanical stability via suspension polymerization. Microporous (gel) or macroporous polymer beads can be synthesized by varying the type and amount of cross-linking agents and porogens.

The polymer support can be modified either chemically (by covalent bonding of the ligand to the matrix) or physically (by sorption of a chelant into the matrix).[30] Chemical modification obviates complexant loss upon continued use.[31, 32, 33, 34] Functionalized polymers can also be prepared directly from functionalized monomers.[28] This method is limited by the possibility of monomer instability and inapplicability under the conditions of suspension polymerization. The ease of reactions on commercially available of polymer beads makes the post-functionalization method more popular.

2.3 Properties of the Lanthanide Cations

The lanthanides, as the first period of f-block elements, possess unique properties. The ionic radius decreases as the atomic number increases, a property termed the lanthanide contraction. This results in an increasing charge density across the series: 17 (La), 17.5 (Pr), 18.3 (Eu), 19.2 (Er), and 19.7 (Lu), in units of 10^{-28} C^2/m.[35] Consequently, the strength of cation-anion, ion-dipole, and ion-induced dipole interactions increase across the series.[36] Hydration energy is another radius-based trend wherein hydration becomes stronger with decreasing ionic size.[37, 38] The third ionization energy shows an increase due to the increase in nuclear charge across the f-block, though a discontinuity at gadolinium is due to the effect of a half-filled shell in the electronic structure of the trivalent ion.[39, 40]

2.4 Polymer-supported Reagents for Trivalent Lanthanide and Actinide Separations

According to hard-soft acid-base (HSAB) theory,[41] lanthanide cations are hard Lewis acids thus preferring to ionicially bind with hard Lewis bases (such as oxygen).

The importance of ionic vs. covalent interactions is seen by comparing their behavior to that of the heavier actinides which develop covalent interactions involving s and p orbitals;[36] this modest enhancement of covalency compared to lanthanides makes their separation possible with softer donor atoms.

This review of polymer-supported reagents for lanthanide and, to a lesser extent, actinide separations is divided into four categories of ligands in an increasing order of donor atom polarizability: (1) oxygen as the donor atom; (2) oxygen and nitrogen as the donor atoms; (3) nitrogen as the donor atom; and (4) sulfur as the donor atom. Thus, oxygen is the least polarizable (hardest) donor and sulfur is the most polarizable (softest) donor, as is evident by the decrease in absolute hardness of OH^-, NH_2^- and SH^- (5.6, 5.3 and 4.1 eV respectively).[42]

2.4.1 Oxygen as the donor atom

Ligands with oxygen as the only donor atom constitute the largest group of immobilized ligands for lanthanide and actinide separations. The functional groups include amides, organophosphates, carboxylates, carbamoylmethylphosphine oxides, and polyphenols.

2.4.1.1 Amides

Soluble *N,N*-dialkylamides are selective extractants for lanthanides and actinides from acidic solutions. They are radiolytically stable, have benign degradation products, are completely incinerable, and their selectivity can be tuned through the choice of alkyl groups.[43, 44, 45, 46, 47, 48, 49]

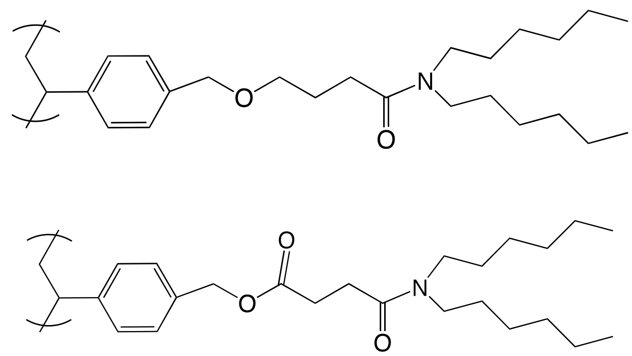


Figure 2.1 Polystyrene-bound 4-ethoxy-*N, N'*-dihexylbutanamide (EDHBA) and *N, N'*-dihexylsuccinamic acid (DHSA).

The effect of structural variations on immobilized amides is evident by comparing the ionic affinities of 4-ethoxy-*N,N*-dihexylbutanamide (EDHBA) and *N,N*-dihexylsuccinamic acid (DHSA) bonded to crosslinked polystyrene (Fig. 2.1).[18, 19] The grafting of the amide was confirmed by FT-IR and ^{13}C-CPMAS NMR spectra. The IR band at 1656 cm^{-1} (EDHBA) and 1645 cm^{-1} (DHSA) corresponds to the amide carbonyl group. ^{13}C-CPMAS NMR spectra showed signals at 39.2 and 25.6 ppm, corresponding to the aliphatic groups in EDHBA. Signals for the methyl groups and the amide carbonyl were observed at 10 and 198 ppm, respectively. EDHBA had greater affinity for Th(IV) (distribution coefficient >10^3) than for U(VI), La(III) and Nd(III) from 4-10 M HNO_3 whereas DHSA had greater selectivity for U(VI) and Th(IV) compared to La(III) and Nd(III) from 2-10 M HCl or HNO_3. As a result, these amides may be useful for the separation of actinides from lanthanides present in highly acidic solutions during nuclear fuel reprocessing. The distribution coefficients (*D*) increase, then decrease, as the acid concentration increases. With EDHBA, the maximum *D* values for La, Nd, and U were in

6 M HNO_3 and HCl; with DHSA, the maximum *D* values for La and Nd were in 2 M HNO_3 and HCl and, for U and Th, in 6 M HNO_3 and 2 M HCl. However, at lower (0.1 M) acid concentration, DHSA had a higher affinity (D = 10^2~10^3) for actinides and lanthanides compared to EDHBA ($D \approx 0$), which may be related to the presence of the additional carbonyl group resulting in chelation.

Studies with soluble extractants have shown that branched diamides could be selective among lanthanides and actinides through steric effects.[46, 50, 51] Polystyrene-bound di-bis(2-ethylhexyl)malonamide was thus prepared for the selective extraction of U(VI) (Fig. 2.2).[52] The malonamide showed greater affinity for U(VI) than Th(IV) due to hindrance from the bulky alkyl chain towards the complexation of $Th(NO_3)_4$. Both U(VI) and Th(IV) had increasing *D* values with increasing acidity, though that trend was more pronounced for Th(IV). Metal-ligand binding was confirmed by far-IR spectra in which bands at 290-120 cm^{-1} correspond to $\upsilon_{O\text{-}[M]}$ stretching vibrations.

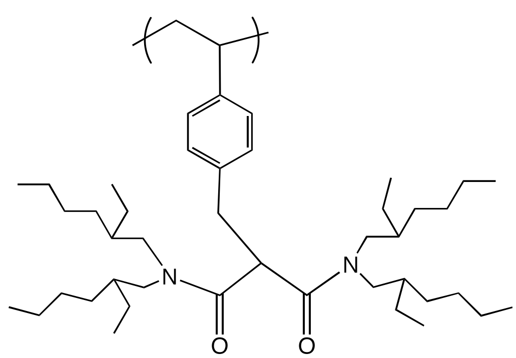
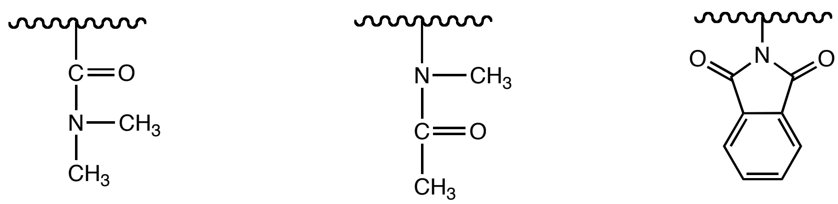


Figure 2.2 Immobilized di-bis(2-ethylhexyl)malonamide.

Silica-supported monoamides were prepared by polymerizing a mixture of porous silica, a monomer with monoamide groups, divinylbenzene (DVB), pore-producing solvents, and an initiator (Fig. 2.3).[53, 54] It was found that *N,N*-dimethylacrylamide

(DMAA) had the highest sorption for U(VI) and the distribution coefficients increased with increasing HNO_3 concentration. *N*-vinyl-*N*-methylacetamide (VMAA) and N-vinylphthalimide (VPhI) had little affinity for U(VI). A comparison of the silica-DMAA IR spectra before and after contact with U(VI) showed a band at 1637 cm^{-1} before and after sorption and a new band at 1595 cm^{-1} after sorption. This is similar to the carbonyl band found in the IR spectrum of the uranyl nitrate complex of bis(*N*-cyclohexyl-2-pyrrolidone),[55] suggesting that DMAA is complexed to U(VI) through the two oxygens of the amide groups by forming $UO_2(NO_3)_2(DMMA)_2$.



N,N-dimethylacrylamide (DMAA)   *N*-vinyl-*N*-methylacetamide (VMAA)   *N*-vinylphthalimide (VPhI)

Figure 2.3 Silica supported *N,N*-dimethylacrylamide, *N*-vinyl-*N*-methylacetamide, and *N*-vinylphthalimide.

The affinity of diamides for actinides was increased by introducing an ether oxygen between the two amide groups.[56] *N, N, N', N'*-tetraoctyldiglycolamide (TODGA) (Fig. 2.4) sorbed into polystyrene embedded in porous silica particles with a mean diameter of 50 μm had high affinities for Am(III) and Ln(III) from simulated high level radioactive liquid waste.[57] This can be ascribed to the additional oxygen making the ligand tridentate.

TODGA has a greater affinity than *N,N,N',N'*-dimethyldibutyltetradecylmalonamide (DMDBTDMA) and octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) for Am(III) after being sorbed into Chromosorb-W, a celite diatomaceous silica.[58] Chromosorb-W outperforms the nonionic XAD-4 and XAD-7 as the solid support. TODGA sorbed into Chromosorb-W behaves as in liquid-liquid extractions:[59, 60, 61] The order of *D* values is Eu(III)>Am(III)>Pu(IV)>U(VI), in agreement with that found in liquid extractions.[59] This sequence is different from that with DMDBTDMA and CMPO, which follow the order of ionic potentials: Pu(IV) > U(VI) > Am(III).[58] The low uptake of U(VI) by TODGA was attributed to steric hindrance.

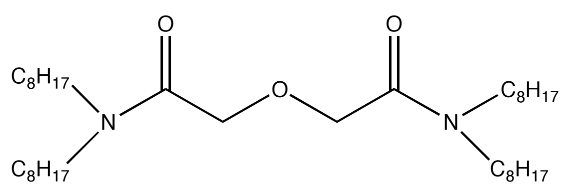


Figure 2.4 *N, N, N', N'*-tetraoctyldiglycolamide (TODGA).

The dependence of Am(III) extraction on HNO_3 concentration was studied with TODGA, CMPO, DMDBTDMA, and Cyanex-923 [a mixture of four trialkylphosphine oxides R_3PO, $R_2R'PO$, $RR_2'PO$ and $R_3'PO$ where R and R' are n-octyl and n-hexyl] sorbed within Chromosorb-W. Both TODGA and CMPO show a steep increase in *D* values up to 1 M HNO_3. Cyanex-923 has decreasing *D* values with increasing acidity.[58] For DMDBTDMA, *D* increases gradually with nitric acid concentration and reaches only moderate values above 3 M HNO_3. When the concentration of HNO_3 is greater than 2 M, the order of extractant strength is CMPO > DMDBTDMA > Cyanex-923. These results are consistent with an earlier study.[62]

2.4.1.2 Organophosphorus acids

Organophosphorus acids are widely used for the separation of lanthanides and actinides via solvent extraction. The complexing ability of organophosphorus acids increases with an increase of their acidity in the order $Alk_2P(O)OH$ < Alk(AlkO)P(O)OH < $(AlkO)_2P(O)OH$.[63] Phosphonic acids have been immobilized onto polystyrene by the Arbuzov reaction using lithium or sodium alkyl chlorophosphites (Fig. 2.5).[64] In contrast to the phosphate ester resin, which has a low uptake (<10%) of U(VI) at a pH of 0-4, the phosphonic acid resin shows a high affinity at an optimum pH of 4. Moreover, the phosphonic acid resin has no affinity for Th(IV), Ni(II), Cd(II), Cu(II), Zn(II) and Co(II) at pH 2, indicating that it can be used for the separation of U(VI) from Th(IV) and divalent transition metal ions.

A polymer into which was sorbed 1-hexyl-4-ethyloctylisopropylphosphonic acid (HEOPPA) (Fig. 2.6) was used for the separation of lanthanide and actinide ions in HCl.[65] Compared to di(2-ethylhexyl)phosphoric acid (DEHPA) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH/EHP), the greater bulkiness of the 1-hexyl-4-ethyloctyl group in HEOPPA leads to higher selectivity: There is a higher affinity for U(VI) than Th(IV) because the group interferes in the complexation of $Th(NO_3)_4$. The affinity for the lanthanides increases as a function of pH and the sequence follows the order of increasing atomic number: Gd < Tb < Dy < Ho < Er < Tm < Yb < Lu. The same order was observed with a polymer containing bis(2,4,4-trimethylpentyl)monothiophosphinic acid.[66] The solution pH was 1-2 with the phosphonic acid and 1-3 with the thiophosphinic acid. Ion exchange was the sole mechanism of separation, as indicated by the log*D* vs pH plots where the lines for each ion had a slope of 3. Ion exchange is a less selective mechanism than coordination and the ionic charge density is the dominant property determining the affinity sequence.

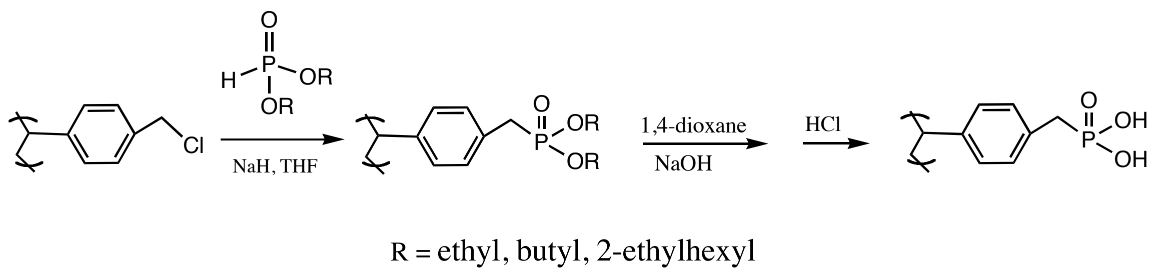


Figure 2.5 Synthesis of the phosphonic acid resin.

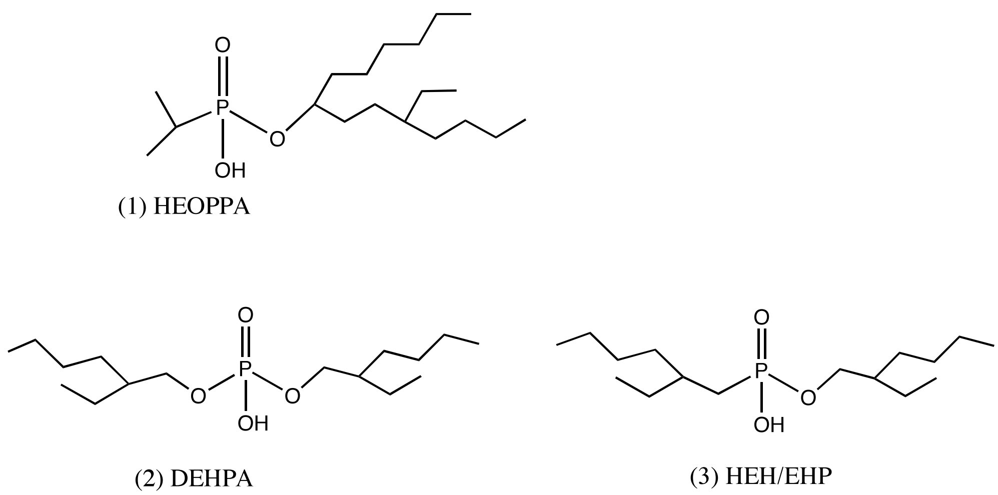


Figure 2.6 Three organophosphorus acids: (1) HEOPPA; (2) DEHPA; (3) HEH/EHP.

Two phosphinic acids, (3-hydroxyphosphinoyl-2-oxo-propyl)phosphinic acid dibenzyl ester (POPDE) and [(2-dihydroxyarsinoylphenylamino)methyl]phosphinic acid (AsP), were bonded to Amberlite XAD-16 (Fig. 2.7).[16, 67] High *D* values were obtained with XAD-16-POPDE for U(VI) at low acidities due to a dual cation exchange / chelating mechanism: P=O and C=O chelate metal ions while the phosphinic acid acts as the cation exchanger. *D* values decrease with increasing acidity due to the formation of anionic metal complexes. U(VI), Th(IV) and La(III) have high D values (10^2-10^4), with the highest values ($D > 10^4$) found with La(III) and XAD-16-AsP.

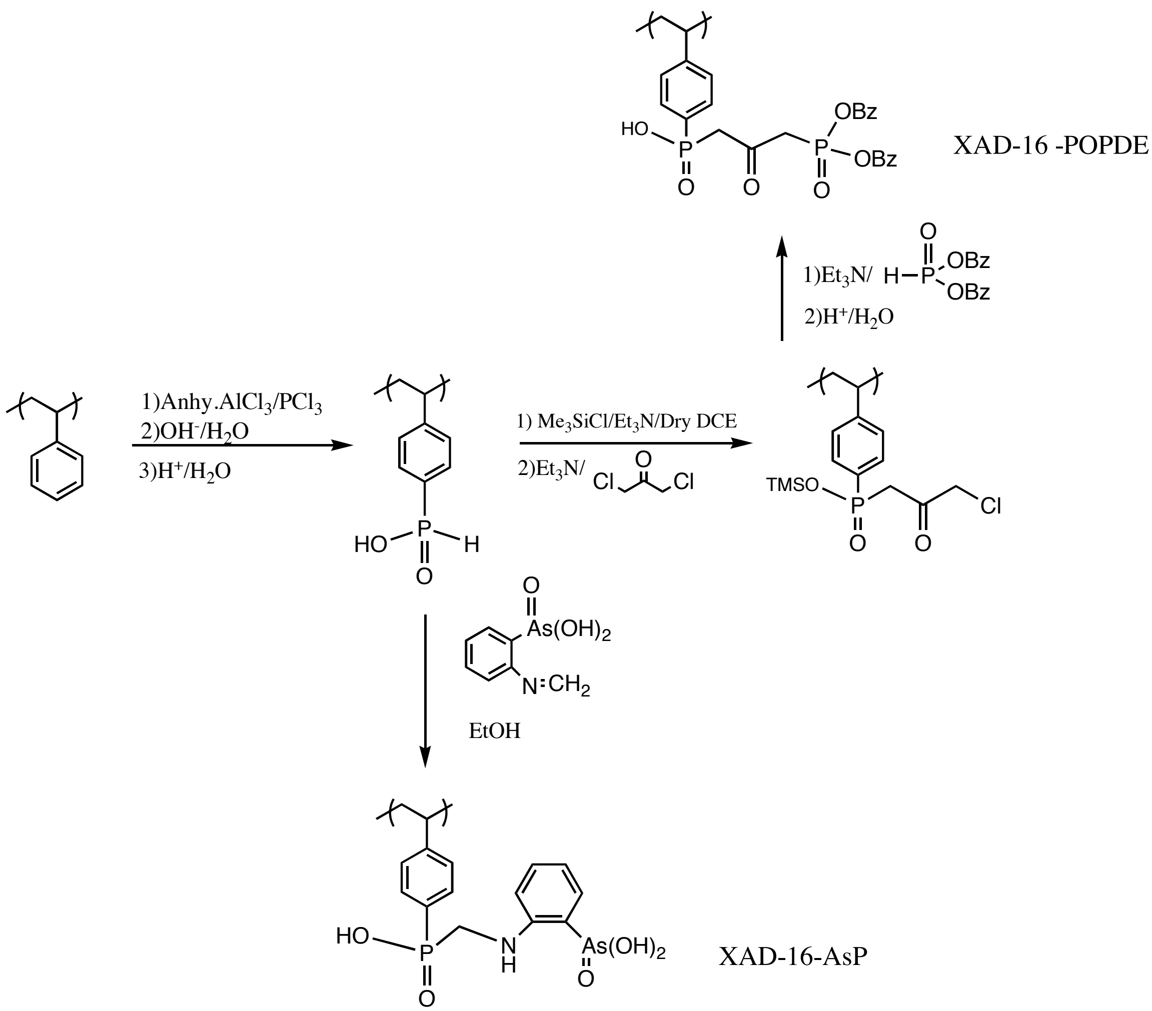


Figure 2.7 Preparation of XAD-14-POPDE and XAD-16-AsP.

2.4.1.3 Polycarboxylic acids

o-Phenylene dioxydiacetic acid (Fig. 2.8) sorbed into Amberlite XAD-2000 was able to preconcentrate U(VI) and Th(IV) from weakly acidic or neutral solutions.[68] The optimum pH for maximum sorption was between 5.5-7.0 for U(VI) and 3-5 for Th(IV).

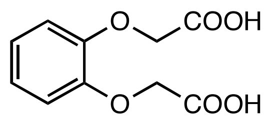


Figure 2.8 *o*-Phenylene dioxydiacetic acid.

A resin identified only as D113 and bearing carboxylic acid groups was studied for the sorption of lanthanides.[69] The capacity for La(III) reached 1.97 mmol/g at pH 6.0. The affinity sequence at pH 6.0 follows the order of decreasing ionic radii, i.e., La > Ce > Gd > Er. FTIR spectra show that the –COOH oxygens coordinate the metal ion to form a stable complex: Upon contact with La(III), the –COOH band at 2544 cm^{-1} vanishes, indicating that the proton exchanges with the lanthanide ion. Additionally, the disappearance of the C=O band at 1721 cm^{-1} and the presence of anti-symmetric and symmetric stretching bands at 1562 cm^{-1} and 1407 cm^{-1} indicate that coordination occurs between the carbonyl oxygen and the metal ions.

Humic acid (a polyelectrolyte with a high density of proton exchanging groups) sorbed within XAD-4 complexes Th(IV) at a pH of 3-7 and U(VI) at pH 5–7.[70] It is thus possible to separate Th(IV) and U(VI) with humic acid/XAD-4 by adjusting the pH. Alkali, alkaline earth and transition metal ions, except Fe(III), do not interfere.

Dibromosuccinic acid has been anchored to XAD-4 (Fig. 2.9).[71] The two-step preparation involves acetylation of XAD-4 and reaction of the resulting ketone with 2,3-dibromosuccinic acid. The resin has a higher capacity for U(VI) than XAD-4/quinoline-8-ol. The sorption of U(VI) reaches a maximum when the pH is above 4.5.

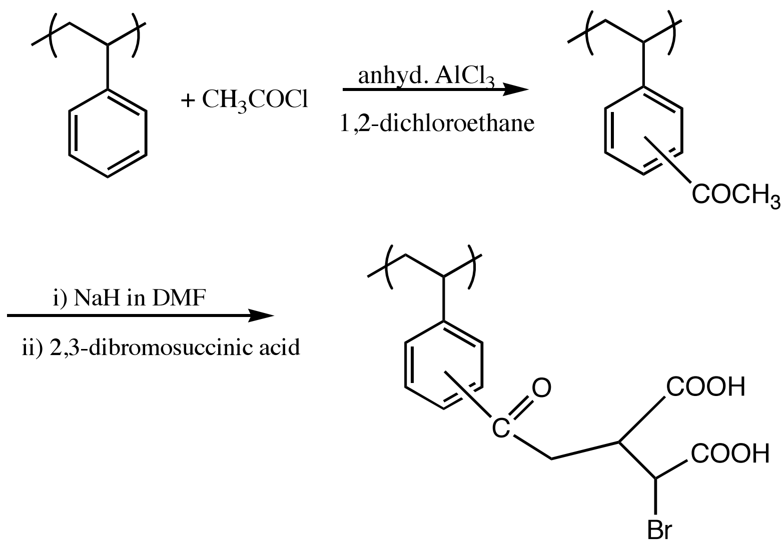


Figure 2.9 Amberlite XAD-4 functionalized with succinic acid.

2.4.1.4 Carbamoylmethylphosphonates and Carbamoylmethylphosphine Oxides

Carbamoylmethylphosphonates and carbamoylmethylphosphine oxides are coordinating complexants having carbonyl and phosphoryl moieties bonded to a central atom. They are known for their ability to extract transuranium elements and are used in the TRUEX (TransUranium Extraction) process. [8, 9, 33, 72, 73, 74] The metal cation interacts with the phosphoryl oxygen while the carbonyl oxygen acts as an external buffer by binding a proton. [9, 75] The intramolecular buffering effect explains their ability to extract trivalent lanthanides and actinides from high concentrations of HNO_3 and HCl.

Diethyl-*N,N*-diethylcarbamoylmethylphosphonate was bonded to poly(vinylbenzyl chloride) through the methylene carbon (Fig. 2.10)[7] and its affinities for Ce(III), Eu(III) and Yb(III) were studied: The *D* values decrease with increasing acid concentration, in contrast to the behavior of the soluble dicyclohexyl-*N,N*-

diethylcarbamoylmethylphosphonate $[(C_6H_{13}O_2)_2P(O)CH_2C(O)N(C_2H_5)_2]$ in which an increase in *D* with increasing acidity was found. However, decreasing *D* values with increasing acid concentration were evident with the soluble complexant having a benzyl group bonded to the methylene carbon.[7] This behavior may be due to steric effects at the coordination site and competitive binding of protons to the more congested molecule.

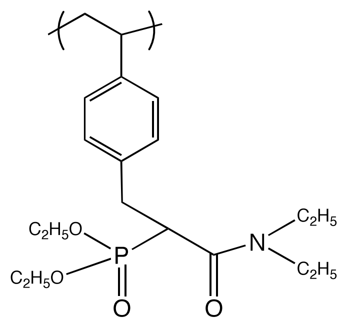


Figure 2.10 The diethyl-*N,N*-diethylcarbamoylmethylphosphonate resin.

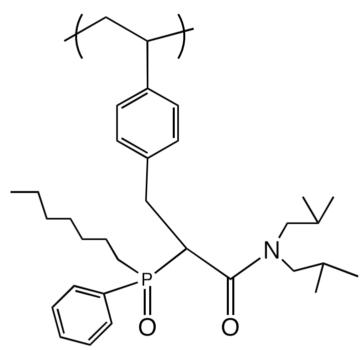


Figure 2.11 Polystyrene-bound octyl(phenyl)-*N, N*-diisobutylcarbamoylmethylphosphine oxide.

Octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) (Fig. 2.11) has been immobilized.[76] The ligand has higher capacities for U(VI) and Th(IV)

(0.96 and 0.98 mmol/g, respectively) than La(III) and Nd(III) (0.49 and 0.50 mmol/g, respectively). At low (< 2M) concentrations of HCl, there is no extraction of the lanthanides while the extraction of U(VI) and Th(IV) is still significant ($D > 100$). This suggests the possibility of separating lanthanides from actinides at low HCl concentration with this polymer.

Sorbents containing CMPO were prepared with polyacrylonitrile (PAN) as the binding matrix and compared to a commercially available extraction chromatography resin.[77] The study showed the distribution coefficients for Pu(VI) to be 60-150 times higher for CMPO-PAN than for the TRU-resin® - a resin in which CMPO and tri-n-butyl phosphate (TBP) are sorbed within an organic polymer matrix. Additional studies with Am(III) have shown that, unlike traditional CMPO acid dependency curves, where *D* values are highly dependent on the range of nitric acid concentration, CMPO-PAN is not very sensitive towards the change of acidity but shows high affinity for Am across a wide range of acid concentrations.

The effect of the polymer matrix is evident when CMPO was sorbed into polyacrylate-based XAD-4 and polystyrene-based XAD-7 for the extraction of U(VI) and Am(III) from 3 M HNO_3.[6] The XAD-7 achieved higher distribution ratios and faster attainment of equilibrium. Not only does the higher porosity of XAD-7 facilitate the diffusion of ions within the resin bead to increase accessibility to the coordination sites, but also the presence of C=O groups in the XAD-7 might contribute to the enhancement of the kinetics compared to the XAD-4. The overall behavior of CMPO within XAD-4 and XAD-7 was comparable to results with CMPO under solvent extraction conditions.

2.4.1.5 Polyphenols and other resins containing oxygen as the only donor atom

9-Phenyl-3-fluorone (Fig. 2.12) sorbed within Duolite XAD-761 (which in itself is a phenol-formaldehyde condensate) chelates Th(IV) and U(VI) in the pH range 4–6.[78] The results show that the presence of ions normally present in water and some transition metal ions do not interfere, suggesting that the preconcentration / separation method can be applied to saline and environmental samples containing transition metals.

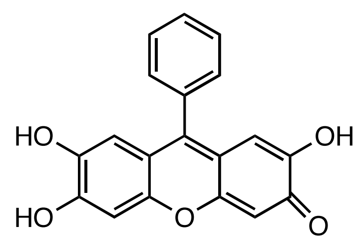


Figure 2.12 9-Phenyl-3-fluorone.

A chelating resin was prepared from 2-hydroxy-4-methoxybenzophenone and ethanediol with polyphosphoric acid as the catalyst (Fig. 2.13).[61] FTIR spectra show the C=O stretching frequencies of the lanthanide-loaded resin to be 1655-1635 cm^{-1}, 20-40 cm^{-1} lower than that of the lanthanide-free carbonyl; this is due to coordination at the carbonyl oxygen. Bands at 465-480 and 565 cm^{-1} also indicate metal-oxygen coordination by phenolic and carbonyl groups. The complex forms with La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy (III) at a 1: 2 metal to ligand ratio (Fig. 2.14). The sorption of lanthanides by the resin increases with increasing solution pH. At pH 5.5, the distribution coefficients are approximately 400 with an order of Tb < Nd < Sm < La < Dy < Gd < Pr (see section 5 for further discussion).

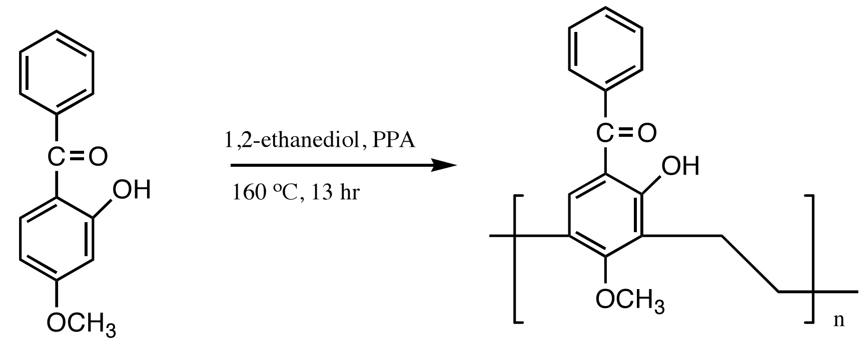


Figure 2.13 Preparation of poly[(2-hydroxy-4-methoxybenzophenone)ethylene].

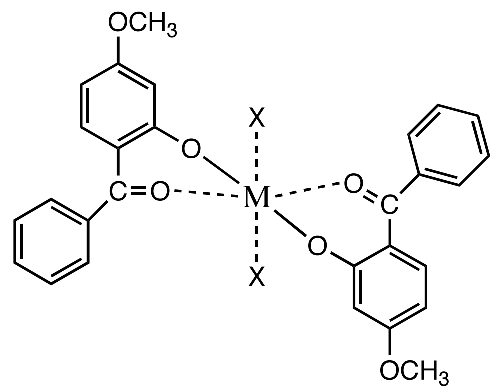


Figure 2.14 Proposed structure of the chelate, where M = La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III), X= H_2O.

Chitosan has been used as a solid support for ion exchange and chelating resins since its amino groups are readily derivatized and it is more hydrophilic than polystyrene. Ethylene glycol diglycidyl ether (EGDE) is used as a crosslinking agent (Fig. 2.15).[79]

A resin containing the 3,4-dihydroxybenzoate (DHBA) moiety was prepared by amidation of cross-linked chitosan (Fig. 2.16).[80] The sorption capacity for U(VI) was as high as 1.39 mmol/g. The ratio of uranium on the resin (1.39 mmol/g) to the amount of DHBA bonded to the resin (2.25 mmol/g) suggested that two DHBA moieties chelate one uranyl ion via neighboring phenolic -OH groups to form a five-membered ring (Fig.

2.17). The 1:2 ratio was again observed when Alizarin (1,2-dihydroxyanthraquinone), also with phenolic OH groups, complexed uranium.[81]

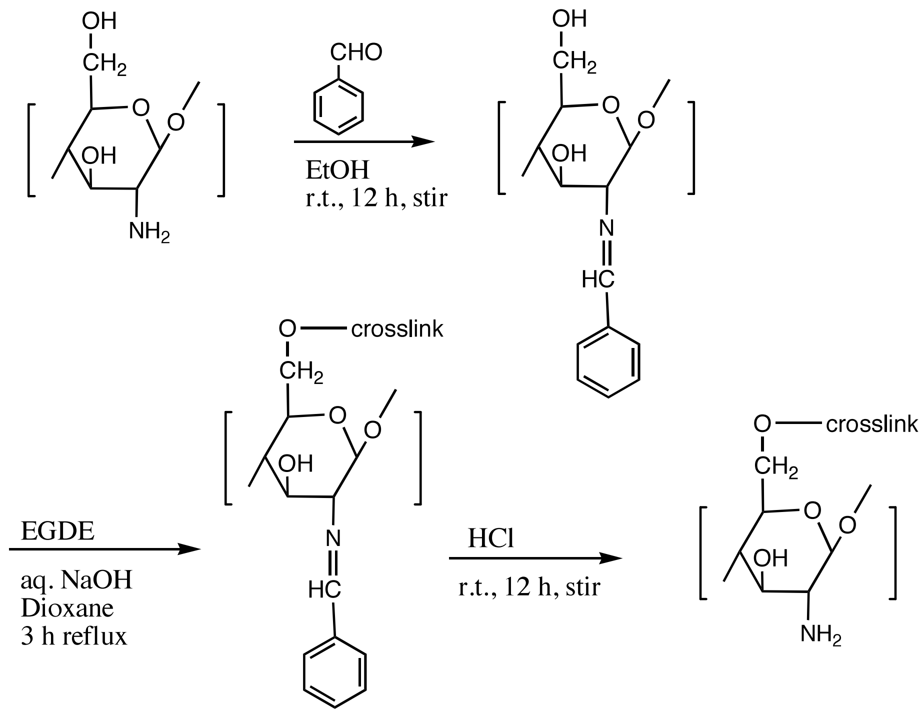


Figure 2.15 Preparation of EGDE - cross-linked chitosan.

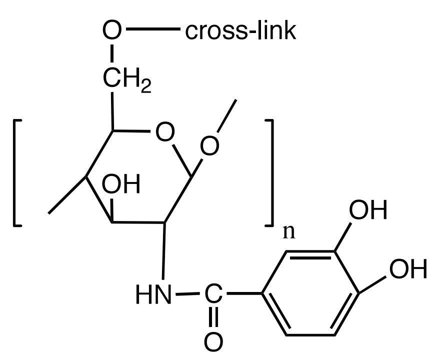


Figure 2.16 Chitosan cross-linked with ethylene glycol diglycidyl ether and functionalized with 3,4-dihydroxybenzoic acid.

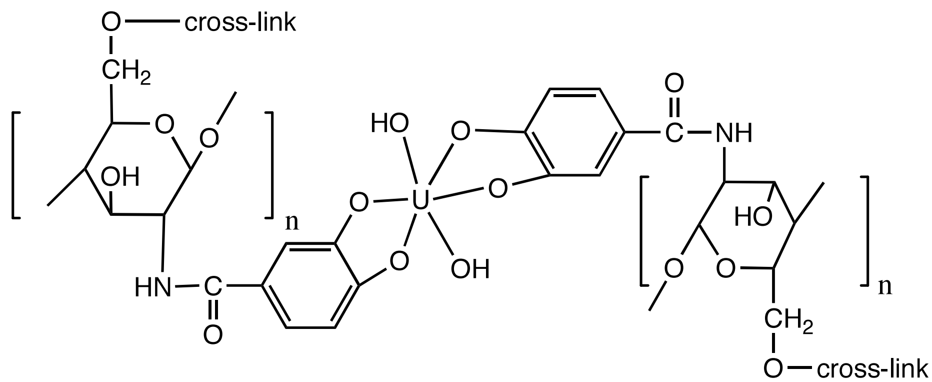


Figure 2.17 Proposed uranyl chelate in chitosan-DHBA resin.

Thenoyltrifluoroacetone (TTA) was immobilized on chloromethylated polystyrene by deprotonation at its methylene carbon (Fig. 2.18).[82] Quantitative extraction of Th(IV) and U(VI) was found in the pH range of 2-4 and 4-5, respectively.

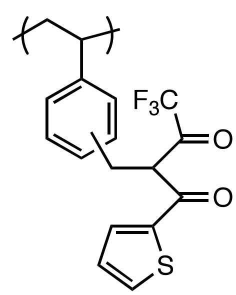


Figure 2.18 Structure of the thenoyltrifluoroacetone resin.

2.4.2 Oxygen and nitrogen as donor atoms

Ligands with oxygen and nitrogen as donor atoms have been incorporated onto different types of matrices. They include polyamino/polycarboxylic acids, hydroxamic acids, iminodiacetic acids and hydroxyquinolines.

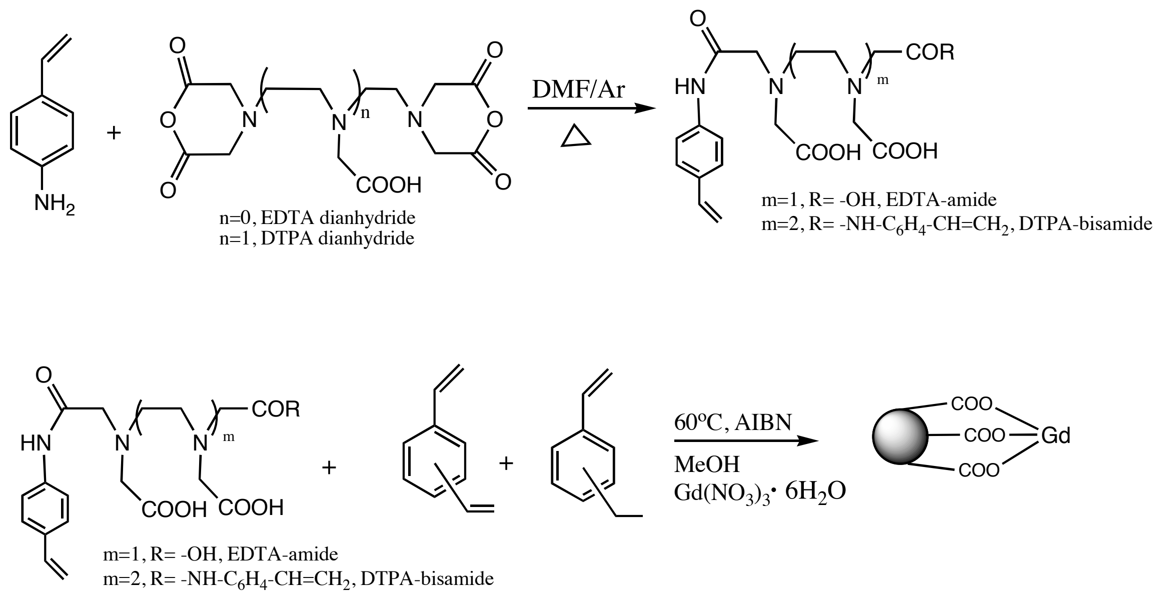


Figure 2.19 Synthesis of polymerizable DTPA- and EDTA-amides for the preparation of Gd(III)-imprinted polymers.

Polyamino/polycarboxylic acids such as diethylenetriaminepentaacetic acid (DTPA) and ethylenediaminetetraacetic acid (EDTA) form stable chelates with the trivalent lanthanides and actinides.[83, 84, 85] Gadolinium-imprinted resins bearing EDTA and DTPA derivatives (Fig. 2.19) were made by copolymerizing DTPA- and EDTA-amides with DVB and p-ethylstyrene in the presence of gadolinium nitrate.[86] The DTPA-amide resin exhibited a much higher Gd/La selectivity than its EDTA counterpart. This is in line with solution studies that found DTPA to be a more powerful chelant for lanthanides by occupying eight binding sites at the metal center compared to EDTA which is considered a pentadentate ligand.[83, 84, 85, 87] This confirms the importance of the number of binding sites on the ligand to ionic recognition. Since EDTA is a fivecoordinate chelating agent, the number of binding sites is probably too low to distinguish Gd(III) and from La(III) thus leading to an ineffective separation of Gd from La.

The ionic form of the resin affects selectivity. The resin is converted to the H^+ form by washing with 1 N HCl and H_2O until neutral, or the Na^+ form by washing with 0.1 N NaOH and H_2O until neutral. The Gd-imprinted DTPA resin in the Na^+ form has a Gd/La selectivity factor of 4.0 – not much higher than the non-imprinted analogue (3.7); on the other hand, the Gd-imprinted DTPA resin in the H^+ form has a selectivity factor of 8.3 – considerably higher than the non-imprinted analogue (4.7). This is probably because the Na^+ form is more ionic, hence more highly hydrated and this introduces greater mobility into the matrix with a resulting loss in selectivity.

While it is most common to immobilize a ligand onto a polymer support or sorb a chelant into the support, it is also possible to bind the chelant electrostatically onto an ion exchange resin. *N*-(2-Hydroxyethyl)ethylenedinitrilotriacetic acid (HEDTA) was exchanged onto the anion-exchange resins Dowex 1×2, Dowex 1×4, Dowex 1×8 and macroporous Dowex MSA-1 and studied for lanthanide separations.[88] The distribution coefficients at pH 7.5 for Dowex 1×2 in the HEDTA form were Dy > Ho > Er > Gd > Tm > Tb > Eu > Sm > Yb ≥ Nd > Pr ≈ La.

The separation of La(III) from other lanthanides was studied with Dowex 1 (which has $^+N(CH_3)_2C_2H_4OH$ as the immobilized group) and Dowex 2x8 (which has $^+N(CH_3)_3$ as the immobilized group) in the acetate and iminodiacetate (IDA) forms at pH 5-6.[89] The affinity series was: Dy > Ho > Gd > Eu > Er > Y > Sm > Tm > Nd > Pr >> La.

The sequence was the same for the anion-exchangers in both forms except that the separation of individual lanthanides was more pronounced with the acetate.

Chitin is a widely available biomaterial that, when deacetylated to form chitosan, can function as a support for different ligands. As one example, chitosan crosslinked with EGDE and modified with serine was prepared (Fig. 2.20).[79] This resin selectively binds the uranyl ion from acidic and alkaline solutions. The nitrogen and oxygen of the serine chelate the central metal while the amino groups of the chitosan hydrogen bond to the uranyl's two oxygen atoms (Fig. 2.21).

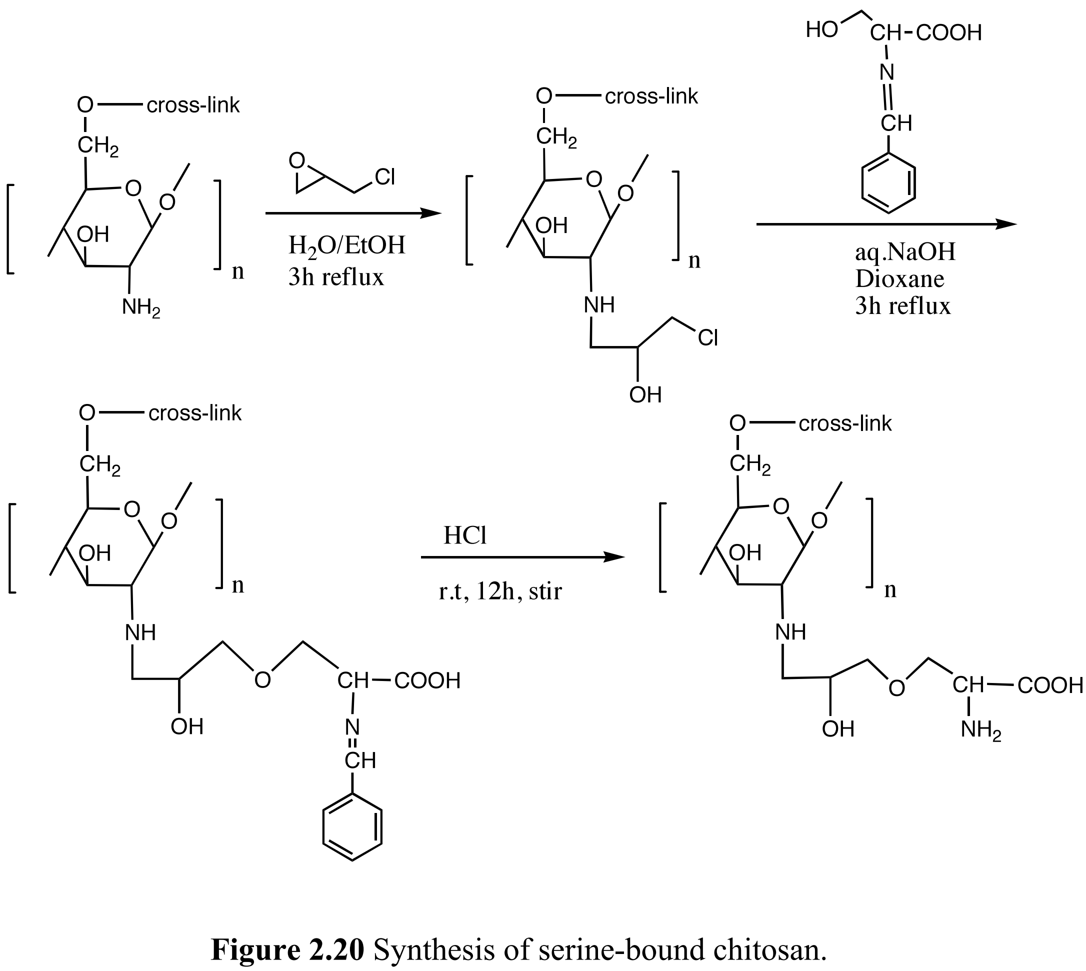


Figure 2.20 Synthesis of serine-bound chitosan.

The coordination chemistry of IDA and related ligands is well established.[90] IDA is capable of both cation-exchange and chelation.[91] In ion-exchange chromatographic separations with a weakly complexing mobile phase, increased retention is expected of ions with an increasing charge density (i.e., La to Lu) due to the increasing electrostatic interaction with the immobilized phase. The chelating affinity of IDA also increases from La to Lu.[92] IDA bonded to silica can be used for the isocratic separation of the lanthanides.[92] A good correlation of lanthanide retention with stability constants was obtained, indicating that chelation was dominant. Gd(III) has a lower retention than Eu(III); this "gadolinium break" arises because gadolinium has a lower stability constant than europium.

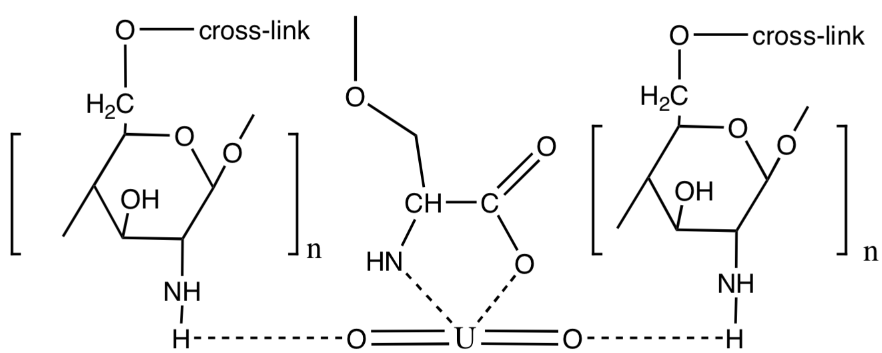


Figure 2.21 Proposed chelate structure in serine-bound chitosan with UO_2^{2+}.

Polystyrene-supported *N, N*-bis(2-hydroxyethyl)glycine (Fig. 2.22) was reported to be capable of separating La(III), Nd(III), Tb(III), Th(IV) and U(VI) from Ni(II), Zn(II), Co(II) and Cu(II) at pH 4–5.[93] One advantage of this resin is the high tolerance for alkali and alkaline earth metal ions which makes it useful for the analysis of U(VI) and Th(IV) in samples such as sea water.

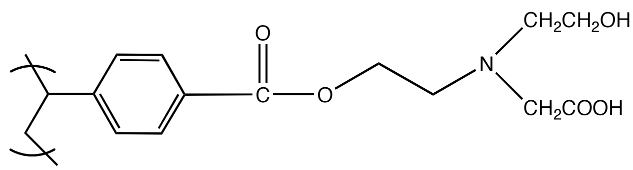
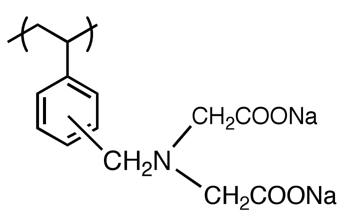
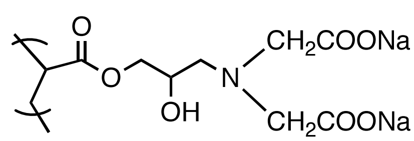


Figure 2.22 Polystyrene-supported *N, N*-bis(2-hydroxyethyl)glycine.

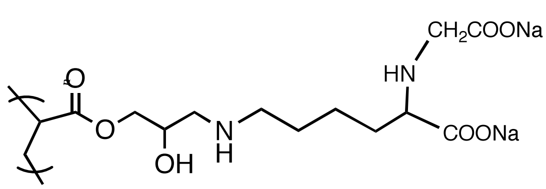
The effect of spacer arms on sorption behavior was investigated by comparing three types of chelating resins containing iminodiacetic acid homologues with spacer arms of varying length (IDA Resins I, II, III in Fig. 2.23).[94] By studying the relationship between the lanthanide affinity of the resins and the corresponding IDA complexes in homogeneous solutions, it was concluded that the selectivity of lanthanides by the resins was consistent with the stabilities of the monomeric ligands when a long spacer arm was present as in Resin III. Poor correlations were found with Resins I and II indicating that a short spacer arm decreases the complex stabilities and so affects the observed selectivity. The lanthanide affinities decrease with increasing solution acidity while selectivity follows the order of ionic radii: Lu > Ho > Gd > Sm > Ce.



IDA resin I



IDA resin II



IDA resin III

Figure 2.23 Structure of IDA Resins.

The *N*-methyl-γ-aminobutyrohydroxamate resin [95] was used in the chromatographic separation of lanthanides from alkali, alkaline earth, and other ions in seawater. The anchoring of the hydroxamic acid is shown in Fig. 2.24.[96] Retention times of Er < Eu < Sm < La were observed when lanthanides were separated by isocratic and gradient elution, following the order of increasing ionic radius and decreasing hydration energies. The smaller the ionic radius, the greater the hydration energy and the lower the affinity of the ion for the stationary phase. The order changes when the lanthanide-containing solutions were separated on Dionex CS-5 as the stationary phase using gradient elution with 0.06 M oxalic acid to 0.02 M oxalic acid – 0.01 M diglycolic acid: La < Ce < Pr <Nd < Eu < Sm < Gd < Tb < Dy < Ho < Er. The change in elution order is related to the change in separation mechanism from chelation to ion exchange. With stronger complexing agents, such as oxalate, the separation of lanthanides proceeds by anion exchange in which the strongest complexes are the most negatively charged.

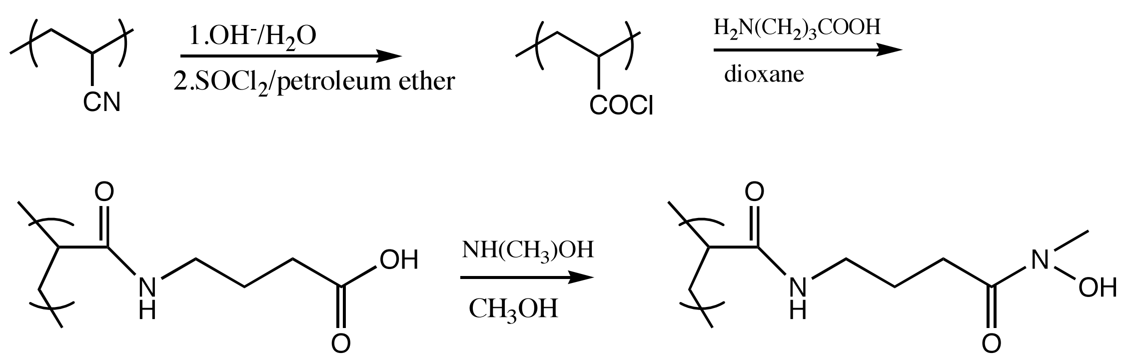


Figure 2.24 Preparation of the *N*-methyl-γ-aminobutyrohydroxamate resin.

Bis-2[(*o*-carbomethoxy)phenoxy]ethylamine was bonded to polystyrene by reacting it with bromoacetylated XAD-4 followed by hydrolysis in 10% NaOH as shown in Fig. 2.25.[97] The sorption capacity for La(III), Nd(III) and Sm(III) depends on the solution pH due to competing protonation. The capacity increases sharply from a solution at pH 4 to a limiting value at pH 5.5. The slopes of the log*D* vs pH plots are equal to 2, indicating complexation occurs by ion exchange and release of two protons.

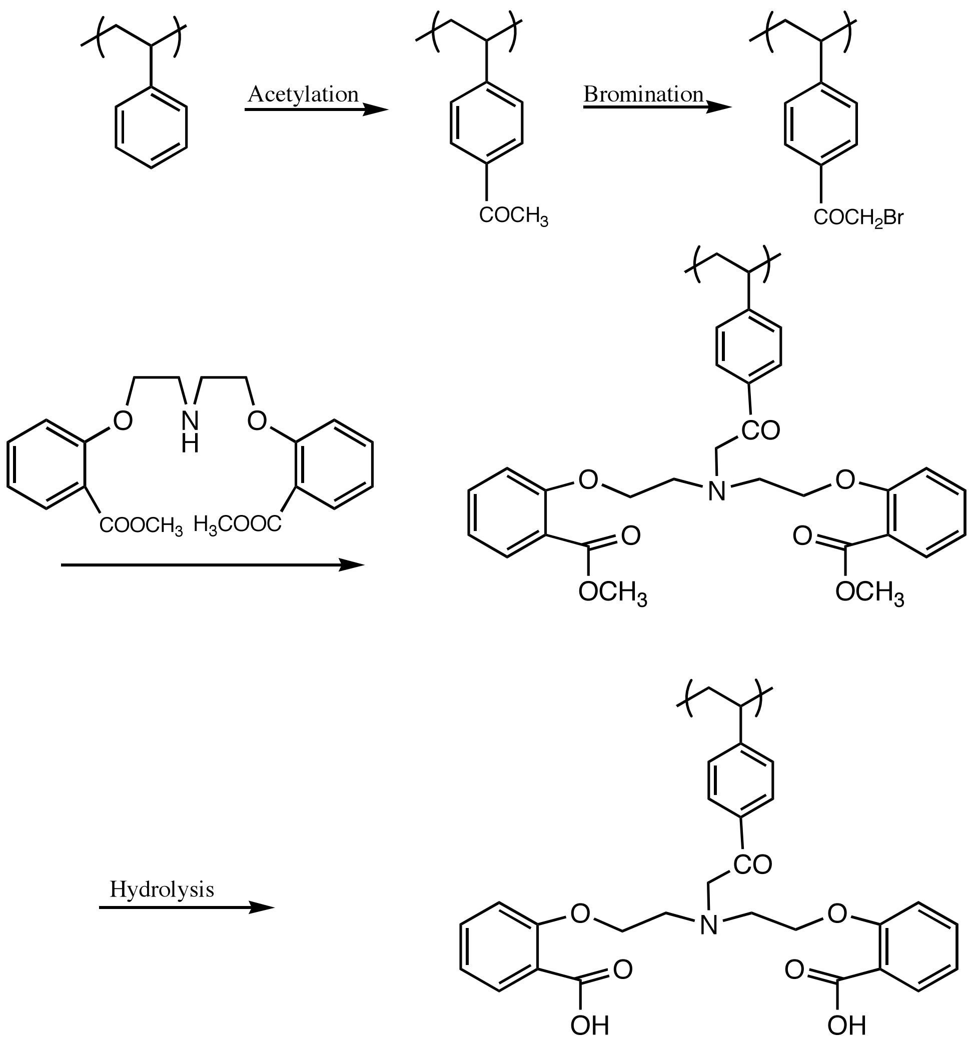


Figure 2.25 Preparation of bis-2[(*o*-carbomethoxy)phenoxy]ethylamine resin.

o-Vanillinsemicarbazone (*o*VSC) has been bonded to XAD-4 through the –N=N- group.[98] The synthesis involves diazotization and coupling reactions (Fig. 2.26). *o*VSC provides three binding sites--phenol oxygen, carbonyl oxygen and nitrogen-- in forming two chelating rings. *D* values for La(III), Ce(III) Th(IV) and U(VI) at their optimum pH (3.0-4.5 for Th(IV), 6.0-8.0 for U(VI), and 6.0-9.0 for La(III) and Ce(III)) are 3300, 3583, 5155, and 4950 respectively.

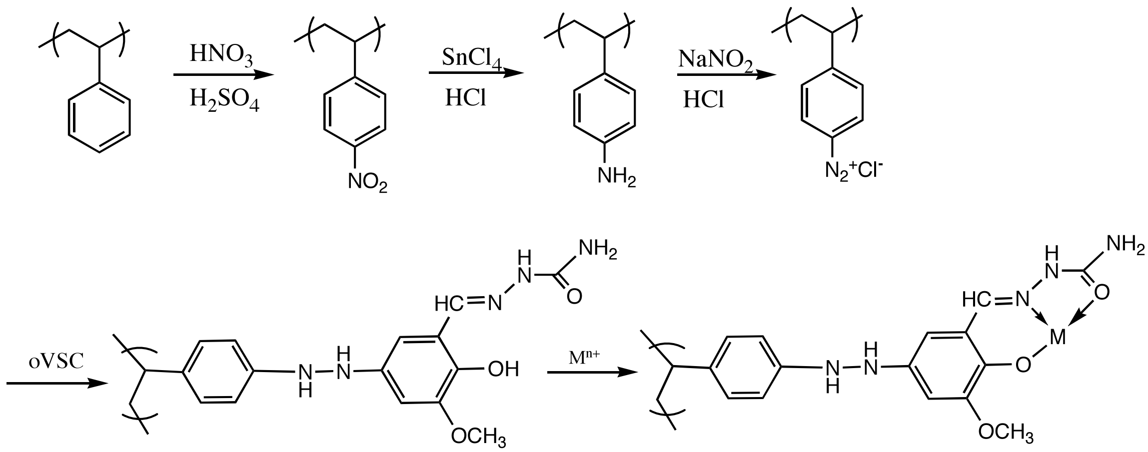


Figure 2.26 Preparation of XAD-4-*o*VSC resin.

4-(2-Thiazolylazo)resorcinol (TAR) sorbed into XAD-16 was reported to have a relatively high selectivity for U(VI) over other divalent and trivalent metal ions except Cu(II).[99] The order of distribution coefficients was U(VI) >> Ni(II) ≈ Co(II) > Yb(III) ≈ Gd(III) > Zn(II) > La(III) > Mn(II) at pH 3.9. However, the selectivity disappears with a decrease in pH from 3.9 to 2.0, at which point complete separation of only Cu(II) from other metal ions is possible.

TAR can also be grafted onto aminated XAD-16 through the –N=N- link (Fig. 2.27) in a manner similar to that shown in Fig. 2.26.[100] This chelating resin has a higher sorption capacity (0.62 mmol/g) for U(VI) than its sorbed counterpart (0.16 mmol/g).[99] The capacity increases with increasing pH but selectivity decreases, which is consistent with TAR-sorbed XAD-16. The selectivity sequence was also similar to that of its sorbed counterpart: Cu(II) > U(VI) > Ni(II) > Pb(II) > Co(II) > Fe(III) > Cd(II) > Yb(III) > Gd(III) > Al(III) > Zn(II) > La(III) > Mn(II).

Quinoline-8-ol (Fig. 2.28), in which the pyridyl nitrogen and adjacent phenolic –OH group are involved in chelation, has been anchored onto chloromethylated polystyrene by reacting it with 5-aminoquinoline-8-ol.[101] The polymer-supported quionoline-8-ol has a high affinity for U(VI) over Th(IV) and La(III) in the pH range of 5-6. The same functional group was also used for the solid phase extraction of U(VI) by sorption into XAD-4 at pH 4-5.5.[102] EDTA was added as a masking agent to eliminate interference from other metal ions since quinoline-8-ol chelates many ions.

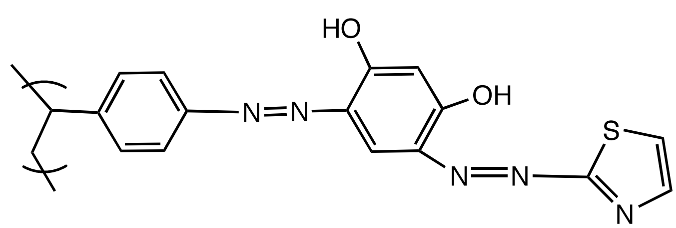


Figure 2.27 4-(2-Thiazolylazo)resorcinol (TAR) bonded to XAD-16.

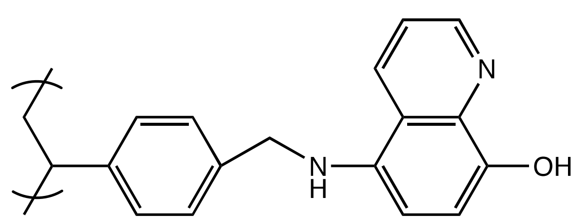


Figure 2.28 Polystyrene-bound quinoline-8-ol.

Under appropriate conditions, immobilized (dimethylaminophosphonomethyl)-phosphonic acid (Fig. 2.29) binds metal ions through both the nitrogen and the phosphoryl oxygens.[103] It is highly selective in extracting U(VI) and Th(IV) from highly acidic and near neutral solutions.

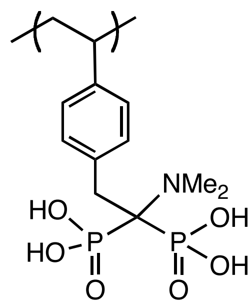


Figure 2.29 Polystyrene-supported (dimethylaminophosphonomethyl)phosphonic acid.

2.4.3 Nitrogen as the only donor atom

Nitrogen-donating ligands are softer than oxygen and often incorporated into an aromatic ring. The pyridine resin (Fig. 2.30) has been used in the separation of rare earth ions.[20, 21, 104, 105, 106, 107] The unprotonated resin has a higher affinity for actinides and lanthanides than the protonated form, supporting the hypothesis that the ions bind to the free nitrogen.[105] Time-resolved laser-induced fluorescence spectroscopy was used to study the coordination states of Eu(III) in the pyridine resin.[20, 21] It has a higher affinity for actinides than lanthanides from aqueous methanol solutions containing either HCl or LiCl due to the modest enhancement of covalency involving actinide s or p orbitals. Adding alcohol to the solvent promotes sorption of the lanthanides by decreasing the activity of “free” water and therefore enhancing the formation of the inner-sphere Ln(III)-chloro complex.

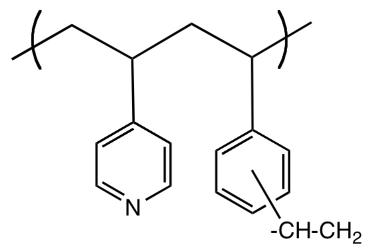


Figure 2.30 The pyridine resin.

The distribution coefficients of lanthanides and actinides complexed by the pyridine resin from methanolic HCl solutions decrease with decreasing ionic radii.[105] In a plot of the distribution coefficients vs ionic radii, three separate correlations are seen: a line associated with trivalent actinides having 5f-electrons, a line associated with lanthanides having 4f-electrons (Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, and Lu) and a line associated with ions having no f-electrons (Y and La). The linearity with the lanthanides was not observed in nitric acid: The decreasing distribution coefficients with decreasing ionic radii formed an S-shaped curve.[106, 107] The trivalent actinides show far greater distribution coefficients than the lanthanides from HCl than from HNO_3. For example, the *D* value for Am(III) is 100 from alcoholic HCl and 10 from alcoholic HNO_3; the *D* value for Eu(III) is 3 from alcoholic HCl and 4 from alcoholic HNO_3. Additionally, Am(III) and Cm(III) have only moderately different *D* values compared to Nd(III) and Sm(III) in alcoholic HNO_3 suggesting that their separation from the middle lanthanides might be difficult to achieve from nitric acid solutions. The difference in behavior between HCl and HNO_3 solutions may be due to different speciation of the metal ions.

The pyridine resin was examined for the sorption of U(VI) and Pu(IV) by anion exchange.[108] It was found that both are strongly sorbed from concentrated HCl and distribution coefficients increase with increasing HCl concentration.

A resin prepared by sorption of 2,6-bis-(5,6-dibutyl-1,2,4-triazine-3-yl)pyridine (Fig. 2.31) into a porous silica/polymer composite support was studied for the extraction of lanthanides and actinides from aqueous nitric acid at pH 1.0.[109] The resin shows significantly higher selectivity for Am(III) and Cm(III) compared to the lanthanides. The sorption of Eu(III) and Gd(III) increases with nitrate concentration, which is similar to results with Am(III) and Cm(III). Ce(III) is not sorbed from 1 M to 4 M nitrate solutions. The resin has no affinity for Cs(I), Sr(II), Zr(IV), Mo(VI), Ru(III) and Rh(III) over a concentration range of 0.5 to 4.6 M nitrate salt at pH 1.0. Pd(II) is strongly sorbed at low nitrate concentration and its sorption decreases with increasing nitrate, which is the reverse of the nitrate dependency of Am(III), Cm(III) and the lanthanides.

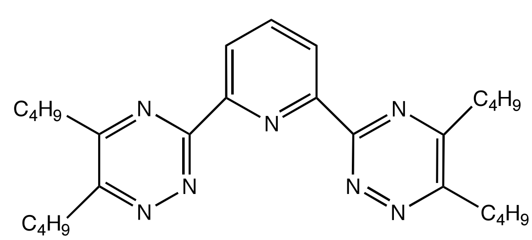


Figure 2.31 2,6-bis-(5,6-dibutyl-1,2,4-triazine-3-yl)pyridine.

Aliquat-336 (a quaternary ammonium salt) sorbed into XAD-4 was used to remove La(III) and Gd(III) from nitrate solutions.[110] Maximum sorption was reached at pH 5.5 for Gd(III) and pH 6.5 for La(III).

Strongly basic anion-exchangers with quaternary amine groups are placed in the *N*-donor category even though these operate solely by ion exchange. The polyacrylate anion-exchange resins Amberlite IRA 458 and IRA 958 (Fig. 2.32) were used to separate Sm(III)-Ho(III), La(III)-Nd(III) and La(III)-Pr(III) with IDA at pH 6.0.[111] The lanthanides form anionic IDA complexes and are then exchanged onto the resin. Nd(III) and Pr(III) complexes of IDA exhibit higher affinity for the anion-exchangers than the La(III) complex. Similarly, there is a higher affinity for the complexes of Ho(III) over Sm(III), thus allowing for their separation. The best separation of La(III) from Nd(III) is obtained with the polyacrylate anion-exchangers in the chloride form; this differs from the polystyrene anion-exchangers which are ineffective for the separation of rare earth IDA complexes. This may be due to the greater ligand flexibility and hydrophilicity of the polyacrylates and the hydrogen-bonding possible through the amide groups.

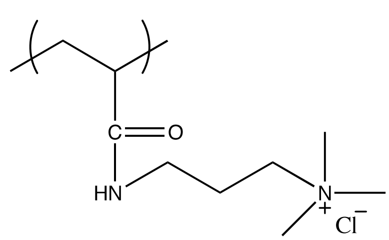


Figure 2.32 The structure of Amberlite IRA 458 and IRA 958.

2.4.4 2.4.4 Sulfur as the donor atom

Sulfur is a softer donor than oxygen and nitrogen and is expected to prefer actinides over lanthanides. Consistent with this, Chromosorb W, a chromatographic resin impregnated with bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) (Fig. 2.33), has a separation factor of ~1000 for Am(III) over Eu(III) from nitrate solutions due to the preference for Am(III) by the thiophosphinic acid.[112] Cyanex 301 showed a much higher affinity for Am(III) and a greater Am(III)/Eu(III) separation factor on Chromosorb W than on XAD-4, XAD-7 and Chromosorb 102. The complexing ability of agents added to the aqueous phase affects the apparent Am(III) and Eu(III) affinities and their separation. Strong complexing agents such as EDTA and DTPA result in low distribution coefficients for both ions and hence poor separations. Good separation was achieved with the nitrate ion, a weaker complexing agent. As the nitrate concentration increased, the affinity decreased more for Eu(III) than for Am(III) and that led to increased separation factors. The pH dependency study suggested that the extracted species were AmL_3 and EuL_2NO_3 (where L is Cyanex 301).

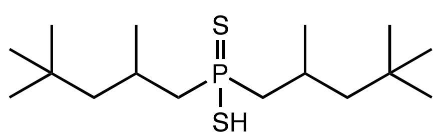


Figure 2.33 Cyanex 301. Reprinted with permission from refs 112 and 113.

In a separate study on the extraction of lanthanides by a silica-based resin containing Cyanex 301,[113] it was found that Ce, Gd, and Eu are only slightly sorbed from solutions at pH 2 to 5 by this resin while the sorption of Am increased sharply with increasing pH to again give an Am(III) / Ln(III) separation factor of ~1000. On the other hand, it is difficult to separate Am(III) from the light lanthanides (La(III), Ce(III) and Nd(III)) with di(2-ethylhexyl)phosphoric acid sorbed within silica.

The sorption of U(VI) by XAD-16 containing *N,N*-dibutyl-*N'*-benzoylthiourea (Fig. 2.34) was studied by FTIR spectroscopy.[34] The characteristic frequency of the amide and C=S stretching bands shift by 2 to 17 cm^{-1} to lower frequency upon complexation. The effect of pH on the complexation of uranium showed an increasing trend from pH 2 to 4.5 and a maximum in the pH range 4.5-7. The sorption capacity was 0.90 mmol/g at pH 5. The complexation of uranium was not affected by the presence of Ni(II), Co(II), Pb(II), Cd(II), Zn(II), Mn(II) and Fe(III).

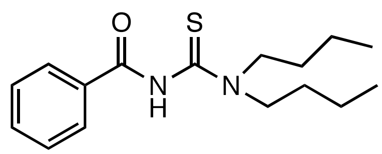


Figure 2.34 *N,N*-Dibutyl-*N'*-benzoylthiourea.

2.5 General trends: Analysis of the distribution coefficients

To a large extent, the design of immobilized ligands for metal ion separations has depended on hard-soft acid-base theory: The softer (more polarizable) the metal, the softer the ligand that will be selective for it. This is useful when the goal is to separate dissimilar ions such as Hg(II) from Co(II). However, choosing a ligand becomes more difficult when the ions have similar properties, as do the lanthanides. With that in mind, the ligands in this review were examined to discern trends that would be useful in a more finely tuned design. Their affinities can be compared for a given ion only when the distribution coefficients are reported under similar conditions; the available data are thus grouped under either highly acidic (4 – 6 M HNO_3) or nearly neutral (pH > 4) solutions. The supports are polystyrene-based unless otherwise noted.

From highly acidic solutions, ligands have an affinity for La(III) in the order of [(2-dihydroxyarsinoylphenylamino)methyl]phosphonic acid > (3-hydroxyphosphinoyl-2-oxopropyl)phosphonic acid dibenyl ester > (dimethylaminophosphonomethyl)-phosphonic acid > 4-ethoxy-*N,N*-dihexylbutanamide > CMPO > *N,N*-dihexylsuccinamic acid (Table 2.1).

Table 2.1 La(III) affinities by polymer ligands from 4 – 6 M HNO_3

Ligand	*D*	Ref
[(2-dihydroxyarsinoylphenylamino)methyl]phosphonic acid	11000	67
(3-hydroxyphosphinoyl-2-oxopropyl)phosphonic acid dibenzyl ester	1100	16
(dimethylaminophosphonomethyl)phosphonic acid	800	103
4-ethoxy-*N,N*-dihexylbutanamide	360	18
CMPO	180	76
N,N-dihexylsuccinamic acid	150	19

The Nd(III) distribution coefficients from 4 M HNO_3 show ligand affinities of 4-ethoxy-*N,N*-dihexylbutanamide > CMPO > *N,N*-dihexylsuccinamic acid (Table 2.2). Though fewer data are available for Nd(III), the trend is consistent with that for La(III).

Table 2.2 Nd(III) affinities by polymer ligands from 4 M HNO_3

Ligand	***D***	ref
4-ethoxy-*N,N*-dihexylbutanamide	530	18
CMPO	180	76
N,N-dihexylsuccinamic acid	100	19

The ligand affinities for La(III) under near-neutral conditions are bis-2[(*o*-carbomethoxy)phenoxy]ethylamine > carboxylic acid > *o*-vanillinsemicarbazone > Aliquat 336 > 4-(2-thiazolylazo)resorcinol > quinoline-8-ol (Table 2.3).

Table 2.3 La(III) affinities by polymer ligands from near-neutral solutions

Ligand	***D***	ref
bis-2[(*o*-carbomethoxy)phenoxy]ethylamine	31600	97
carboxylic acid[a]	9100	69
o-vanillinsemicarbazone	3300	98
Aliquat-336[b]	1000	110
4-(2-thiazoylazo)resorcinol	135	99
quinoline-8-ol	0	101

[a] polymer not well defined

[b] chelant sorbed within XAD-4

The affinities for Gd(III) from solutions at pH > 4 are 1-hexyl-4-ethyloctyl isopropylphosphonic acid ≈ bis(2,4,4-trimethylpentyl)monothiophosphinic acid > carboxylic acid > 2,6-bis-(5,6-dibutyl-1,2,4-triazine-3-yl)pyridine > Aliquat 336 > 4-(2-thiazolylazo)resorcinol (Table 2.4). Generally, the results show that acids have the highest affinities, quaternary amines have moderate affinities, and resorcinol and quinolinol have low affinities.

Table 2.4 Gd(III) affinities by polymer ligands from near-neutral solutions

Ligand	***D***	**ref**
1-hexyl-4-ethyloctyl isopropylphosphonic acid[a]	$>10^4$	65
bis(2,4,4-trimethylpentyl)monothiophosphinic acid[a]	$>10^4$	66
carboxylic acid[b]	2500	69
2,6-bis-(5,6-dibutyl-1,2,4-triazine-3-yl)pyridine[c]	1050	109
Aliquat-336[d]	1000	110
4-(2-thiazolylazo)resorcinol	230	101

[a] macroporous polystyrene support is likely but not specified

[b] polymer not well defined

[c] chelant sorbed within a silica-polystyrene composite

[d] chelant sorbed within XAD-4

HDEHP and bis(2,4,4-trimethylpentyl)-dithiophosphinic acid (Cyanex 301) illustrate the correlation of ligand polarizability and lanthanide affinity due to the similarity of their structures. An affinity sequence of Gd > Eu > Ce is observed for HDEHP in 0.1 M HNO_3 and the sequence remains when the data are extrapolated to pH 4 solutions from a plot of *D* vs. [HNO_3]; this compares to an order of Ce > Eu ≈ Gd for Cyanex 301 at pH 4.[113] The affinity sequences reflect the polarizability of each ligand. The sequence for HDEHP follows an order of decreasing hardness from Gd to Ce but the sequence reverses for Cyanex 301. This is in line with HSAB theory since HDEHP, as an *O*-donor, is harder than Cyanex 301, in which sulfur is the donor atom, thus preferring the lanthanides toward the latter part of the series with their greater charge density. That coordination, not ion exchange, is operative with Cyanex is evident from the curved correlation of the log*D* vs pH plot.[113]

HSAB theory is not always successful in predicting ligand – lanthanide affinities. For example, an order of Tb < Nd < Sm < La < Dy < Gd < Pr was found with poly[(2-hydroxy-4-methoxybenzophenone)ethylene] at pH 5.5[66] which cannot be explained with HSAB theory alone since there is no simple ordering of the lanthanide sequence. This implies that there are other factors, such as geometrical constraints, involved in determining ion affinities by chelants. Additionally, the complexation mechanism affects the affinity sequence[95] (this will be elaborated in the following section). However, ion/ligand polarizability is often the dominant variable, making HSAB theory an important starting point in any ligand design. The results in this review, taken as a whole, suggest that chelants designed for intra-lanthanide separations and to separate lanthanides from other ions, especially in acidic solutions, should bear the –P(O)OH group.

2.6 The Variables Affecting Ionic Affinities

The two principal mechanisms of interaction between a ligand and a metal ion are ion exchange (or ion-pairing) in which complexation is due to an electrostatic interaction, and coordination in which complexation is due to a primarily covalent interaction. With either mechanism, there are four factors influencing the affinity sequence: the basicity or polarizability of the ligand vs the acidity or polarizability of the ion; the degree to which solution conditions result in protonation of the ligand; association of the metal ion with counterions; and the extent of hydration of the ion.

The interaction of the ligands with the lanthanides is determined by their basicity and the acidity (or electronegativity) of the ions. The more basic the ligand and the more electronegative the cation, the more dominant becomes the ion exchange mechanism. For a given ligand, with all other factors constant, the affinity of the ligand with lanthanides should increase with the decrease in ionic radius across the series (which is reflected in the increasing electronegativity from La^{3+} to Lu^{3+}).[114] This continuously increasing affinity sequence is observed when the ion-exchange mechanism is operative: In the extraction of lanthanides by 1-hexyl-4-ethyloctylisopropylphosphonic acid or bis(2,4,4-trimethylpentyl)monothiophosphinic acid, sorption occurs by cation exchange and the distribution coefficients decrease in the order:[65, 66] Gd < Tb < Dy < Ho < Er < Tm < Yb < Lu. The pH studied was 1-2 for the former and 1-3 for the latter. That ion exchange was the sole mechanism of complexation is seen from the log*D* / pH plots wherein all metals had a slope of 3. The same order is found with a carboxylic acid resin.[115]

The acidity of the solution can change the complexation mechanism by affecting the speciation of the lanthanide ion and protonation of the ligand. For example, in separation systems involving malonamide ligands, when the nitric acid concentrations are below 1 M, the malonamide ligand is unprotonated and the sorption of Tb(III) and Am(III) occurs by coordination.[1] The dominant species is the monoprotonated malonamide·HNO_3 in acid solutions of 1 – 6 M and the diprotonated malonamide·$2HNO_3$ forms above 7 M HNO_3. Ion-pairing thus occurs when the nitric acid concentration exceeds 1 M.[1] Protonation is a competitive effect because the basic functional groups attract not only M^{n+} but also H^+ in solution thus decreasing the apparent affinities for the metals from highly acidic solutions.[16, 17, 18, 19, 34, 61, 65, 66, 70, 75, 82, 93, 98, 99, 100, 113]

Nitrate and chloride ions are two common counterions. Nitrate tends to form inner-sphere complexes with the lanthanides while chloride forms outer-sphere complexes.[116, 117, 118] Outer-sphere chlorocomplexes can convert to inner-sphere depending on the solution: in LiCl-H_2O and LiCl-(H_2O+CH_3OH), the level of inner-sphere lanthanide chlorocomplexes is higher in the latter due to the decrease of "free" water activity caused by the presence of alcohol.[105] Counterion coordination of the lanthanides influences their speciation. In high HNO_3 concentrations (> 6 M), two nitrates coordinate to the cation in a bidentate manner; the formation of a dinitrato complex contributes to the decrease in affinity of the lanthanides because the complexes are very stable in the aqueous phase and do not favor coordination to the ligand.[16, 17, 18, 19]

The complexation of metal ions competes with hydration: Water coordinates to ions in solution thereby affecting their interaction with immobilized ligands. The dehydration enthalpy ($-\Delta H_h$) quantifies the strength of the cation-water interaction and these enthalpies increase across the series from La to Lu.[119] In a study of inner sphere coordination at low (0.25 M HCl) and high (14 M LiCl) chloride concentrations, it was found that the Ln-O bond length of La, Ce, Nd, Eu and Yb decreases (2.54, 2.52, 2.49, 2.43 and 2.32 Å, respectively) in low [Cl^-], indicating tighter binding of water across the series.[120] The decreasing water exchange rate of Ln aquo-complexes with increasing atomic number further confirms that hydration of the lanthanides becomes stronger with increasing atomic number.[37, 38] If hydration outweighs other factors (including polarizability), the affinity sequence across the series is expected to decrease with increasing hydration energy from La to Lu. An example of this is the order of retention times Er < Eu < Sm < La in the separation of lanthanides using the *N*-methyl-γ-aminobutyrohydroxamate resin as the stationary phase:[95] The trend can be rationalized only in terms of the increasing hydration energies of the ions from La to Er.

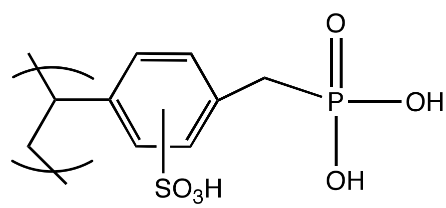


Figure 2.35 Bifunctional phosphonic/sulfonic acid resin.

The importance of hydration is further emphasized by noting that the polymer must be compatible with the hydrophilicity of the metal ion in order to observe rapid rates of metal ion complexation. Dual mechanism bifunctional polymers were thus developed and found to be selective with rapid kinetics by combining two mechanisms—an access mechanism to bring metal ions into the polymer and a recognition mechanism to selectively interact with the metal ions.[27] In one example, a bifunctional phosphonic/ sulfonic acid resin (Fig. 2.35) was prepared rapidly complexed Eu(III) from both low (0.1M HNO_3) and high (1 M HNO_3) acid solutions. It was shown that the sulfonic acid ligand is not responsible for a significant amount of complexation but rather acts to enhance the accessibility of the phosphonic acid ligand to the metal ions.

2.7 Conclusions

A review of the ligands most often incorporated chemically and physically into polymers, as summarized in the preceding tables, shows that the distribution coefficients towards lanthanides follow different trends under different conditions. A comparison of these distribution coefficients indicates that phosphonic acids offer the greatest potential for the design of lanthanide-selective resins under either highly acidic or nearly neutral conditions. HSAB theory can be used to predict ionic affinities. While often the dominant effect, it is also important to consider the degree to which the metal ion coordinates to the counterions, the extent to which ligands are protonated, and the enthalpy of hydration.

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3 Polystyrene-bound *N,N,N',N'*-Tetramethylmalonamide (TMMA)

3.1 Introduction

N,N-dialkylamides have received much attention recently due to their ability to extract lanthanides and actinides from nuclear waste solutions. They are weak bases with the potential for use in the separation of actinides and lanthanides in nuclear waste management as an alternative to organophosphorus extractants such as tri-n-butyl phosphate (TBP).[1, 2, 3, 4, 5] Compared to organophosphorus compounds, *N,N*-dialkylamides are environmentally compatible owing to the fact that they contain only carbon, hydrogen, oxygen and nitrogen and thus do not create undesirable waste after incineration. In addition, their complexing properties can be tuned by optimizing the alkyl groups. It was reported that linear dialkyl amides could be used for the recovery and purification of Pu while branched chain dialkyl amides are good extractants for U.[6, 7, 8, 9]

N,N-dialkylamides can be immobilized on a polymeric support. Polystyrene-bound 4-ethoxy-*N,N*-dihexylbutanamide was developed for the selective extraction of U(VI), Th(IV), La(III) and Nd(III) from highly acidic streams. The maximum metal sorption capacity values are 0.36, 0.69, 0.32 and 0.42 mmol/g for U(VI), Th(IV), La(III) and Nd(III), respectively, in 6 M HNO_3.[10] Di-bis(2-ethylhexyl)malonamide showed selective extraction towards U(VI) up to 4 M acid with distribution coefficients of the order of 10^3 after being anchored on polyVBC.[11]

N, N, N', N'-tetramethylmalonamide (TMMA) has been immobilized to polyVBC through a two-step process in which NaH is added to generate a carbanion which then reacts with polyVBC.[12, 13] The immobilized TMMA exhibits higher sorption for U(VI) and Ce(III) than the dihexyl-*N,N'*-diethylcarbamoylmethyl-phosphphpnate resin and is more selective toward U(VI) than Ce(III).

This study is part of our broader study into the mechanism of metal ion complexation by polymer-supported reagents with the objective of understanding the conditions required for ionic recognition to occur. A study of phosphates bound to immobilized polyols has shown that hydrogen bonding to the phosphate ligand by auxiliary –OH groups tunes the polarizability of the phosphoryl oxygen and is an important determinant affecting metal ion affinities.[14] This chapter explores the ability of hydrogen bonding to tune the metal ion affinities of immobilized amide.

The affinities of the diamide for the lanthanides are determined because of their monotonically varying properties (ionic radius, charge density, hydration enthalpy, etc.), similar complex geometries, and polarizabilities that vary over a narrow range of hardness. Covalent interactions are minimal since the f-orbitals being populated are not the outermost orbitals.[15] The design of polymer-supported reagents which allow for the selective complexation of lanthanide ions from aqueous solutions is important in its own right due to applications in nuclear waste management,[16] luminescent probes,[17] and catalysis.[18]

3.2 Experimental

3.2.1 Materials

TMMA was purchased from TCI Americas. All other chemicals were obtained from Sigma-Aldrich or Acros Chemical. All chemicals were used without further purification unless otherwise noted. The preparation of the crosslinked poly(vinylbenyl chloride) beads has been described[19] and is summarized below. The beads had a particle size of 0.25-0.42 mm. Reactions at temperatures other than room temperature or reflux were regulated with a Therm-O-Watch temperature control device. Water for metal ion studies and analytical determinations was filtered through a Millipore Direct Q-5 system and had a resistivity of 18.2 MΩ-cm.

3.2.2 Synthesis of functional resins

3.2.2.1 Synthesis of poly(vinylbenzyl chloride) gel resin with 2% divinylbenzene

The poly(vinylbenzyl chloride) gel copolymer was prepared by suspension copolymerization of vinylbenzyl chloride (VBC) and 2 wt% divinylbenzene (DVB) with 1 wt% benzoyl peroxide (BPO) as initiator.[19] The aqueous phase, prepared by dissolving 1.25 g of polyvinyl alcohol and 28.0 g of calcium chloride in 250 mL water, was poured into a 1 L three-neck round-bottom flask fitted with condenser, nitrogen inlet, thermometer and overhead digital stirrer and sparged for 10 min with nitrogen. The organic phase made up of 143.08 g VBC, 5.42 g DVB (55.4% purity), and 1.50 g BPO, was sparged with nitrogen for 5 min after being mixed thoroughly and then added to the round-bottom flask containing the aqueous phase under a nitrogen sweep.

The stir shaft was adjusted so that the top edge was just above the aqueous phase. The stir motor was turned on for 2 min and then off for 1 min to suspend droplets of the organic phase throughout the aqueous phase. This “on/off” cycle was repeated two more times. The stir speed was adjusted to produce beads of the desired size. The reaction was heated with a heat lamp to 80°C over a 2-h period. The temperature was kept at 80°C for 10 hr. The polymerization was completed by a 2-h reflux after adding 100 mL water.

After washing with 10^{-4} M aqueous HCl once and with water three times, the resulting beads were Büchner dried and extracted with toluene for 17 h. After extraction, the beads were dried and sieved using US Standard screens. Beads used for functionalization have a particle size of 0.25-0.42 mm (-40+60 mesh). All resins are gels unless otherwise indicated.

3.2.2.2 Synthesis of macroporous polyVBC resin crosslinked with 5% DVB

Macroporous beads was prepared by suspension copolymerization of VBC, 5 wt% DVB, 1 wt% BPO as initiator and 50% 4-methyl-2-pentanol as the porogen. The finish-off period of the polymerization was a 6-h distillation to remove 4-methyl-2-pentanol.

3.2.2.3 Synthesis of poly(VBC-co-MMA) crosslinked with 2% DVB

Poly(VBC-co-methyl methacrylate) was prepared by suspension copolymerization of VBC, methyl methacrylate (MMA), 2 wt% DVB and 1 wt% BPO. The molar ratios of VBC to MMA were 80/20, 50/50 and 20/80. After polymerization, the beads were washed with distilled water followed by Soxhlet extraction with toluene.

3.2.2.4 Synthesis of poly(glycidyl methacrylate) crosslinked with 2%DVB

Poly(glycidyl methacrylate) (polyGMA) was prepared by suspension copolymerization of GMA, 2 wt% DVB and 1 wt% BPO. After polymerization, the beads were washed with distilled water followed by Soxhlet extraction with toluene.

3.2.2.5 Synthesis of polyVBC-bound *N,N,N',N'*-tetramethylmalonamide (TMMA)

TMMA (9.5 g, 60 mmol) was dissolved in 100 mL of 1-methyl-2-pyrrolidone (NMP) and 2.3 g of NaH (60% dispersion, 57 mmol) was added in portions. After the reaction mixture was heated at 60 °C for 2 h, 2.0 g of polyVBC beads swollen in 50 mL of NMP were added and the reaction was stirred at 80 °C for 17 h. The beads were recovered and washed with NMP and water, placed in a glass frit funnel, and conditioned with 1 L each of H_2O, 1 M NaOH, H_2O, 1 M HCl, and H_2O.

3.2.2.6 Synthesis of polyVBC-bound diethylmalonate

Diethylmalonate (9.1 mL, 60 mmol) was dissolved in 100 mL of NMP and 2.3 g of NaH (60% dispersion, 57 mmol) was added in portions. The reaction mixture was heated at 60 °C for 2 h, 2.0 g of polyVBC beads swollen in 50 mL of NMP were added and the reaction was stirred at 80 °C for 17 h. The beads were recovered and washed with NMP and water, placed in a glass frit funnel, and conditioned with 1 L each of H_2O, 1 M NaOH, H_2O, 1 M HCl, and H_2O.

3.2.2.7 Synthesis of poly(VBC-co-MMA)-bound TMMA resin

The poly(VBC-co-MMA)-bound TMMA resin was prepared by the reaction of TMMA anion and poly(VBC-co-MMA) resin in a manner similar to the preparation of polyVBC-bound TMMA. TMMA was dissolved in 100 mL of NMP and NaH (60%

dispersion) then added in portions. The amount of each reactant was calculated to ensure a ratio of $–CH_2Cl$, NaH and TMMA of 1:5:5 (Table 3-1). After the mixture was heated at 60 °C for 2 h, 2.0 g of poly(VBC-co-MMA) beads swollen in 50 mL of NMP were added and the reaction was stirred at 80 °C for 17 h. The beads were recovered and washed with NMP and water, placed in a glass frit funnel, and conditioned with 1 L each of H_2O, 1 M NaOH, H_2O, 1 M HCl, and H_2O.

Table 3.1 Poly(VBC-co-MMA)-bound TMMA Resin Formula

VBC/MMA (mol/mol)	$M_{VBC\ beads}$ (g)	M_{NaH} (g)	M_{TMMA} (g)
80/20	2.5	2.3	9.50
50/50	1.0	0.70	2.75
20/80	1.9	0.43	1.70

3.2.2.8 Synthesis of polyGMA-bound TMMA

The polyGMA-bound TMMA was prepared by the reaction of TMMA anion and GMA resin in a manner similar to the preparation of polyVBC-bound TMMA. TMMA (9.50 g, 60 mmol) was dissolved in 100 mL of NMP and LiH (0.456 g, 57 mmol) was added in portions. After the reaction mixture was heated at 60 °C for 2 h, 2.0 g of polyGMA beads swollen in 50 mL of NMP were added and the reaction was stirred at 80 °C for 17 h. The beads were recovered and washed with NMP and water, placed in a glass frit funnel, and conditioned with 1 L each of H_2O, 1 M NaOH, H_2O, 1 M HCl, and H_2O.

3.2.2.9 Synthesis of polystyrene-bound amide

PolyVBC beads (10 g) were added to a reaction flask containing 30 g $NaHCO_3$ and 150 mL DMSO and the mixture refluxed for 20 h. After washing with ethanol, the beads were contacted with 60 mL of dioxane for 1h, refluxed for 24 h after the addition of 130 mL of 3 M HNO_3, washed with water, dried and contacted with 60 mL of dioxane for 17 h followed by a 24-h reflux after the addition of 130 mL 30% H_2O_2. Amidation was completed by refluxing 2.0 g of vacuum-dried carboxylic acid resin in 100 mL of $SOCl_2$ for 48 h, followed by addition of 30 mL of 2 M solution of dimethylamine in tetrahydrofuran (THF) after removing excess $SOCl_2$. The mixture was stirred at 45 °C for 17 h. The beads were recovered, washed with THF and water, placed in a glass frit funnel, and conditioned with 1 L each of H_2O, 1 M NaOH, H_2O, 1 M HCl, and H_2O.

3.2.2.10 Hydrolysis of polyVBC-bound diethylmalonate

The hydrolysis of diethylmalonate resin was carried out under basic condition. KOH (1.8 g) in 12 mL H_2O and 10 mL ethanol was added to 1.5 g of diethylmalonate ester beads swollen in 60 mL of 1,4-dioxane. The mixture was refluxed for 36 h. The beads were recovered, washed with water, placed in a glass frit funnel, and conditioned with 1 L each of H_2O, 1 M NaOH, H_2O, 1 M HCl, and H_2O.

3.2.3 Characterization of functionalized resins

The resins were then characterized by their percent solids, acid capacity, chlorine capacity, nitrogen capacity and FT-IR spectrum.

3.2.2.11 Percent solids

The water content of the resins was obtained and described by their percent solids. The percent solids were calculated as (weight of the oven-dried resin)×100/(weight of the Büchner-dried resin). To get the weight of Büchner-dried resin, approximately 1 g of resin was placed in a Büchner funnel, covered with a piece of latex, suction applied for 5 min at 710 mm Hg and the weight taken. The oven-dried resin was determined by placing the Büchner-dried resin in a 110°C oven for 17 h.

3.2.2.12 Acid capacity

The acid capacity, the amount of acid in 1 gram of resin, was measured by stirring 1 g resin with 200 mL standardized 0.1 N NaOH containing 5 wt% NaCl for 17 h. Two 50 mL aliquots of the contacted NaOH solution (without resin) were titrated with a standardized 0.1 N HCl to a phenolphthalein end point.

3.2.2.13 Chlorine elemental capacity

The chlorine capacity was measured by burning 100 mg of polymer in an oxygen combustion bomb. After 5 minutes, the walls were washed with water and the chlorine was determined by Volhard titration.

3.2.2.14 Nitrogen elemental capacity

The nitrogen capacity was determined by the Kjeldahl method. About 0.2 g of dried resin was digested with concentrated sulfuric acid.[19] The nitrogen was distilled in the form of ammonia and absorbed by 0.1 N standardized HCl solution. The consumed HCl was determined by titration with 0.1 N standardized NaOH.

3.2.2.15 FT-IR spectra

All the resins were studied by FTIR (Bomem (MB Series); Hartmann-Braun) in which KBr pellets were prepared with 0.01 g of resin and 0.100 g of KBr followed by grinding and compression into pellets.

3.2.2.16 Metal ion study

Metal ion studies were carried out by contacting approximately 0.10 g of resin with 5 mL of 10^{-4} N solutions of the metal ions for 17 h on a digital orbital shaker (VWR, DS-500) at speed of 200 rpm, which was sufficiently long to reach equilibrium. Each resin was pre-equilibrated with an aqueous solution of HCl, HNO_3 or H_2SO_4 of the same acidity as the metal-containing solution. The amount of metal complexed was determined with an inductively coupled plasma—atomic emission spectrometer (Spectroflame M 120E).

3.3 Results and Discussion

3.3.1 Synthesis of the TMMA resin

TMMA was bonded to polyVBC via nucleophilic addition as shown in Fig. 3.1. The synthesis consisted of deprotonating of TMMA with NaH and nucleophilic addition. NMP was chosen as solvent because it dissolves the sodium salt.

Anchoring TMMA onto polyGMA followed the same steps as onto polyVBC but LiH was used as the base instead of NaH because it gave much higher degree of functionalization—the nitrogen capacity was 4.63 mmol/g for LiH compared to 1.81 mmol/g for NaH.

3.3.2 Synthesis of polystyrene-bound amide

The amide resin was prepared by the amidation of the acyl chloride derived from chlorination of carboxylic acid with thionyl chloride ($SOCl_2$). The carboxylic acid was anchored through the reaction of polyVBC and DMSO followed by oxidation of the aldehyde produced. The addition of 30% H_2O_2 after 3 M HNO_3 is to ensure the complete oxidation of aldehyde (Fig. 3.2).

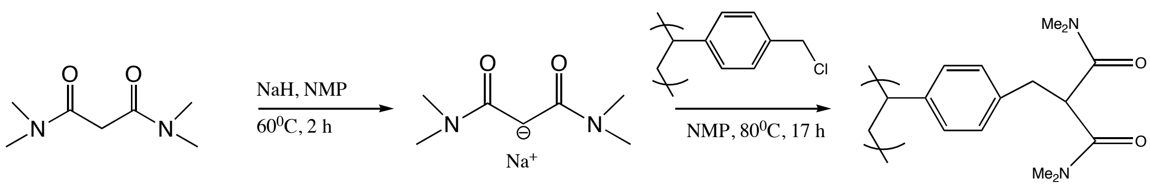

Figure 3.1 Synthesis of polystyrene-bound TMMA.

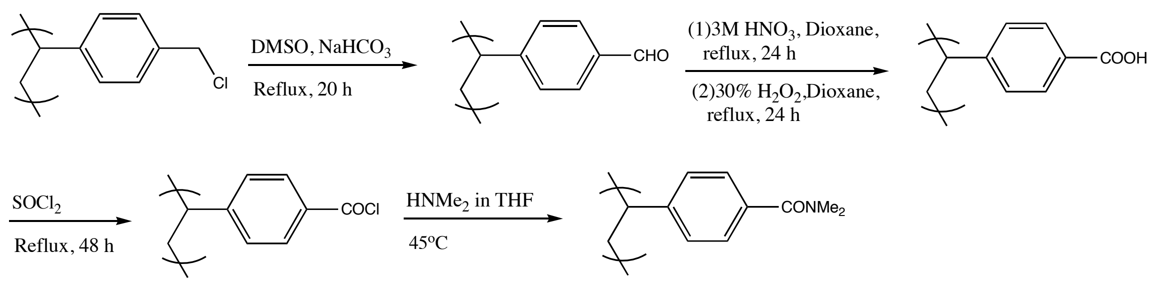

Figure 3.2 Synthesis of polystyrene-bound amide.

3.3.3 Characterization of functionalized resins

The preparation of each functionalized resin was repeated many times in order to test for reproducibility in characterization and metal ion studies.

Table 3.2 Characterization of Polystyrene-bound Gel Resins

Resin	Functional Group	%Solids	Cl Capacity (mmol/g)	N Capacity (mmol/g)	Acid Capacity (mmol/g)
YY-01-004	Chloromethyl	78.8	5.79	--	--
YY-01-247	Monoamide	57.7	1.11	2.93	1.27
YY-01-027	Malonate diester	72.3	2.01	--	--
YY-01-031		72.1	1.24	--	--
YY-01-039		63.1	1.56	--	--
YY-01-029	Malonic acid	51.7	--	--	6.20
YY-01-033		33.0	--	--	7.12
YY-01-040		47.8	--	--	6.24
YY-01-043	TMMA	39.8	0	7.18	1.54
YY-01-045		41.1	0	6.26	--
YY-01-089		43.0	0.51	5.94	0.51

The results from the analysis of polystyrene-bound gel resin are summarized in Table 3.2. The diester, monoamide, and TMMA resins had average percent solids of

69.2, 57.7, and 41.3%, respectively, average chlorine capacities of 1.60, 1.11 and 0.17 mmol/g, respectively, and average nitrogen capacities (for the two amide resins) of 2.93 and 6.50 mmol/g, respectively. The malonic acid resin was made from the hydrolysis of the diester resin and its acid capacity reflects the amount of diester originally present. By comparison to the theoretical values (3.39, 5.12, and 7.19 mmol/g for the diester, monoamide, and diamide, respectively), the degrees of functionalization are calculated to be 80% for the diester, 60% for monoamide, and 85% for the diamide. The decreasing solid levels from polyVBC, diester, monoamide and diamide are due to the increasing hydrophilicity of the $–CH_2Cl$, $-C(O)OEt_2$ and the $–C(O)NMe_2$ moieties.

Table 3.3 Characterization of Polystyrene-bound Macroporous Resins with 5% DVB

Resin	**Functional Group**	**%Solids**	**Cl Capacity (mmol/g)**	**N Capacity (mmol/g)**	**Acid Capacity (mmol/g)**
YY-01-282	Chloromethyl	57.3	5.44	--	--
YY-01-285	TMMA	24.8	--	5.97	--
YY-01-041	Malonate diester	33.0	3.45	--	--
YY-01-042	Malonic acid	36.1	--	--	0.97

Malonate and malonamide ligands were immobilized onto macroporous polyVBC with 5% DVB and the characterization of those resins is summarized in Table 3.3. The degree of functionalization for the TMMA resin is > 98% given its nitrogen capacity of

5.97 mmol/g (complete functionalization yields 6.06 mmol/g). However, the macroporous malonate diester resin achieves only 25% functionalization as indicated by its chlorine capacity of 3.45 mmol/g and the acid capacity of its hydrolysis product (0.97 mmol/g). Due to its greater porosity, macroporous resins exhibit lower percent solids than the gel counterparts bearing the same functional group.

Table 3.4 Characterization of Poly(VBC-co-MMA)-bound Resins

Resin	VBC/MMA	Functional Group	%Solids	Cl Capacity (mmol/g)	N Capacity (mmol/g)
YY-01-004	100/0	Chloromethyl	78.8	5.79	--
YY-01-222	80/20	Chloromethyl	84.5	4.40	--
YY-01-266	50/50	Chloromethyl	91.1	3.22	--
MH-02-034	20/80	Chloromethyl	92.3	1.12	--
YY-01-045	100/0	TMMA	41.1	0	6.28
YY-01-224	80/20	TMMA	32.2	--	5.12
YY-01-268	50/50	TMMA	28.7	--	3.60
YY-01-230	20/80	TMMA	38.1	--	2.04

The density of the TMMA group on the polymer backbone was altered by anchoring TMMA onto polymers with VBC/MMA molar ratios of 100/0, 80/20, 50/50 and 20/80 (Table 3.4). Since TMMA can react only with the VBC moiety, the decreasing content of VBC on the polymer from 100% to 80%, 50% and 20% (chlorine capacities of 5.79, 4.40, 3.32 and 1.12 mmol/g, respectively) leads to the decline in TMMA on the resin (nitrogen capacities of 6.28, 5.12, 3.60 and 2.04 mmol/g, respectively).

The FTIR spectra of the resins are presented in Table 3.5. The characteristic bands for polyVBC include a strong band at 1265 cm^{-1} due to C-H symmetric bending of CH_2-Cl group and a C-Cl stretch frequency at 708 cm^{-1}. The diester resin shows a strong band at 1734 cm^{-1} due to the carbonyl stretch and 1180 cm^{-1} due to C-O-C symmetric and asymmetric stretching. The broad band appearing at 3300-3400 cm^{-1} for malonic acid resins is due to O-H stretching. The band observed at 1701 cm^{-1} region is attributed to the carbonyl. The appearance of amide –C=O stretching bands at 1649 and 1637cm^{-1} confirms the functionalization to TMMA and monoamide resins, respectively.

Table 3.5 IR Spectra of Polystyrene-based Resins

Resin	**Functional group**	**Band position (cm^{-1})**	**Intensity**	**Assignment**
YY-01-004	Chloromethyl	1265	s	C-H sym. bending (CH_2-Cl)
		708	s	C-Cl stretch
YY-01-027	Malonate diester	1734	s	C=O stretch (ester)
		1180	s	C-O-C sym. and asym. stretch
YY-01-029	Malonic acid	3000-3400	b	O-H stretch
		1701	s	C=O stretch (acid)
YY-01-043	TMMA	3400 3500	m	N-H stretch
		1649	s	C=O stretch (amide)
YY-01-023	Monoamide	3400	b	N-H stretch
		1707	s	C=O stretch (acid)
		1637	s	C=O stretch (amide)

3.3.4 Lanthanide affinities for polystyrene-bound TMMA in HCl

The nitrogen capacities of the TMMA and monoamide resins were determined before and after the resins being contacted with 8 M HCl and 8 M HNO_3 for 17 h. The values remain unchanged, indicating that the resins are stable under highly acidic conditions.

3.3.4.1 Effect of HCl concentration on lanthanide affinities

The lanthanides affinities for the diamide resin were determined as a function of HCl concentration (Fig. 3.3): the distribution coefficients are low from 0.001 M to 2 M HCl, increase in 4 M and 6 M HCl, then decrease as the HCl concentration increases to 8M. The highest affinities are obtained for Tb, Eu and Ho, and this is more pronounced in 4 M and 6 M HCl as shown in Fig. 3.4. The results may be divided into three regions: low acid (0.001 – 2M), mid-acid (4 – 6 M), and high acid (8 M).

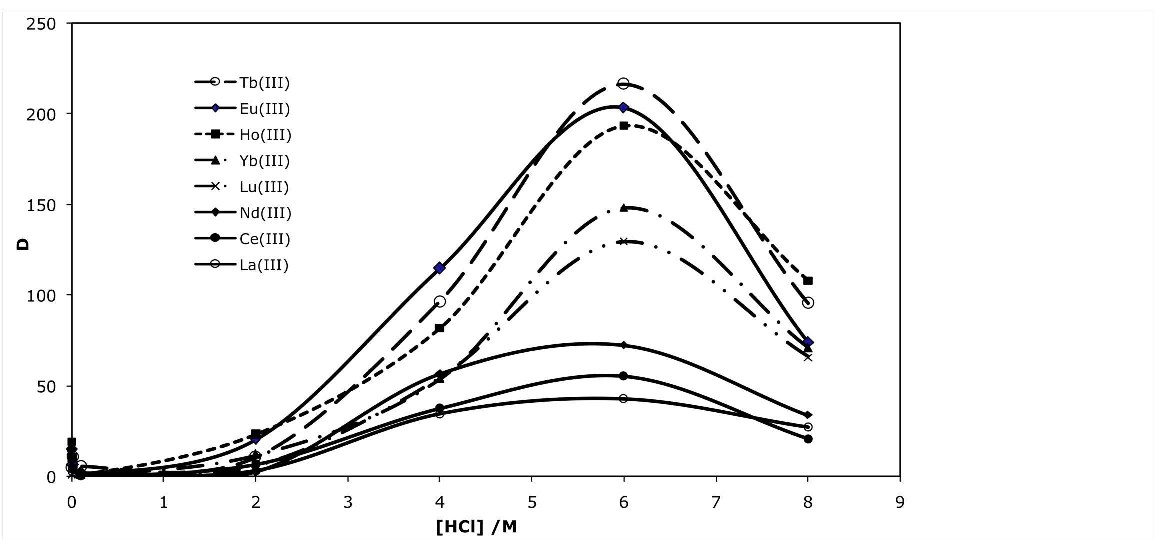

Figure 3.3 Distribution coefficients of the lanthanides by the TMMA resin as a function of HCl concentration

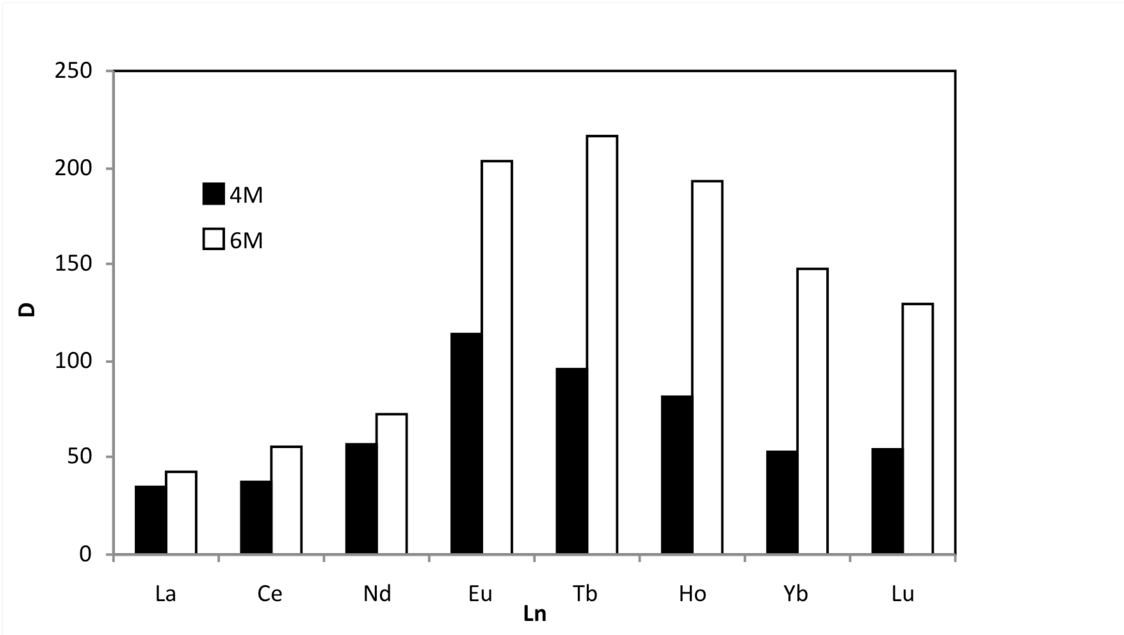

Figure 3.4 Distribution coefficients of the lanthanides by the TMMA resin from 4M and 6M HCl

In the low acid region, there is little sorption of the lanthanides because coordination by TMMA is weaker than binding by the waters of hydration (Fig.3.5).In the mid-acid region, there is significant sorption of the lanthanides from 6 M HCl with a maximum affinity toward the middle of the series. The protonation of malonamide in 4 M HCl is confirmed by the ^{1}H NMR spectrum: A peak appearing at δ=5.3 ppm is assigned to the proton bound to the amide.[20] Protonation occurs at the carbonyl oxygen rather than the nitrogen[21, 22] to form a six-membered ring with the neighboring carbonyl group. Consistent with this, we propose that as the HCl concentration exceeds 2 M, protonation of the amide occurs which is stabilized by hydrogen bonding to the adjacent carbonyl oxygen (no protonation occurs in the absence of the adjacent carbonyl). This protonation then results in the formation of iminium moiety (Fig.3.6).

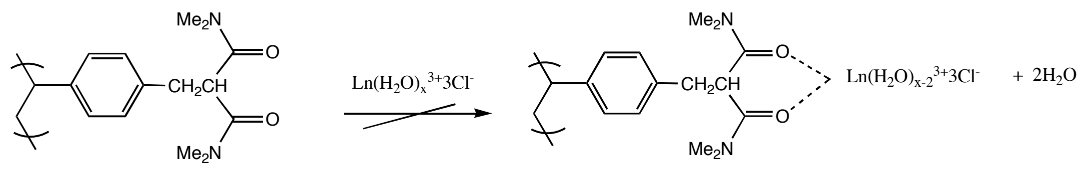

Figure 3.5 Coordination of the lanthanides by TMMA in dilute acid solutions

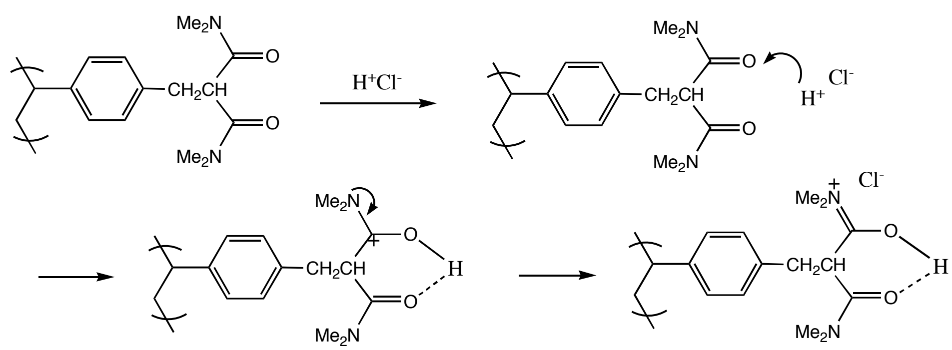

Figure 3.6 Protonation of the malonamide ligand and formation of the iminium moiety

The iminium chloride is the site of ion exchange with the lanthanide chlorocomplex. The concentration of HCl affects the speciation of the lanthanide and ion exchange then operates by exchanging the chloride ion with the anionic lanthanide complex (Fig. 3.7).

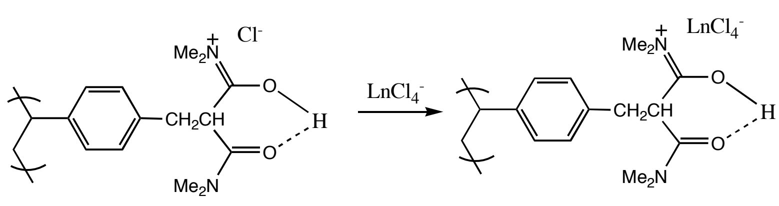

Figure 3.7 Ion exchange of Cl$^-$ at the iminium moiety by the lanthanide chlorocomplex

The results in the high acid region agree with the ion exchange mechanism: the distribution coefficients decrease due to decreasing ion exchange from competition by the high chloride ion concentration.

The proposed schemes are consistent with a report describing the complexation Tb(III) and Am(III) by *N,N'*-dicyclohexyl-*N,N'*-dimethyltetradecylmalonamide from HNO_3 wherein two modes of complexation were proposed: coordination and ion-pairing (equivalent, in this case, to ion-exchange), each operating at different solution acidities.[23] The extraction of nitric acid when its concentration exceeds 2 M supports the ion-pairing mechanism.

3.3.4.2 Comparison study on monoamide, diamide and diester Resins

A comparative study was conducted for the complexation of lanthanides by contacting 100 mg of monoamide, diamide and diester resins with 5 mL of the individual lanthanide ions (10^{-4} N) in 4 M and 6 M HCl solutions in which the TMMA resin showed strong complexation to lanthanides (Table 3.6). The metal ion affinity was quantified in terms of *D* values after determining the equilibrium aqueous phase metal ion concentrations.

The monoamide resin had only low affinities for the lanthanides from 4 M and 6 M HCl while the diamide resin had significant affinity. The diester resin had no affinity for La, Eu, and Lu from 4 M HCl and a low affinity from 6 M HCl.

Table 3.6 Distribution Coefficients of Lanthanides Complexed by Monoamide, Diamide, and Diester Resins from HCl Solution

Ln(III)	Monoamide				Diamide				Diester			
	4M HCl		6M HCl		4M HCl		6M HCl		4M HCl		6M HCl	
	D	$\%M^{3+}$	D	$\%M^{3+}$	D	$\%M^{3+}$	D	$\%M^{3+}$	D	$\%M^{3+}$	D	$\%M^{3+}$
La	0	0	10.9	8.2	34.4	23.2	42.9	24.2	0	0	16.8	24.0
Ce	5.7	4.7	4.9	4.1	37.4	24.4	55.2	30.3	--	--	--	--
Nd	16.2	8.9	10.8	11.6	56.4	33.5	72.2	40.1	--	--	--	
Eu	0	0	21.2	15.8	114.6	49.3	203.3	63.0	6.0	4.9	22.1	33.2
Tb	0	0	2.1	1.8	96.5	45.5	216.2	65.1	--	--	--	--
Ho	0	0	17.2	13.4	81.5	41.8	193.2	60.8	--	--	--	--
Yb	1.5	1.2	23.1	16.2	53.7	32.0	148.0	51.9	--	--	--	--
Lu	0	0	10.1	8.0	54.1	32.3	129.4	49.9	0	0	13.5	18.2

These results are consistent with Fig. 3.6. The key step is protonation of the carbonyl oxygen, resulting in an iminium moiety that ion pairs with the anionic lanthanide complex. The low affinities of the monoamide indicate that protonation of the C=O in the monoamide is not favored in 4M HCl and only slightly occurs in 6 M HCl. Protonation of the carbonyl oxygen occurs to a much greater extent in the diamide because of the stabilization which results by binding to the neighboring carbonyl [24]and this results in the iminium nitrogen as the site of ion-pairing. The diester has low affinities because there is no protonation of diester or ion-exchange occurs only at the nitrogen rather than the protonated carbonyl.

In order to evaluate the possibility of inter-ligand cooperation in the binding of a given lanthanide, the TMMA ligands were separated by ester groups through the covalent attachment of TMMA onto VBC-co-MMA copolymers with varying VBC/MMA molar ratios (80/20, 50/50, 20/80). TMMA reacts only with the VBC moiety through the benzyl chloride but not the ester moiety. Decreasing *D* with decreasing TMMA content is observed on the polymer backbone from 100% to 80%, 50% and 20% when the distribution coefficients are calculated on a per gram-resin basis (Fig. 3.8). However, when the distribution coefficients are recalculated on a millimole-ligand basis (*D'*), no significant difference is shown in affinities among the 100%-, 80%-, and 50%-functionalized resins (Fig. 3.9). Lower affinities are evident only for Eu, Tb, Ho, and Yb with the 20%-functionalized resin, which may indicate that inter-ligand cooperation becomes substantial only when the ligands are separated by a significant distance.

Inter-ligand interaction

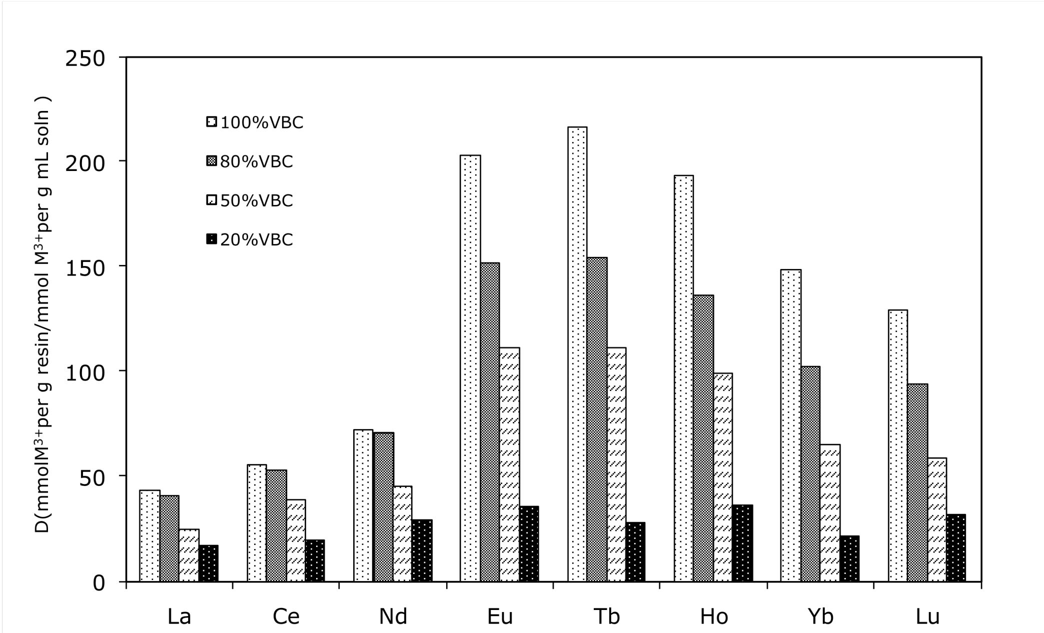

Figure 3.8 Distribution coefficients of the lanthanide ions for four VBC-MMA 100/0, 80/20, 50/50 and 20/80 copolymers functionalized with TMMA in 6M HCl

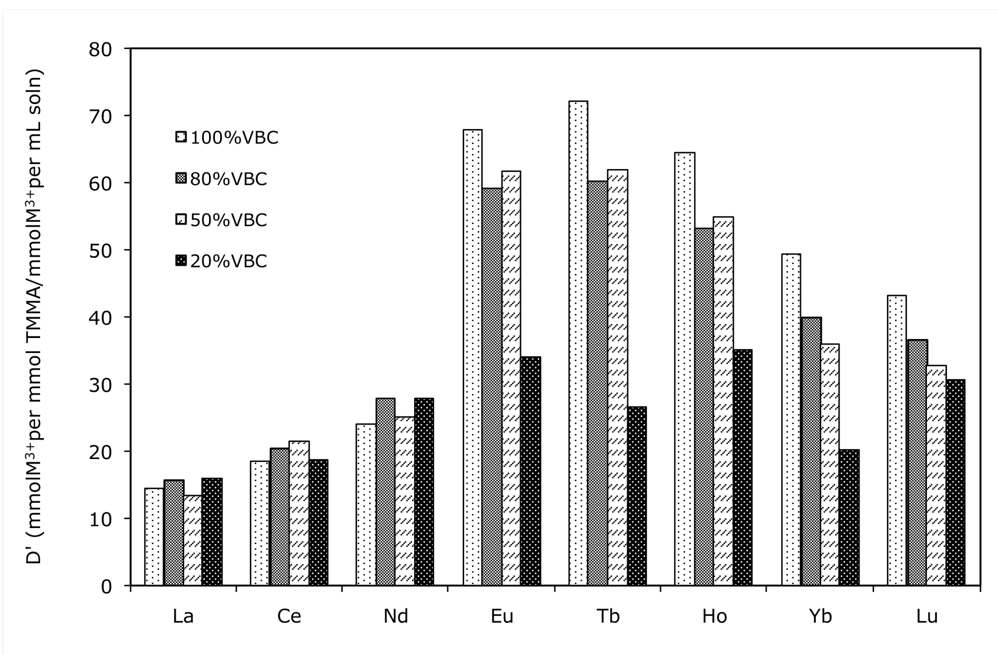

Figure 3.9 Molarity-based distribution coefficients of the lanthanide ions for four VBC-MMA 100/0, 80/20, 50/50 and 20/80 copolymers functionalized with TMMA in 6M HCl

3.3.4.3 Affinity sequence in 6 M HCl with the macroporous resin

As shown in Fig. 3.4, the affinity series with the microporous (gel) TMMA resin from 6 M HCl is Tb ≥ Eu ≥ Ho > Yb ≥ Lu > Nd Ce > Ce > La. In order to demonstrate that whether the distribution coefficients are affected by accessibility of the ions into the polymer matrix, the results (Fig. 3.10) from the 2% DVB gel resin were compared to a macroporous resin. Both resins give a similar sequence, though the affinity difference of Tb ≥ Eu ≥ Ho in the gel resin is more like Eu > Tb > Ho in the macroporous resin. Additionally, there are slightly higher distribution coefficients with the macroporous resin for all lanthanides except Lu, though these differences are small except for except for Eu.

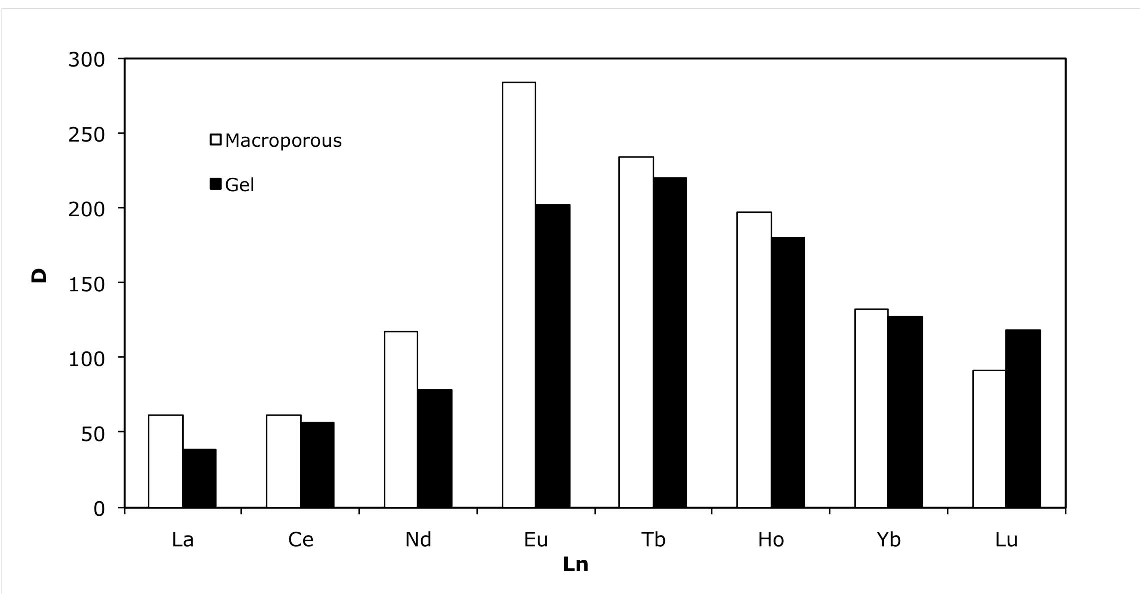

Figure 3.10 Comparison of distribution coefficients between 2% DVB gel and 5% DVB macroporous resins in 6 M HCl

3.3.4.4 The complete lanthanide series

Complexation of the lanthanides by TMMA was extended to the complete lanthanide series (except Pr (due to analytical difficuilties with the ICP) and Pm (due to its radioactivity) from 6 M HCl (Fig. 3.11).

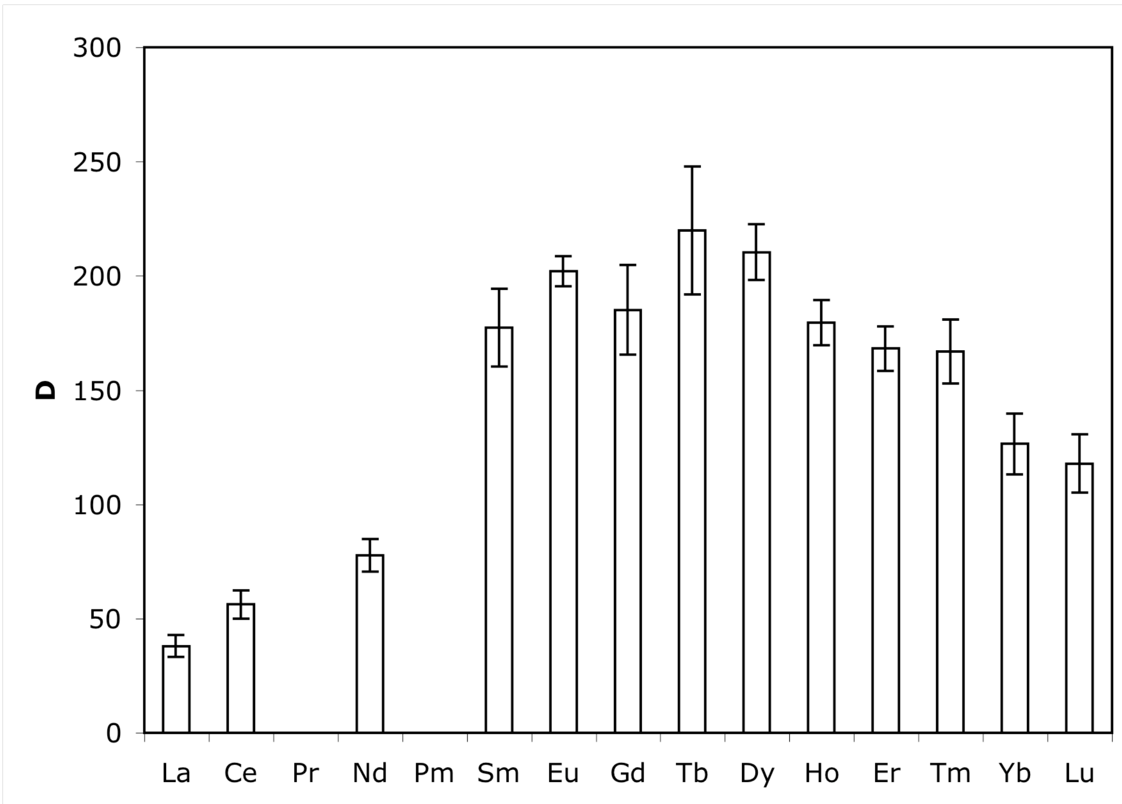

Figure 3.11 Distribution coefficients of the lanthanide series with the TMMA resin in 6 M HCl

Each run was repeated six times. The distribution coefficient increases gradually from La to Nd, jumps to a level twice as much as that found at Nd for Sm, Eu and slightly decreases at Gd. It rebounds to a new high at Tb and gradually decreases for Dy and Ho. After that, the distribution coefficient declines slowly toward Lu. In general, the trend remains the same as that observed earlier for the seven lanthanides—*D* values increase from La to Tb and decrease from Tb to Lu. According to their *D* values, the series can be divided into four subgroups (La→Nd(Pm), Sm→Gd, Gd→Ho and Er→Lu) by three breakpoints at Sm, Gd and Er. This variation of affinities affirms the "Gadolinium Break" or "Three-Quarter Shell Effect" reported with soluble complexants,[25] including di-*n*-octylphosphinic acid and di-2-ethylhexylchloromethylphosphonate. This observation with immobilized ligands indicates that complexants could maintain their coordination properties after being immobilized onto polymer supports.

3.3.5 Lanthanide affinities of by polystyrene-bound TMMA from HNO_3

3.3.5.1 Effect of HNO_3 concentration on lanthanide affinities

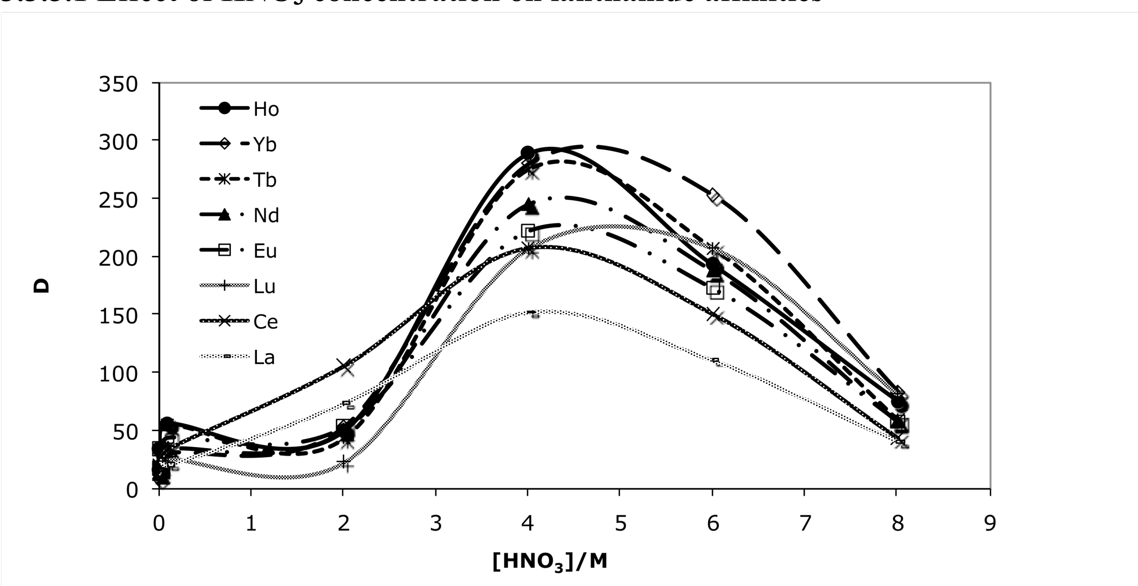

Figure 3.12 Distribution coefficients for the lanthanides as a function of HNO_3 concentration

The HNO_3 concentration dependency mirrors that in HCl (Fig. 3.12): a positive dependency is observed up to 2-4 M acidity followed by a negative trend as [HNO_3]

exceeds 5 M. The extraction of HNO_3 by maloamide is significant when the acid concentration is greater than 2M and increases with the increasing acid concentration.[26] For most lanthanides (except Lu which shows similar affinities at 4 M and 6 M HNO_3) the highest affinity is seen at 4 M HNO_3 compared to 6M in HCl.

The decreasing distribution coefficient at higher nitric acid concentrations is due to the competition between metal ions and protons for the coordination sites of amide and the formation of less extractable $Ln(NO_3)_5^{2-}$ species.[27, 28] A similar nitric acid dependency has been reported with soluble ligand Cyanex 923 (a mixture of phosphine oxides) in a solvent extraction study of Am(III):[29] the lanthanide affinities increase with increasing acid concentration and exhibit a peak at 0.75 M HNO_3, followed by a sharp decline as the acid concentration further increases. Another solvent extraction study of substituted malonamides with La(III), Nd(III) and Eu(III) shows a maximum in the distribution coefficient at 4 to 6 M HNO_3 and then a decline at 7 M or higher concentrations.[30]

The TMMA resin in this paper showed a higher lanthanide affinity than that found in literature probably due to the lower crosslinking degree -- 2% DVB in this paper vs. 8% DVB in the literature. The distribution coefficient of Ce (III) by the polyVBC-supported TMMA from nitric acid is 31.5,[13] lower than the affinity found in this paper (distribution coefficient is 208).

3.3.5.2 Affinity sequence

As seen in Fig. 3.11 the affinity sequence in 4 M HNO_3 follows the same pattern as that found in 6 M HCl—the affinities are higher for the lanthanides in the middle of the series than the ones at the two ends: Ho ≈ Yb ≈ Tb > Nd > Eu > Lu ≈ Ce > La.

3.3.6 Effect of counterion on the complexation of lanthanides by the TMMA resin

The trends observed for complexation of the lanthanides by TMMA in HCl and HNO_3 (Fig. 3.3 and 3.12) are similar to each other. The D values, however, are greater in HNO_3 than in HCl (Fig. 3.14) and this is especially true for the lanthanides at the two extremes (La, Ce, Nd and Yb, Lu). The cause of these differences between hydrochloric acid and nitric acid systems can be attributed to their different solvation properties and hydration energies of the chloride and nitrate ions because binding of a metal complex by a ligand entails at least partial dehydration. The free energies of hydration is higher for nitrate than for chloride (-340 vs. -300 kJ/mo, respectively):[31] chloride has the more negative hydration free energy thus requiring more energy to dehydrate the chloro complex in order to bind to the resin, leading to lower affinities.

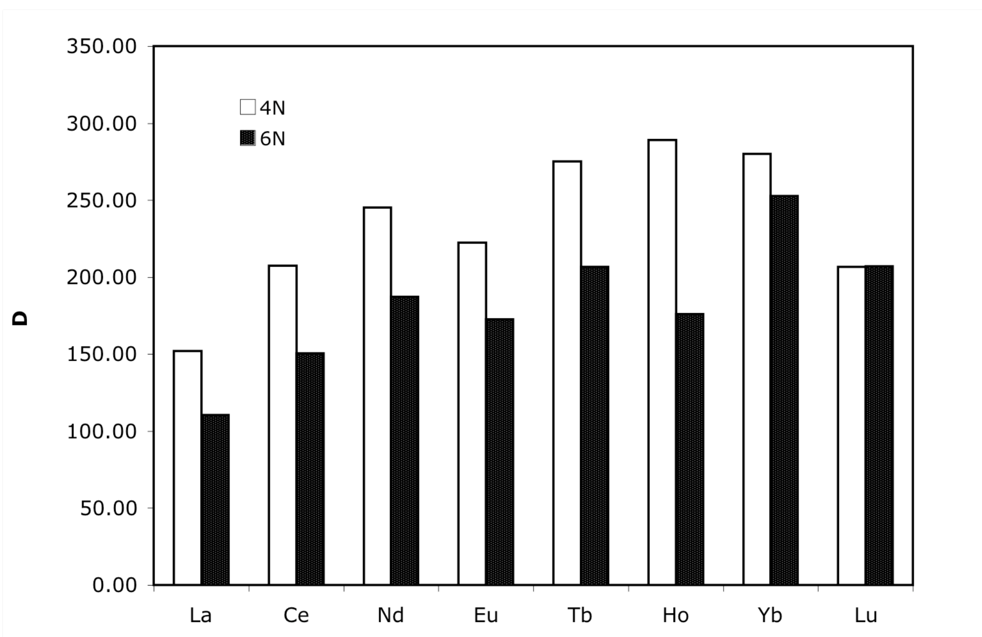

Figure 3.13 Distribution coefficients of the lanthanides by the TMMA resin from 4M and 6M HNO_3

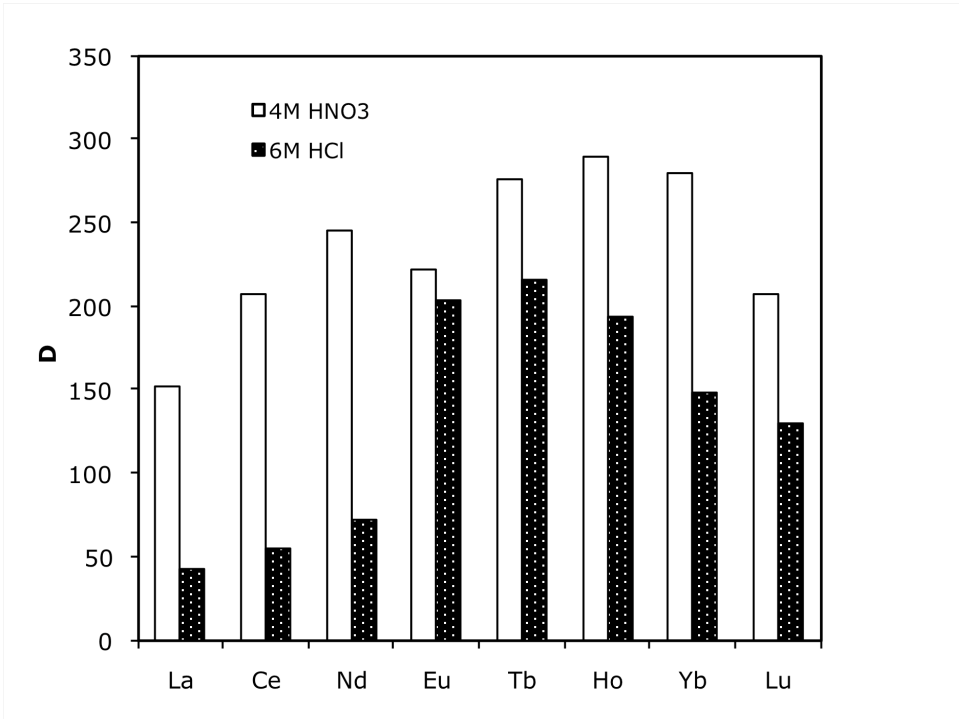

Figure 3.14 Distribution coefficients of lanthanides with TMMA resin in 4M HNO_3 and 6M HCl

The importance of the counterion in determining the extent of complexation was tested by changing the acid to 3 M and 6 M H_2SO_4. In both cases, only a low level of complexation was observed for La, Eu and Lu (Table 3.7). Sulfate binds lanthanides to form anionic $Ln(H_2O)_x(SO_4)_2^-$ species[32,33] that are significantly stronger than either chloride or nitrate;[31] its hydration energy of -1080 kJ/mol[33] indicates it is strongly hydrated and thus prefers to remain in aqueous solutions rather than enter the less polar resin.

Table 3.7 Distribution Coefficients of Lanthanides Complexed

by theTMMA Resin from H_2SO_4 Solutions

Metal	**D**					
	H_2SO_4		**HCl**		**HNO_3**	
	3 M	**6 M**	**4 M**	**6 M**	**4 M**	**6 M**
La	13.6	22.8	34.4	42.7	151.9	110.3
Eu	12.4	33.0	114.6	203.3	222.3	172.4
Lu	12.1	34.2	54.1	129.4	206.7	206.9

3.3.7 Mechanism of recognition

Fig. 3.4 shows that the affinities in 6 M HCl increase from La to Tb, remain high for Tb and Ho, and then decline toward Lu. The affinities in 4 M HNO_3 exhibit a similar trend. Unlike a trend that is monotonic, this bell-shaped trend is not explained by any single property used to characterize the lanthanides: ionic radius, ionization potential, third ionization energy, electronegativity, or hydration energy (Table 3.8). A continuously increasing or decreasing trend along the series has been reported with polymer-supported complexants with pyridine[34] and sulfonic acid ligand[35]. The current results, in which there is a maximum within the series, is best explained as arising from ionic recognition. Recognition requires two opposing mechanisms that operate on each substrate and a change in trend occurs at the crossover point where the originally dominant mechanism becomes secondary.

Table 3.8 Physical Properties of the Lanthanides

Physical Property	**Z**[a]	**r**[b]**/Å**	**3**rd **IP**[c]**/eV**	**SIP**[d]**/eV**	**c**[e]	**-ΔH**$_{hyd}$[d]**/kcal×mol**$^{-1}$	**D**$_{6MHCl}$
La	57	1.16	19.18	35.82	1.1	792.9	37.95
Ce	58	1.143	20.2	36.56	1.12	805.1	56.23
Pr	59	1.126	21.62	37.62	1.13	815.3	----
Nd	60	1.109	22.1	38.27	1.14	822.2	77.7
Pm	61	----	22.3	----	----	830.8	----
Sm	62	1.079	23.4	40.38	1.17	839.6	177.3
Eu	63	1.066	24.92	42.95	----	847.4	202.1
Gd	64	1.053	20.63	39.03	1.2	853.1	185.1
Tb	65	1.04	21.91	30.42	----	861.3	219.8
Dy	66	1.027	22.8	40.66	1.22	868.8	210.4
Ho	67	1.015	22.84	40.77	1.23	876.1	179.5
Er	68	1.004	22.74	40.83	1.24	881.8	168.1
Tm	69	0.994	23.68	42.04	1.25	887.9	167
Yb	70	0.985	25.05	43.39	----	893.2	126.4
Lu	71	0.977	20.96	40.51	1.27	898.8	117.8

[a] Atomic number

[b] Ionic radius.[36]

[c] Third ionization potentials.[37]

[d] Ionization potentials.[38]

[e] Electronegativity.[39]

Electrostatic attraction is thus one operative mechanism (Fig.3.7). The second mechanism is the loss of the waters of hydration (Fig. 3.15). This occurs upon ion exchange, as observed by neutron diffraction studies of the chloride ion associated with an anion exchange resin[40] and the lithium ion associated with a cation exchange resin. [41]

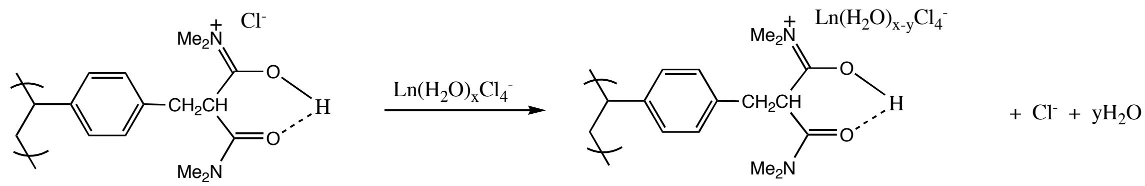

Figure 3.15 Ion exchange at the iminium moiety coupled to

loss some waters of hydration

The bell-shaped trend results from the increasing electrostatic attraction to the iminium due to the lanthanide contraction: the increasing positive-charge density on the lanthanide across the series causes it to draw the Cl^- closer making it a harder ion overall; for the same reason, ΔH(hydr) becomes more negative across the series. The increasing electrostatic attraction gives an increasing affinity from La to Tb. As the series passes Tb, ΔH(hydr) outweighs electrostatic attraction (Fig. 3.15), thus decreasing the apparent affinity from Dy to Lu.

Increased binding of H_2O to the lanthanides, especially after Eu, has been observed.[42] At low [Cl^-], the hydration numbers of La, Ce, Nd, Eu, and Yb decrease from 9.2 to 8.7 while the Ln-O bond lengths decreased from 2.54 Å to 2.32 Å, indicating tighter binding of water across the lanthanide series. In high chloride concentrations (14 M LiCl), chloride incorporation into the inner sphere decreases and after Eu there is no chloride and no loss of coordinated water. The decreasing ability of chloride to replace water in the inner sphere across the lanthanide series is consistent with dehydration as the increasingly dominant component of the TMMA-Ln interaction.[42]

It is important to point out that a key variable which distinguishes the current series with other cases wherein there is a linear change in affinity between the ligand and the lanthanides is the ligand itself: a ligand with a moderately affinity is required for ionic recognition to occur. The stronger the ligand, the more it will be able to coordinate with the metal, and the less selective it will be. The strength of the ligand is dependent on its charge density; with the protonated TMMA, the charge density at the iminium site is moderated by the electron-donating methyl groups.

3.4 Conclusions

Ionic recognition is operative in the TMMA-Ln ion-pairing interaction under acidic conditions. The two opposing mechanisms are electrostatic attraction of the $Ln(H_2O)_xCl_4^-$ or $Ln(H_2O)_x(NO_3)_4^-$ by the protonated ligand and (partial) loss of the waters of hydration as complexation occurs. The key feature in the proposed mechanism is that hydrogen bonding switches on the formation of the iminium group and it is the site of complexation.

Recognition requires a moderately strong ligand interacting with metal ions along with two opposing trends that dominate at different points along a homologous series. The decrease in ionic radius across the lanthanide series acts to increase the electrostatic attraction of the lanthanides for the ligand while the increasingly negative hydration enthalpy serves to keep the species in solution. The dominant trend determines the observed affinity and the magnitude of the distribution coefficients. Electrostatic attraction dominates from La to Eu giving increasing distribution coefficients, whereas the hydration enthalpy becomes dominant after Eu and Tb to give decreasing distribution coefficients.

Dehydration of the counterions and stability of the anionic complex influence the strength of the ligand - metal interaction and therefore the apparent affinities. The affinities are greater from HNO_3 than HCl and minimal from H_2SO_4.

The results with TMMA emphasize the importance of hydrogen bonding in affecting ionic affinities. This general effect, which has been observed in our work with phosphorylated polyols, is being incorporated into other amides in order to determine the ionic selectivities of structurally different iminium ions.

The lanthanide series can be divided into four subgroups—La→Nd(Pm), Sm→Eu, Gd→Ho and Er→Lu—by three breakpoints at Sm, Gd, and Er according to their affinities with TMMA resin at 6 M HCl. This pattern is consonant with the tetrad effect reported with several soluble complexants. This observation with immbolized ligands indicates that complexants can maintain their complexing properties after being anchored to polymers.

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4 Polystyrene-bound malonate ligands monoamidated with diethylenetriamine

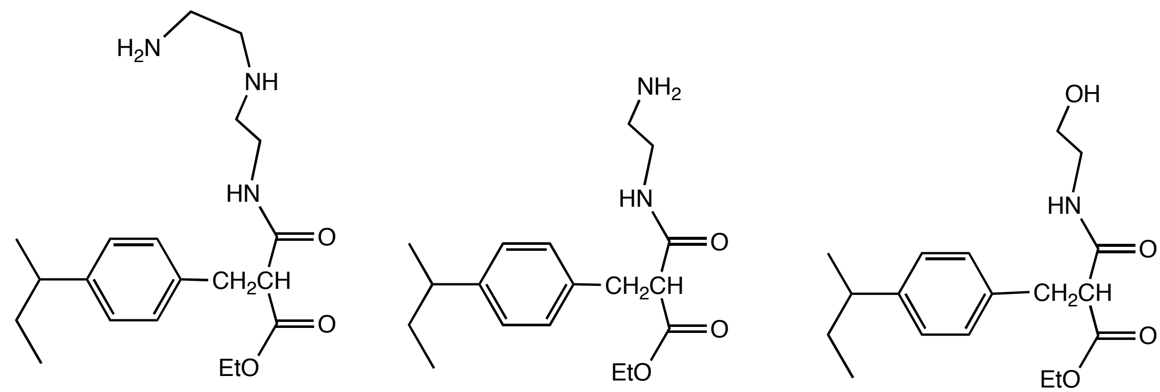
4.1 Introduction

Polymer-supported amides and diamides have been investigated for the complexation of lanthanides.[1, 2, 3] The metal complexation was significantly enhanced by placing ligands next to each other. The distribution coefficient towards Cu(II) by a resin funtionalized by diamide of malonic acid from an acetate buffer of pH 3.7 increased 400 times to 1.5×10^5 compared to the monocarboxylic acid counterpart.[3]

Our previous study on the TMMA resin also suggests that the diamide ligand prefererentially binds Tb, Dy and Eu from highly acidic solution. The proposed mechanism entails initial protonation of one of the carbonyl oxygen's, then hydrogen bonding between the proton and a neighboring carbonyl oxygen triggers formation of the iminium site which acts as the site of ion exchange.[4] Ionic recognition is achieved through a mechanism in which two opposing reactions-electrostatic attraction of $Ln(H_2O)_xCl_4^-$ or $Ln(H_2O)_x(NO_3)_4^-$ by the protonated ligand and (partial) loss of the waters of hydration--dominate at different points along the lanthanide series.

In this chapter, the lanthanide ion complexation of immobilized malonate ligands monoamidated with diethylenetriamine (DETA) is studied and compared with the corresponding DETA amides of monocarboxylic acid (DETA-AMA). The aim of this work is to probe the general nature of the mechanism with three new amide ligands:

malonate is amidated with DETA, ethylenediamine (EDA) and ethanoleamine (EA) (Fig.4.1).



DETA-MAm EDA-MAm EA-MAm

Figure 4.1 Chemical Structure of DETA-MAm, EDA-MAm and EA-MAm

4.2 Experimental

4.2.1 Materials

All chemicals were obtained from Sigma-Aldrich or Acros Chemical and used without further purification unless otherwise noted. The preparation of the polyVBC beads has been described.[5] They had a particle size of 0.25-0.42 mm. All solutions were prepared with Class A glassware. Reaction requiring temperatures other than room temperature or reflux were regulated with Therm-O-Watch temperature control devices. Water for metal ion studies and analytical determinations was filtered through a Millipore Direct Q-5 system and had a resistivity of 18.2 MΩ-cm.

4.2.2 Synthesis of functional resins

4.2.2.1 Synthesis of polyVBC-bound diethylmalonate

9.1 mL of diethylmalonate (1.60 mmol) was dissolved in 100 mL of 1-methyl-2-pyrrolidone (NMP) and 2.3 g of NaH (60% dispersion, 57 mmol) was added in portions. After the reaction mixture was heated at 60 °C for 2 h, 2.0 g of polyVBC beads swollen in 50 mL of NMP were added and the reaction was stirred at 80 °C for 17 h. The beads were recovered and washed with NMP and water. In order to determine the degree of functionalization, the resin was hydrolyzed with KOH. 1.8 g of KOH in 12 mL H_2O and 10 mL ethanol was added to 1.5 g of diethylmalonic ester beads swollen in 60 mL of 1,4-dioxane. The mixture was refluxed for 36 h. The beads were recovered and washed with water, placed in a glass frit funnel, and conditioned with 1 L each of H_2O, 1 M NaOH, H_2O, 1 M HCl, and H_2O.

4.2.2.2 Synthesis of diethylenetriamine (DETA) resin

PolyVBC (5.0 g) was contacted with 100 mL NMP for 2 h and then 50 mL DETA was added. The mixture was stirred at 80 °C for 17 h. The beads were recovered and washed with NMP, water and MeOH, placed in a glass frit funnel, and conditioned as above.

4.2.2.3 Amidation of malonate with DETA, ethylenediamine (EDA) and ethanolamine(EA)

Malonate resin (2.0 g) was contacted with 50 mL of DETA, EDA or EA for 2 h. The mixture was stirred at 110 °C for 17 h. The beads were recovered and washed with NMP, water and MeOH, placed in a glass frit funnel, and conditioned as above.

4.2.2.4 Amidation of monocarboxylic acid resin with DETA

The preparation of the monocarboxylic acid resin has been described.[6] Dry carboxylic acid resin (2.0 g) was refluxed in 100 mL $SOCl_2$ for 48 h. After excess $SOCl_2$ was removed, the resulting resin was washed with toluene twice and dioxane once. Dioxane and DETA (50 mL each) were then added and the mixture stirred at 110°C for 17 h. The beads were recovered, washed with dioxane and water, placed in a glass frit funnel, and conditioned as above.

4.3 Results and Discussion

4.3.1 Synthesis of polyVBC-bound DETA-MAm resin

Diethyl malonate ester was bound to polyVBC through a two-step reaction—deprotonation of diethyl malonate and nucleophilic addition (Fig. 4.2). The subsequent amidation of the malonate resin was achieved by the reaction of DETA with the ester. A 40-50-fold excess of amine was used.

4.3.2 Synthesis of polyVBC-bounded DETA-AMA resin

The synthesis of the DETA amide of the monocarboxylic acid (DETA-AMA) resin is similar to that of polystyrene-bound amide, including formation of the carboxylic acid, acyl chloride, and amide (Fig. 4.3).

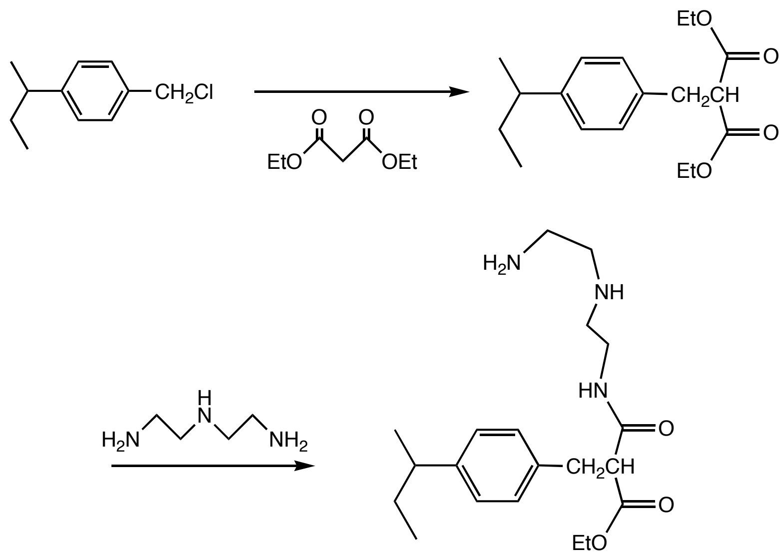


Figure 4.2 Synthesis polyVBC-bound DETA-MAM resin

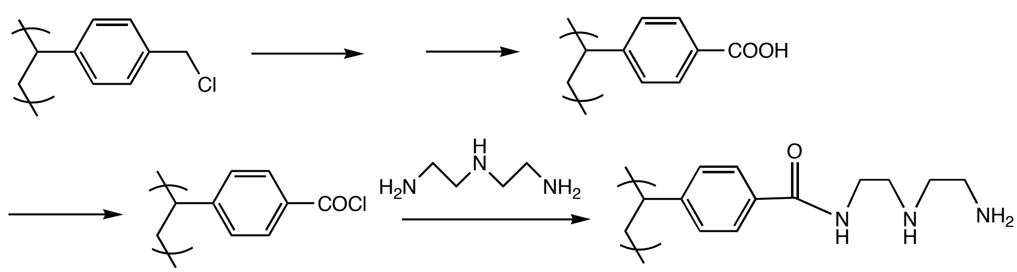


Figure 4.3 Synthesis of polyVBC-bound DETA-AmA resin

4.3.3 Characterization

The preparation of each functionalized resin was repeated many times in order to test for reproducibility in characterization and metal ion studies.

The results from the analysis of polystyrene-bound amide resins are summarized in Table 4.1. The starting polyVBC containing 5.79 mmol of Cl per gram reacted with the sodium salt of diethyl malonate under conditions described in Scheme 5-1. The resulting malonate diester resin was hydrolyzed with KOH and an acid capacity 6.17 mmol/g was found. Considering the final chlorine capacity found in the malonate resin (1.24 mmol/g), it was calculated that the degree of functionalization with diethyl malonate is 80%.

The DETA-MAM resin resulting from amidation reaction of malonate ester has an average nitrogen capacity of 6.81 mmol/g. Allowing for 80% functionalization to the malonate, the theoretical nitrogen capacity for monoamidation of diester is 7.42 mequiv/g. The FTIR spectrum of the DETA-malonate amide (Table 4.2) shows a band at 1672 cm^{-1} due to the amide carbonyl and a band at 1725 cm^{-1} associated with the ester carbonyl. The malonate diester has a band at 1732 cm^{-1} due to the ester C=O streatch. The red shift of the C=O band from 1732 to 1725 cm^{-1} is due to the functional group on the neighboring carbonyl. Similar shifts were observed for the EDA-malonate amide (1726 cm^{-1}) and EA-malonate amide (1727 cm^{-1}). These results make it reasonable to propose that the amidation reaction of the malonate diester resin with DETA, EDA and EA yields uniformly DETA malonate monoamide (DETA-MAm), EDA malonate monoamide (EDA-MAm), and EA malonate monoamide (EA-MAm).

In the amidation of monocarboxylic acid with DETA, the amount of nitrogen capacity was 6.45 mquiv/g (2.15 mmol/g ligand capacity), corresponding to 57.3% yield (theoretical value at 100% functionalization is 3.75 mmol/g). The FTIR spectrum of the amidated acid (DETA-AmA) shows a strong band at 1647 cm^{-1}, confirming the amide group. No peaks are evident at 1732 or 1701 cm^{-1}, indicating the absence of diester and acid groups, respectively.

Table 4.1 Characterization of Polystyrene-bound Gel Resins

Resin	Functional Group	%Solid	Cl Capacity (m.equ./g)	Acid Capacity (mmol/g)	N Capacity (m.equ./g)	Ligand Capacity (mmol/g)
YY-01-027	Malonate diester	72.3	2.01	--	--	--
YY-01-031		72.1	1.24	--	--	--
YY-01-039		63.1	1.56	--	--	--
YY-02-289	DETA-MAm	53.91	--	--	6.76	2.25
YY-03-036		54.88	--	--	6.71	2.24
YY-03-071		50.11	--	--	6.96	2.32
YY-02-300	EDA-MAm	48.77	--	--	6.20	3.10
YY-03-180		53.84	--	--	5.93	2.97
YY-03-103	EA-MAm	68.91	--	--	3.28	3.28
YY-03-175		66.46	--	--	3.18	3.18
YY-03-086	DETA-AMA	53.17	--	1.40	6.45	2.15

The DETA resin was prepared in order to determine whether the observed metal affinities by the DETA-MAm resin were affected by the triamine ligand alone. The reaction goes to completion, as indicated by the absence of chloride and a nitrogen capacity of 8.27 mequiv/g. Some bridging of two phenyl rings by a single DETA is indicated since the theorectical capacity for complete functionalization is 11.9 mequiv/g.

Table 4.2 FTIR Spectra of PolyVBC-bound Resins

Resin	Functional Group	Band position (cm^{-1})	Intensity	Assignment
YY-01-027	Malonate ester	1732	s	C=O stretch
		1100-1300	s	C-O-C sym. and asym. stretch
YY-02-289	DETA-MAm	3300-3400	s	N-H stretch
		1725	m	C=O stretch (unreacted ester)
		1671	s	C=O stretch (amide)
YY-02-300	EDA-MAm	1726	m	C=O stretch (unreacted ester)
		1671	s	C=O stretch (amide)
YY-01-010	Carboxylic acid	3100-3400	b	O-H stretch
		1701	s	C=O stretch
YY-03-086	DETA-AmA	3300	b	N-H stretch
		1647	s	C=O stretch (amide)

4.3.4 The affinities of polyVBC-bound DETA-MAm with lanthanides in HCl:

4.3.4.1 Effect of HCl concentration on lanthanide affinities

The lanthanide affinity of the DETA-MAm resin from HCl was investigated (Fig. 4.4). The extent of metal ion affinity was studied in terms of distribution coefficients (*D* values) after determining the aqueous phase metal ion concentrations at equilibrium.

In general, the *D* values show a constant increase with increasing HCl concentrations from 2 M to 8 M though they are low until the acidity exceeds 6 M.

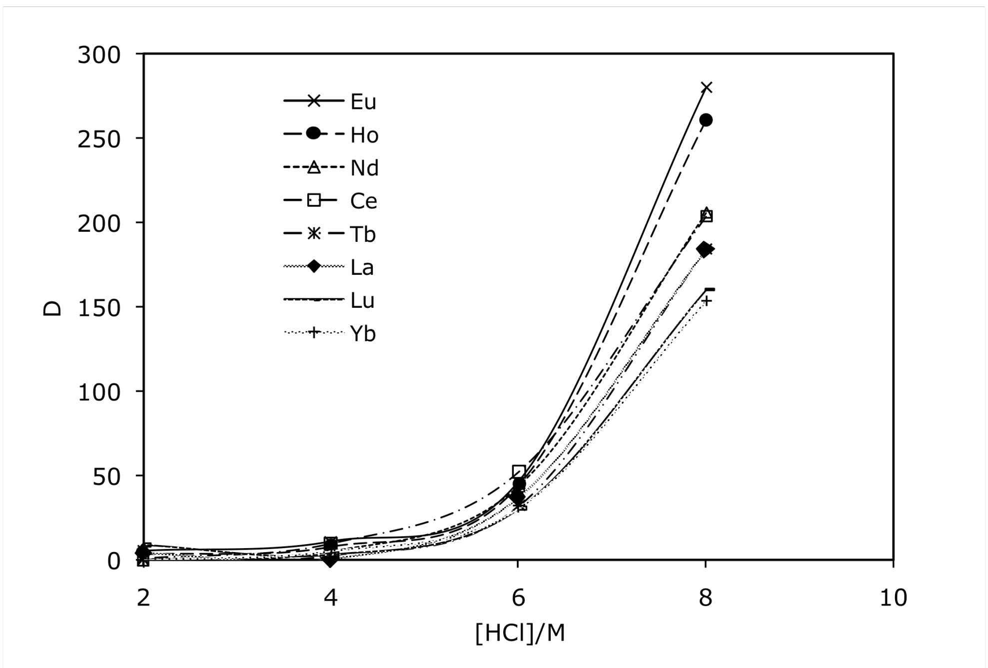


Figure 4.4 Distribution coefficients of the lanthanides by DETA-MAm resin as a function of HCl concentration

4.3.4.2 Affinity sequence in 8 M HCl

The lanthanide affinity sequences from 6 M and 8 M HCl are summarized in Fig. 4.5. In 6 M HCl, the complexation of all lanthanides is very low, as reflected by the low

D values (<50). The *D* values increase to >150 when the acidity rises to 8 M. Among all the lanthanides, Eu and Ho exhibit the highest *D* values.

4.3.4.3 Comparison of DETA-MAM, DETA-AMA, malonate ester and amide resins

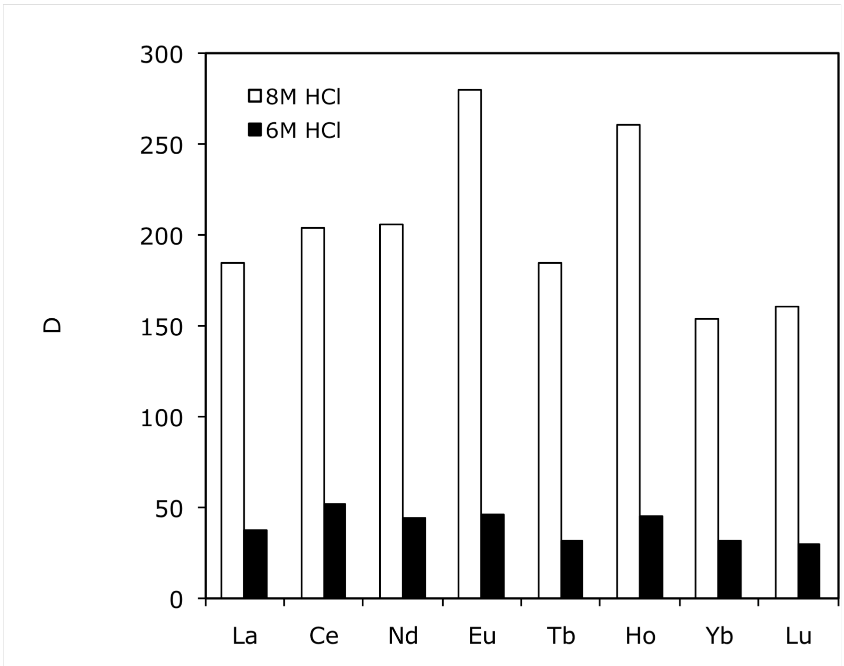


Figure 4.5 Distribution coefficients of lanthanides by DETA-MAm resin in 6 M HCl and 8 M HCl

Distribution coefficients for La (III), Eu(III) and Lu(III) by DETA, DETA-AmA, malonate and DETA-MAm resins in 8 M HCl are displayed in Fig. 4.6. (DETA was contacted only with Eu(III)). Only DETA-MAm exhibits significant affinities for all three lanthanides while the other resins show little complexation. The results with DETA indicate that the DETA-MAm affinities are not due to the triamine ligand alone. The results with malonate show the affinities are not due to the adjacent carbonyl sites alone. And the results with DETA-AmA show that the amide alone does not yield high affinities. The other –NH- moieties on the ligand may be protonated, but they do not act as the site of ion exchange given that DETA alone is ineffective at complexing the lanthanides. They have, however, a secondary role, as discussed below.

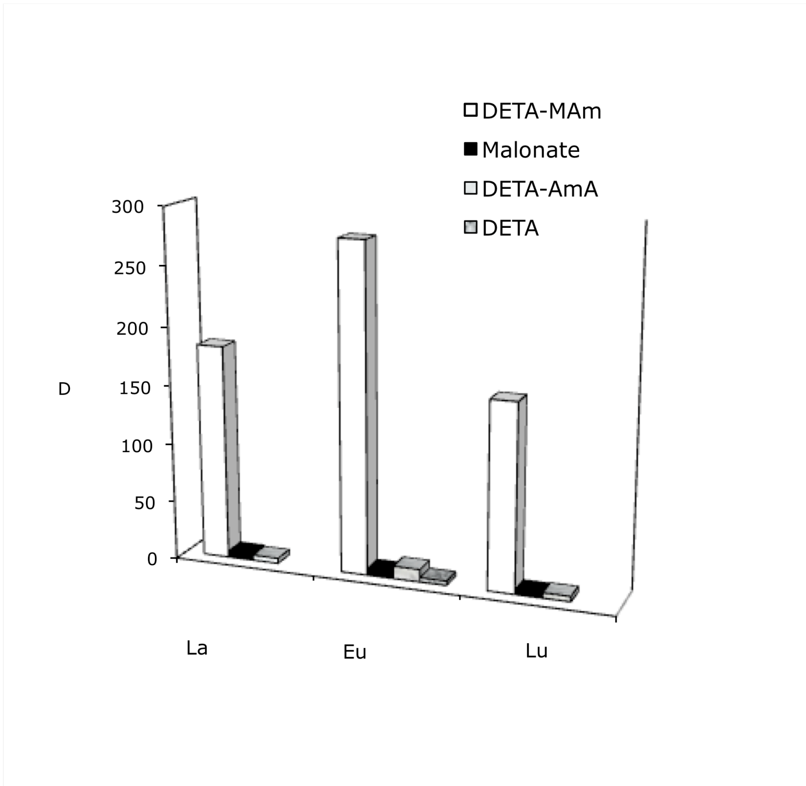


Figure 4.6 Distribution coefficients for La (III), Eu(III) and Lu(III) by DETA-MAm, Malonate, DETA-AmA and DETA resin in 8 M HCl

(DETA was contacted only with Eu(III))

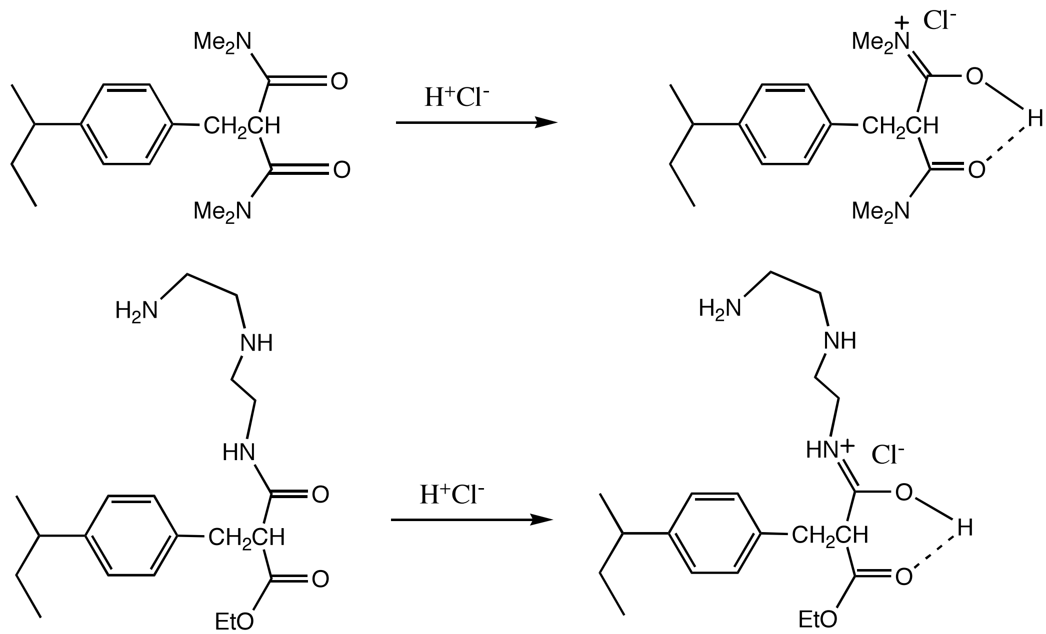


Figure 4.7 Formation of the ion exchange site for TMMA and DETA-MAm

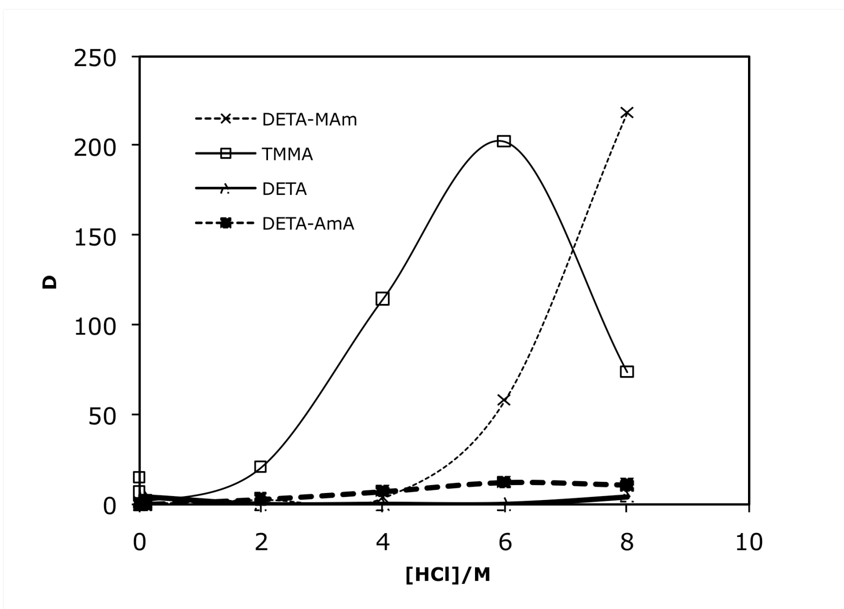


Figure 4.8 Distribution coefficients for Eu(III) by DETA, TMMA, DETA-MAm, and DETA-AmA as a function of HCl concentration

The affinities of DETA and DETA-AmA remain low across the set of HCl concentrations (Fig. 4.8). Unlike DETA-MAm, TMMA shows greater Eu affinities in 4 and 6 M HCl probably due to a higher basicity of its diamide and thus a greater tendency to be protonated (Fig. 4.7). A decreasing of affinity is expected to occur for the DETA-MAm resin as the acid concentration increases beyond 8 M, as observed for TMMA beyond 6 M HCl, due to competition by the large excess of chloride for the ion-exchange sites.

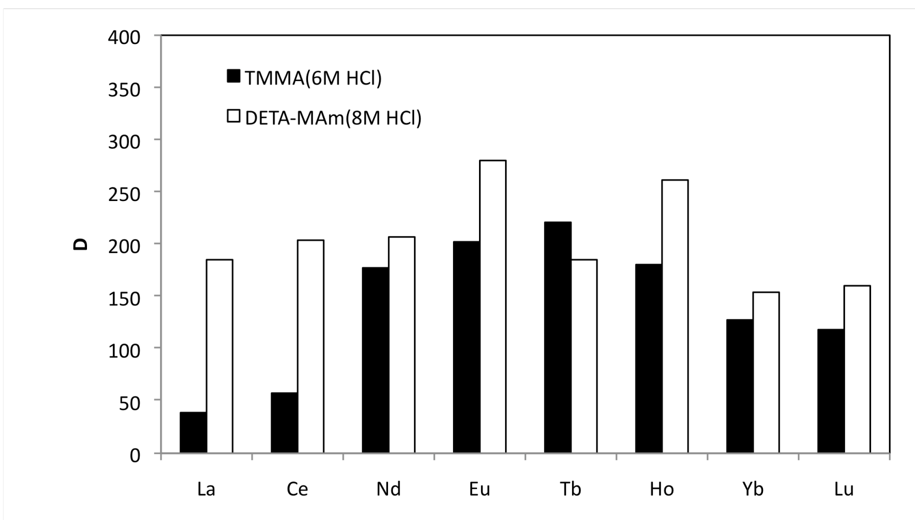


Figure 4.9 Distribution coefficients for TMMA in 6 M HCl and DETA-MAm in 8 M HCl

4.3.4.4 Comparison of TMMA and DETA-MAm: the mechanism of recognition

Lanthanide affinities are compared for the TMMA and DETA-MAm resins under conditions in which each resin has its best performance: 6 M HCl for TMMA and 8 M HCl for DETA-MAm (Fig. 4.9). The lanthanide affinities of DETA-MAm are generally greater than those of TMMA, especially for La(III) and Ce(III).

Table 4.3 Separation factors for TMMA from 6 M HCl and DETA-MAm from 8 M HCl

$SF_{Ln/La}$	TMMA	DETA-MAm
La	1.00	1.00
Ce	1.48	1.11
Nd	4.67	1.12
Eu	5.32	1.52
Tb	5.79	1.00
Ho	4.73	1.42
Yb	3.33	0.83
Lu	3.10	0.87

In order to quantify the selectivities of the resins, the Ln/La separation factor (SF), defined as the distribution coefficient ratio for a given lanthanide relative to La(III), was calculated (Table 4.3). Combined with the results in Fig. 4.9, it is seen that DETA-MAm is a stronger and less selective ligand than TMMA. This provides additional insight into the mechanism of complexation.

The complexation mechanism is common to both TMMA and DETA-MAm: protonation, hydrogen bond stabilization with an adjacent carbonyl, and iminium ion formation. TMMA is weaker because the methyl groups on the iminium are electron donors and weaken the positive charge thus decreasing its affinity for the lanthanide complexes; the methyl groups can also sterically hinder the lanthanide complexes from a close interaction with the positively charged center. The TMMA is thus more responsive to changes between the electrostatic attraction and the enthalpy of dehydration and hence more selective. DETA-MAm is stronger and less selective than TMMA because the iminium moiety has only one $-CH_2-$ moiety to act as an electron donor and thus there is less of weakening of the positive charge.

The additional -NH- sites on the ligand are protonated in 8 M HCl. Whether they provide additional stabilization to the chlorocomplex was investigated by amidating the malonate resin with ethylenediamine (EDA) and ethanolamine (EA). The EDA-MAm resin was contacted with La(III), Eu(III), and Lu(III) in 8 M HCl; the distribution coefficients were 140, 466, and 286, respectively, compared to DETA-MAm values of 184, 280, and 160. That the affinities are greater, at least for the latter part of the series with the higher negative charge densities, suggests that there is additional stabilization provided by the protonated terminal amine since it can form a five-membered ring with the chlorocomplex (Fig. 4.10). DETA-MAm may complex in a similar manner, but its affinities are lower because the auxiliary nitrogen is now secondary and thus a lower charge density than the primary amine in EDA-MAm; additionally, there may be steric hndrance to complexation by the $-CH_2CH_2NH_3(+)$ moiety. Any enthalpic stabilization that could be provided by this protonated site seems to be offset by the corresponding entropic loss.

To further investigate the role of the terminal $–NH_2$ moiety, EA-MAm was contacted with Eu(III) in 8 M HCl; the distribution coefficient was 111 compared to the EDA-MAm value of 466. The lower affinity of the EA-MAm resin further supports that protonation of the terminal amine enhances the ion-exchange occurring at the iminium moiety by stabilizing the chlorocomplex.

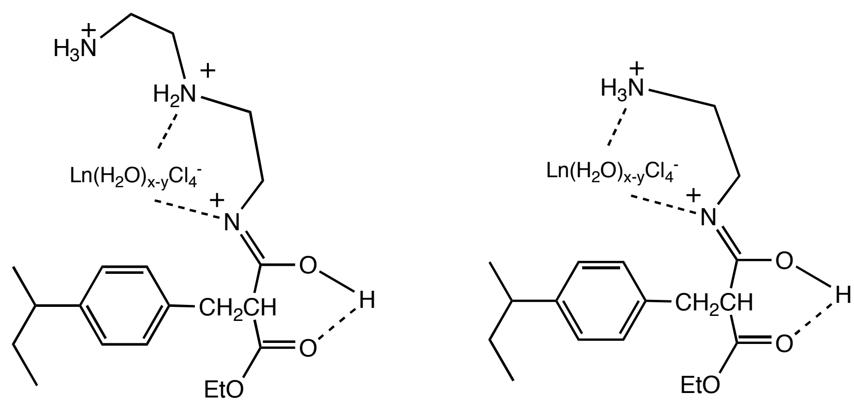


Figure 4.10 Complexation of the chlorocomplex by DETA-MAm and EDA-MAm.

4.4 Conclusions

A polyVBC-supported malonate amide resin has been prepared by the amidation of malonate ester with DETA. The FTIR spectra and nitrogen elemental analysis confirmed the uniform formation of DETA maonate monoamide. It had the highest complexion of lanthanides from 8 M HCl. A positive acid concentration dependency was found in HCl and the lanthanide affinities are similar in 8 M HCl, except for Eu and Ho, both of which have slightly higher *D* values.

DETA-MAm was also compared with TMMA resins by their distribution coefficients towards lanthanides from HCl. TMMA is a weaker but more selective ligand due to a moderated charge density at the iminium site by two electron-donating methyl groups on the nitrogen.

For malonamide-type ligands, it seems to be generally true that hydrogen bonding is critical in activating complexation through formation of an iminium moiety which becomes the site of an ion exchange mechanism. The groups on the nitrogen affect the apparent affinities and selectivities. This is being probed further with amides that bear no alkyl groups in the next chapter.

4.5 References

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5 Polystyrene-bound Ureas

5.1 Introduction

Urea, thiourea and their derivatives, with the lone pair of either oxygen or sulfur to coordinate with different metal ions, are an important class of ligand.[1] Complexes of lanthanides with urea, substituted ureas and thioureas have been prepared and characterized.[2, 3, 4, 5, 6] The infrared spectra of these complexes indicated that these ligands coordinate to lanthanides through the oxygen or sulfur atom in a monodentate manner.[2,3,6] The shift of the carbonyl absorption peak to lower frequencies suggests oxygen coordination.

The epoxy-urea resin, prepared by the reaction of epoxy resin with urea, has showed excellent affinities towards Bi(III), In(III), Sn(IV), Zr(IV) V(V) and Ti(IV) at pH 4-7.[7] Urea has been incorporated into methyl methacrylate (0.5 mol)-glycidyl methacrylate (0.4 mol)-divinylbenzene (0.1 mol) terpolymer beads via a two-step modification of the epoxy groups involving reaction with excess triethylenetetramine followed by isocyanate.[8] The pendant urea groups selectively separated mercuric ions from aqueous solutions.

Our earlier study of the complexation of lanthanides by immbolized malonamide-type ligands --diethylenetriamine malonate monoamide (DETA-MAm) and *N,N,N'N'*-tetramethylamonamide (TMMA)--showed the importance of hydrogen bonding in triggering formation of iminium ion which acts as ion exchange.[9, 10] The mechanism consists of the protonation of one of the carbonyls, which is stabilized by hydrogen bonding to the neighboring carbonyl oxygen, formation of iminium site and ion exchange by exchanging the chloride ion with the lanthanide chlorocomplex. Compared to DETA-MAm which has only one –CH_2 group with its amide nitrogen, the two electron-donating methyl groups in TMMA moderate the positive charge density at the iminium resulting in a weaker but more responsive ligand towards changes between the electrostatic attraction and the enthalpy of dehydration. This responsiveness makes the TMMA show ionic recognition towards the middle of the lanthanide series.

In this chapter, the study is extended from the amide to the urea ligand in order to determine what effect the latter's greater basicity will have on the lanthanide ion affinities. Ureas are incorporated onto the beads by treating the immobilized diethylenetriamine with acidic potassium isocyanate.

5.2 Experimental

5.2.1 Materials

All chemicals were obtained from Sigma-Aldrich or Acros Chemical and used without further purification unless otherwise noted. The preparation of the polyVBC beads has been described.[11] They had a particle size of 0.25-0.42 mm. All solutions were prepared with Class A glassware. Reaction requiring temperatures other than room temperature or reflux were regulated with Therm-O-Watch temperature control devices. Water for metal ion studies and analytical determinations was filtered through a Millipore Direct Q-5 system and had a resistivity of 18.2 MΩ-cm.

5.2.2 Synthesis of Functional Resins

5.2.2.1 Synthesis of diethylenetriamine (DETA) resins

5.0 g of VBC resin was swelled in 100 mL NMP for 2 h before mixing with 50 mL EDA or DETA. The mixture was stirred at 80 °C for 17 h. The beads were recovered and sequenctially washed with NMP, water and MeOH (three times), placed in a glass frit funnel, and conditioned with 1 L each of H_2O, 1 M NaOH, H_2O, 1 M HCl, and H_2O.

5.2.2.2 Synthesis of urea resins

The synthesis follows a published procedure.[8] 2.0 g of amine resin was mixed with 40 mL concentrated HCl at room temperature for 1h. The HCl was removed and the beads were washed twice with 100 mL water. 20 mL aqueous potassium cyanate (KCNO) (20% w/w) was added to the beads. The reaction was stirred at room temperature for 17 h. The beads were recovered and washed with saturated sodium bicarbonate and water, placed in a glass frit funnel, and conditioned with 1 L each of H_2O, 1 M NaOH, H_2O, 1 M HCl, and H_2O.

5.3 Results and Discussion

5.3.1 Synthesis and characterization of functional polymers

The preparation of each functionalized resin was repeated many times in order to test for reproducibility in characterization and metal ion studies. The results from the analysis of polystyrene-bound amine and urea resins are summarized in Table 5.1.

Table 5.1 Characterizations of Polystyrene-bound l Resins

Resin	Functional Group	%Solids	Cl Capacity (mmol/g)	N Capacity (m.equ./g)	Ligand Capacity (mmol/g)
YY-02-274	DETA	46.2	0	8.72	2.90
YY-02-277		48.4	0	8.46	2.82
YY-03-054		50.3	0	8.82	2.94
YY-02-266	urea-3	48.94	0	10.31	2.58
YY-03-044		51.0	0	8.68	2.17
YY-03-055		44.1	0	12.02	3.01
YY-02-162	Primary amine	72.3	0	5.96	5.96
YY-02-163		78.2	0	5.78	5.78
YY-03-070		86.5	0	4.77	4.77
YY-03-073	urea-1	69.4	0	8.23	4.12

5.3.2 Synthesis of primary amine and urea-1 resins

Primary amine resin was prepared through the Gabriel synthesis in which potassium phthalimide reacts with alkyl halides followed by cleavage with hydrazine monohydate (Fig. 5.1). Comparing the average experimental to the theoretical value (5.75 mmol/g and 6.64 mmol/g, respectively), the degree of functionalization is about 87%. The urea was obtained by treating the amine with acidic potassium isocynate. The degree of functionalization is about 88%, as calculated from its nitrogen capacity of 8.23

meuqiv/g (complete functionalization yields 9.23 mequiv/g). This resin will be referred as urea-1.

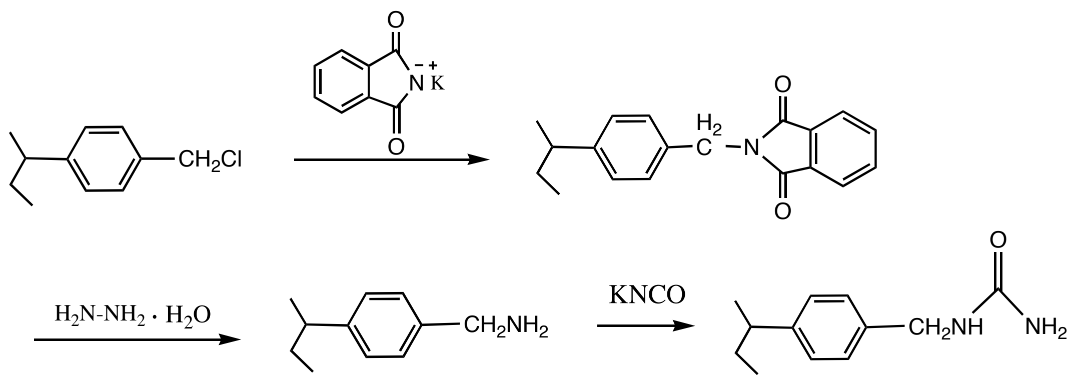

Figure 5.1 Preparation of the Urea-1 resin

5.3.3 Synthesis of DETA and urea resins

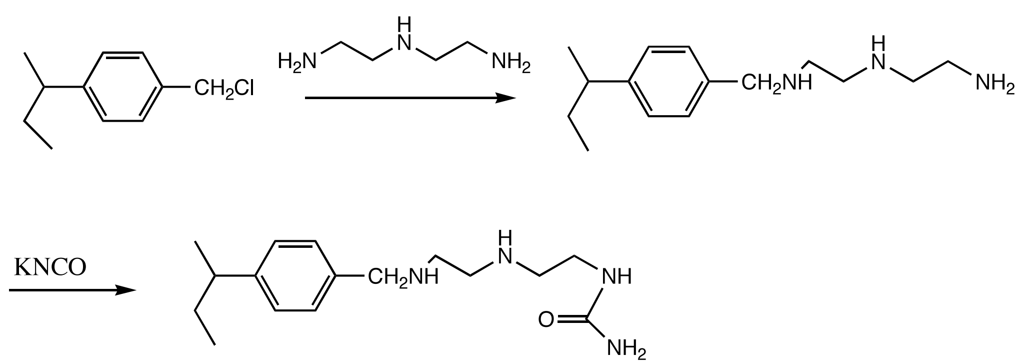

Figure 5.2 Immobilization of diethylenetriamine and preparation of the urea

DETA resins were prepared by the amination of polyVBC with the corresponding amines (Fig. 5.2). The absence of chloride in the DETA indicates the completion of the reaction. The experimental nitrogen capacity (8.72 mequiv/g) is lower than the theoretical capacity for complete functionalization (11.9 mequiv/g) probably due to some bridging of two benzyl rings by a single DETA.

Table 5.2 FTIR Spectra of Amine and Urea Resins

Resin	Functional Group	Band position (cm^{-1})	Intensity	Assignment
YY-02-274	DETA	3300-3400	m	N-H stretch
		1662	s	N-H in-plane bending
		1446	m	Asym. C-H bending
YY-03-055	urea-3	3300-3400	m	N-H stretch
		1658	s	C=O stretch
		1489	m	Asym. C-H bending
		1437	m	
YY-03-072	Primary amine	3379	m	N-H stretch
		1652	s	N-H in-plane bending
		1447	m	Asym. C-H bending
YY-03-073	urea-1	3300-3400	m	N-H stretch
		1658	s	C=O stretch
		1446	m	Asym. C-H bending

The corresponding urea resin was obtained by treating the DETA with acidic isocyanate(Fig. 5.2). The average nitrogen capacity of the urea is 10.60 mequiv/g, which is consistent with the theoretical capacity for the resin containing only one urea (10.28 mmol/g). This resin will be referred as urea-3.

The FTIR spectra of amine and urea resins are presented in Table 4.2. The broad bands appearing at 3300-3400 cm^{-1} for all the amine and urea resins are due to –N-H stretching. The bands at 1649-1662 cm^{-1} for all three amine resins are attributed to N-H in-plan bending. The bands at 1437 and1496 cm^{-1} are attributed to asymmetric C-H bending vibration. The amide carbonyl –C=O stretching frequency for the urea resin, appearing at 1649-1670 cm^{-1}, suggests the formation of urea.

5.3.2 The lanthanide affinities of PolyVBC-bound urea in HCl

5.3.3.1 Effect of HCl concentration on lanthanide affinities

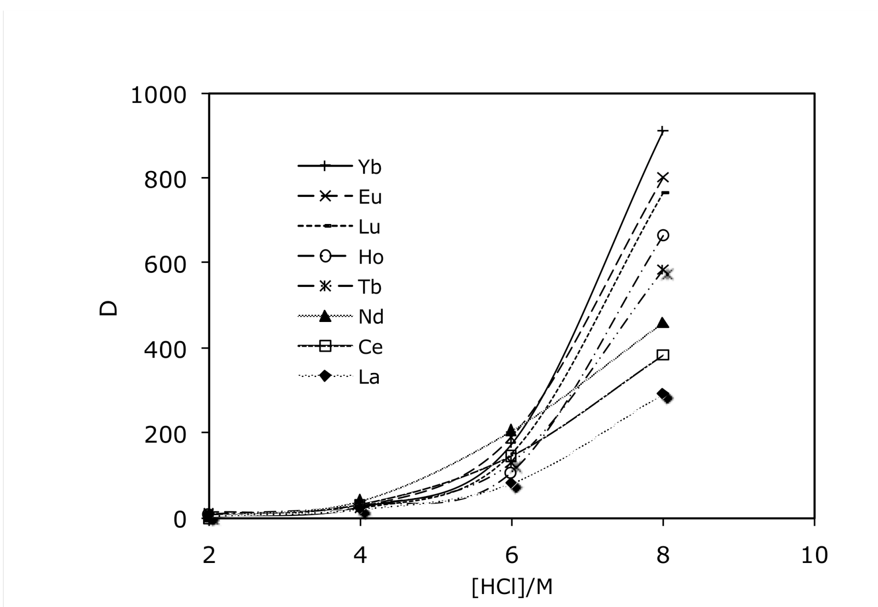

Figure 5.3 Distribution coefficients of the lanthanides by the Urea-3 resin as a function of HCl concentration

The lanthanide affinities from solutions of 2 to 8 M HCl were examined for the urea-3 resin. The metal ion affinities were quantified with *D* values after determining the aqueous phase metal ion concentrations at equilibrium.

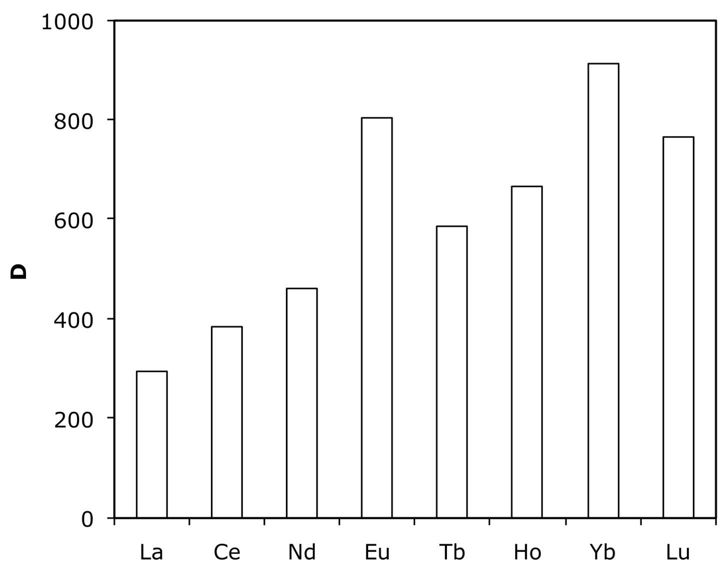

Figure 5.4 Distribution coefficients of lanthanides by the Urea-3 resin in 8 M HCl

The distribution coefficients increase with increasing concentration of acid (Fig. 5.3). From 2 M to 4 M HCl, the distribution coefficients are low ($D < 50$), but increase when the acid concentration exceeds 6 M. The distribution coefficients at 8 M HCl increase across the lanthanide series from La to Lu except at Eu and Yb where the *D* values are higher than expected based on the values of adjacent lanthanides (Fig. 5.4). Because of the well-defined trend at this acid concentration, it is used in a comparative study of amide resins.

The complexation of lanthanides by the TMMA and DETA-MAm resins in HCl consists of protonation of the ligand that occurs at the carbonyl oxygen and is stabilized by hydrogen bonding with the adjacent carbonyl, formation of a quaternary iminium, and ion exchange that operates through the exchange of iminium chloride and the lanthanide chlorocomplex (Fig. 5.5). In an analogous manner, the high affinities of the urea-3 resin are ascribed to protonation of the urea ligand at the carbonyl group which is stabilized by an amine nitrogen through hydrogen bonding and formation of a secondary iminium ion due to its greater stability than the primary imnium ion. The benzyl nitrogen does not act as an amine nitrogen participating in the hydrogen bonding due to its inadequate basicity. Consistent with this, Raman study has shown that the extent of urea protonation increases with increasing HCl concentrations and 90% of urea becomes protonated in 6 M HCl for 1 M urea.[13]

The role of hydration bonding in the Urea-3 resin on helping the formation of iminium site is investigated by contacting the Urea-1 resin with La(III), Eu(III) and Lu(III) in 8 M HCl. No complexation was observed. The inability of the Urea-1 to complex lanthanides is due to its inability to form iminium ion: hydrogen bond stabilization is not possible due to the absence of an adjacent group. These results supports that hydrogen bond stabilization is necessary for the Urea-3 to show the affinities.

This is consistent with the increase in lanthanide affinities with the Urea-3 as HCl concentration increases from 4 M to 6 and 8 M. *D* values are expected to decline with further increase in acidity due to competition at the complexation sites by chloride, as observed for many resins including 4-ethoxy-*N,N*-dihexylbutanamide grafted polymer,[14] polystyrene supported-*N,N*-di-hexylsuccinamic acid[15] and octyl(phenyl)-*N,N*-diisobutylcarbamoyl-methylphosphine oxide resin.[16]

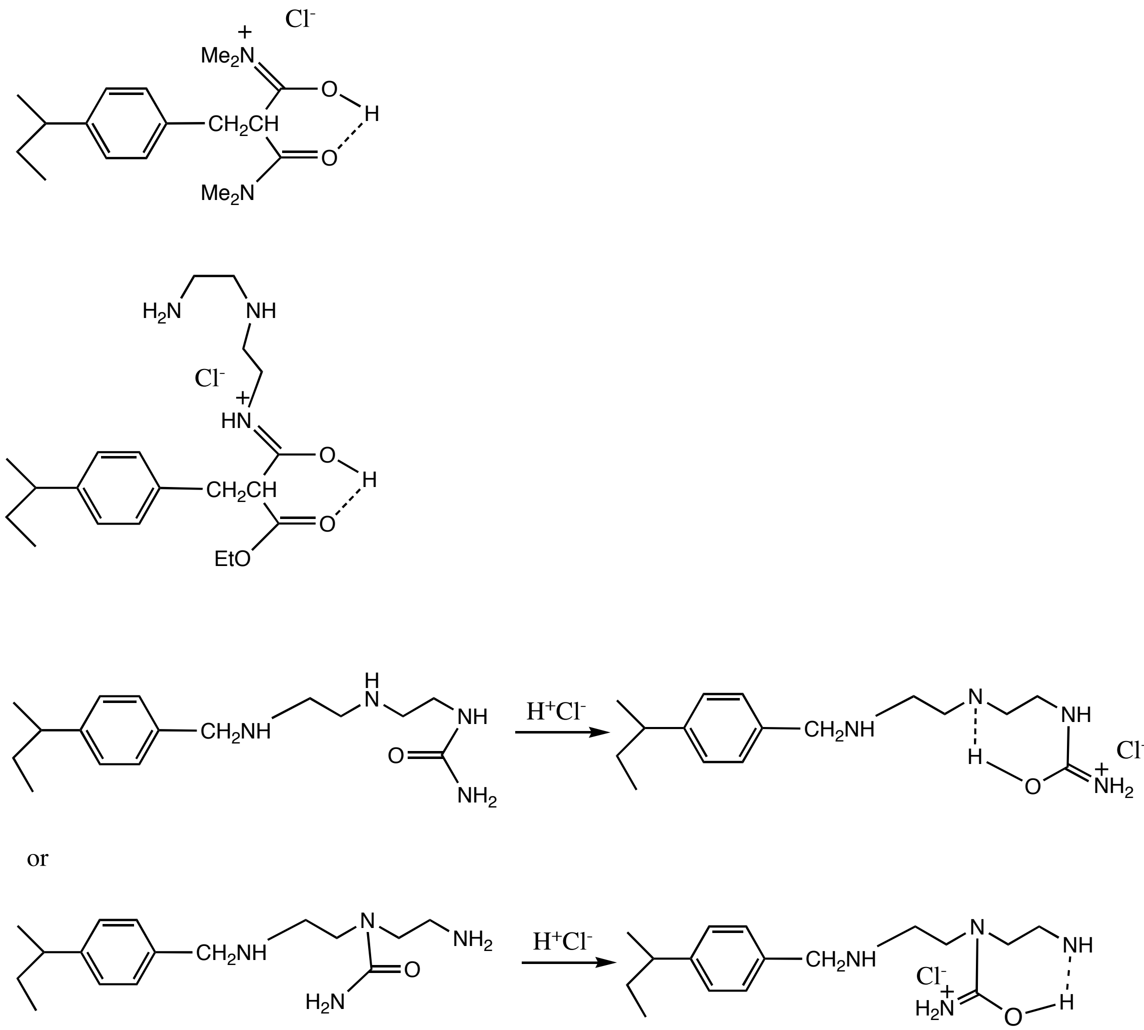

Figure 5.5 Protonation and formation of the site of ion-paring in Urea-3

5.3.4 Complexation towards lanthanides in HNO_3

The effect of HNO_3 concentration from 2 M to 8 M on lanthanide affinities by the Urea-3 was examined for La(III), Ce(III), Eu(III) and Lu(III) and compared with the HCl concentration dependency for Eu(III) as depicted in Fig. 5.6. No complexation was observed, in contrast to the increasing distribution coefficients (the solid line) found in HCl.

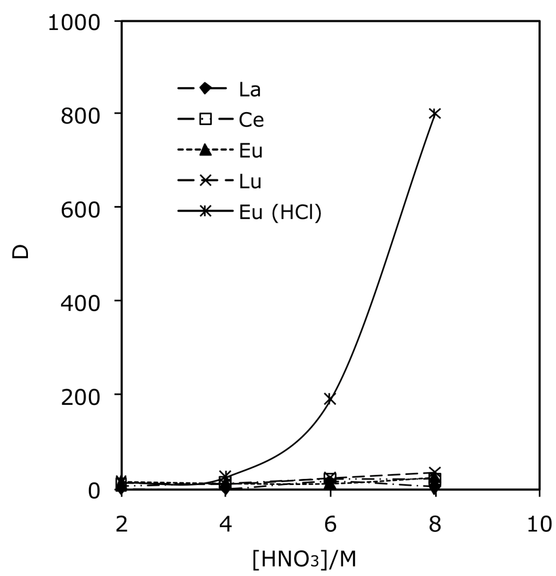

Figure 5.6 Distribution coefficients of La(III), Ce(III), Eu(III) and Lu(III) by Urea-3 as a function of HNO_3 concentration (and comparison to Eu(III) in HCl)

The difference in lanthanide affinities from HNO_3 and HCl may be due to the different hydrogen bonding abilities of chloride and nitrate ions. Ureas and thioureas chelate anions and the amide hydrogens form relatively strong hydrogen bonds.[17, 18, 19] The hydrogen bond distance for chloride is greater than for nitrate by about 0.40 Å[18,] indicating that nitrate forms stronger hydrogen bond than chloride. Cyclic bis-thioureas in ion-selective electrodes prefer nitrate to chloride due to the stronger hydrogen bonding it forms with the oxygens of nitrate.[19] The hydrogen bonding between the Urea-3 and the large concentration of nitrate ions may thus be strong enough to preclude ion-pair formation with the lanthanide complexes in HNO_3. The weaker hydrogen bond formed by chloride with the Urea-3, on the other hand, is outweighed by ion-pairing with the lanthanide chlorocomplex in HCl.

5.3.5 Comparison of Urea-3, DETA-MAm and TMMA

Lanthanides affinities are compared for Urea-3, DETA-MAm and TMMA under conditions in which each resin exhibits its best performance, i.e. 8 M HCl for DETA-MAm and Urea-3, and 6M HCl for TMMA (Fig. 5.7). Urea-3 resin is much stronger as evidenced by its greater *D* values, and remains higher than EDTA-MAm and TMMA across the series of HCl comcentration (Fig. 5.8).

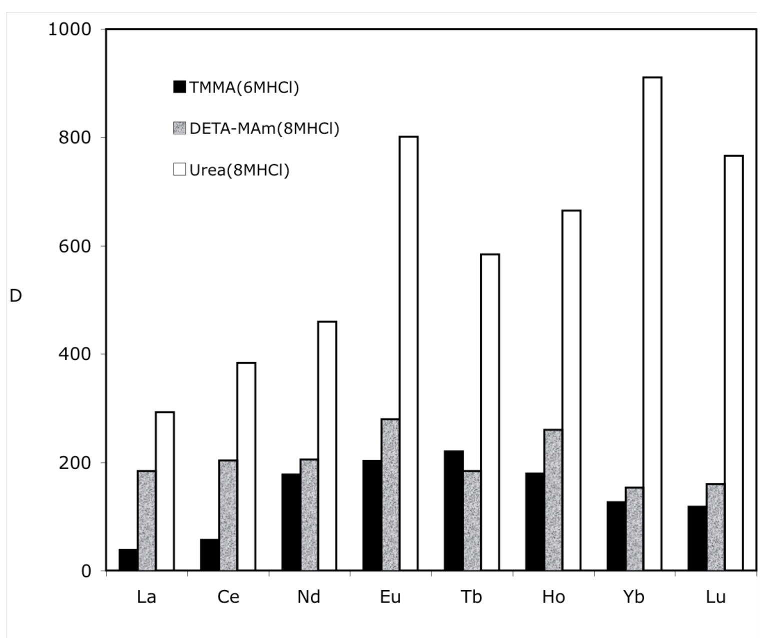

Figure 5.7 Distribution coefficients for lanthanides by TMMA and resin in 6 M HCl and Urea-3 resin in 8 M HCl

The complexation of lanthanides by the Urea, DETA-MAm and TMMA resins operates in a similar ion-pairing manner. The bell-shaped TMMA trend results from a combination of electrostatic attraction and dehydration enthalpy of the lanthanide complex.[9,] That the *D* values increase across the entire lanthanide series with the Urea-3 resin, however, implies that it is the strongest ligand among these three amide-type ligands since electrostatic attraction dominates the ligand-lanthanide interaction. This is supported by the linear correlation between the *D* values and the ionization potential (Fig. 5.9) (The correlation improves (from 0.967 to 0.991) when Lu(III) is excluded from the plot.)

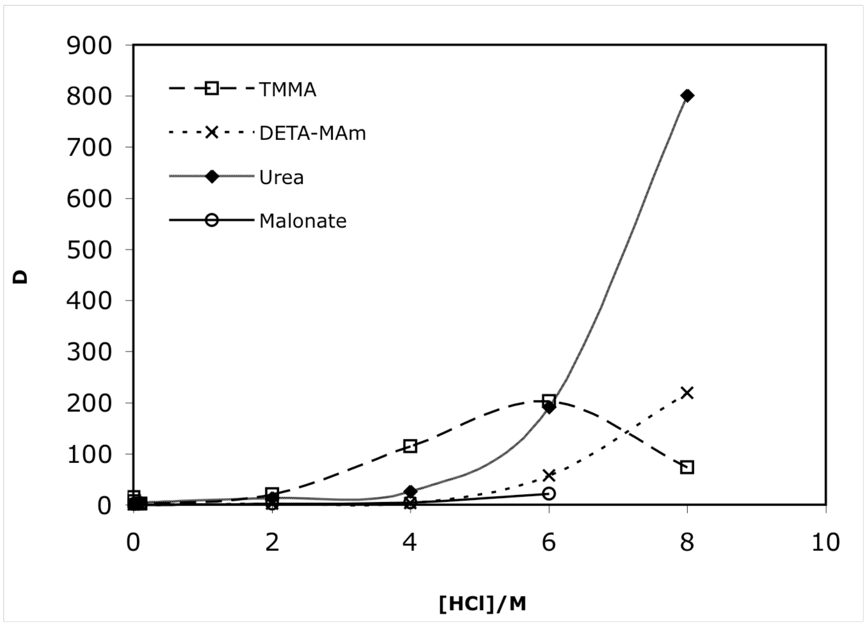

Figure 5.8 Eu(III) distribution coefficients by the Urea-3, DETA-MAm, TMMA and diethyl malonateresins as a function of HCl concentration

The proposed mechanism is supported by the order of ligand strength: Urea-3 > DETA-MAm > TMMA. TMMA is the weakest yet the most responsive to the change between electrostatic attraction and enthalpy of dehydration due to attenuation of the (+) charge at the iminium site by the two electron-donating methyl groups ($=NR_2(+)$); DETA-MAm is somewhat stronger than TMMA and less responsive because the iminium has only one $-CH_2-$ moiety attenuating the (+) charge (=NHR(+)) and it is also a two-site interaction with the ammonium group probably contributing to the electrostatic stabilization of the chlorocomplex; and Urea-3 is the strongest because the iminium has no groups to attenuate the (+) charge (=NH_2(+)). This strong electrostatic force between the Urea-3 and lanthanides outweighs the enthalpy of dehydration dominating the whole lanthanide series, resulting in a continuously increasing affinity trend.

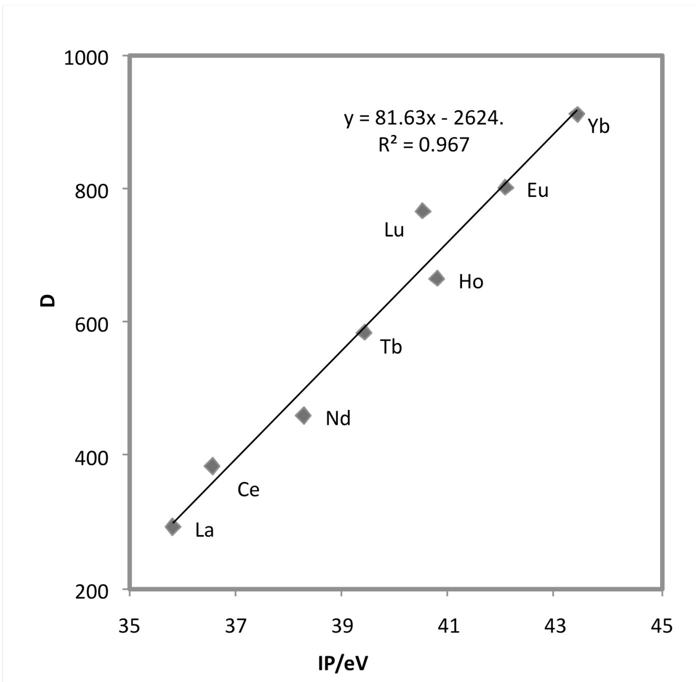

Figure 5.9 Correlation of Urea-3 affinities in 8 M HCl with ionization potential (IP)[20]

5.4 Conclusions

A divinylbenzene crosslinked VBC resin has been modified with urea groups. The resin has shown great affinities towards a series of lanthanides(III) in concentrated HCl solution (8M). A positive acid concentration dependency was found in HCl and the lanthanide affinity across the series in 8 M HCl increases continuously from La to Lu except Eu and Yb.

Similar to other amide ligands, the complexation proceeds by ion-pairing mechanism consisting of protonation of the carbonyl oxygen, stabilization by hydrogen bonding with an amine nitrogen, formation of the site of ion exchange and ion exchange. The strength of protonated amide-type ligands is dependent on their charge density at the iminium site that is tuned by the substituents on the iminium nitrogen. The stronger the ligand is, the more it will be able to bind to metals, the more likely the affinity trend will parallel the metal's ionization potentials. For the protonated TMMA, DETA-MAm and Urea-3, the ligand strength increases due to the increasing charge density as electron-donating methyl groups are replaced by hydrogen atoms, while a bell-shaped affinity trend transforms into a continuously increasing curve.

5.5 References

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6 Experimental Section

6.1 Polymer Preparation

6.1.1 Materials

N,N,N',N'-tetramethylmalonamide (TMMA) was purchased from TCI Americas. All other chemicals were obtained from Sigma-Aldrich or Acros Chemical. All chemicals were used without further purification unless otherwise noted. Beads that were used in the functionalization reactions had a particle size in the range of 0.25-0.42 mm. All solutions were prepared with Class A glassware. Reaction requiring temperatures other than room temperature or reflux were regulated with Therm-O-Watch temperature control devices. Water for metal ion studies and analytical determinations was filtered through a Millipore Direct Q-5 system and had a resistivity of 18.2 MΩ-cm.

6.1.2 Synthesis poly(vinylbenzyl chloride) gel beads crosslinked with 2 % divinylbenzene

Copolymer of vinylbenzyl chloride (VBC) and 2 wt% divinylbenzene (DVB) was prepared by suspension polymerization with 1 % benzoyl peroxide (BPO) as initiator.[1, 2, 3] The aqueous phase prepared by dissolving 1.25 g polyvinyl alcohol and 28.0 g calcium chloride in 250 mL water was poured into a 1000 mL three-neck round-bottom flask fitted with condenser, nitrogen inlet, thermometer and overhead digital stir apparatus (stir motor, shaft, bearing and blade) and sparged for 10 min with nitrogen. The organic phase made up of 143.08 g VBC, 5.42 g DVB (55.4% purity), and 1.50 g BPO was sparged with nitrogen for 5 min after being mixed thoroughly and then added to the round-bottom flask containing the aqueous phase under a nitrogen sweep.

The stir shaft was adjusted so that the top edge was just above the aqueous phase. The stir motor was turned on for 2 min and then off for 1 min to suspend droplets of the organic phase throughout the aqueous phase. This “on/off” cycle was repeated two more times. The stir speed was adjusted to produce beads of the desired size. The reaction was heated with a heat lamp to 80°C over a 2-h period. The temperature was kept at 80°C for 10 h. The polymerization was completed by a 2-h reflux after 100 mL water was added.

After washing with 10^{-4} M aqueous HCl once and with water three times, the resulting beads were Büchner dried and extracted by using a soxhlet extraction apparatus with toluene for 17 h. After extraction, the beads were dried and sieved by using US Standard screens.

6.1.3 Synthesis polyVBC macroporous (MR) beads crosslinked with 5% DVB

The polyVBC MR beads were prepared in a manner similar to the gel beads by suspension polymerization. However, the organic phase consisted of monomer (49 wt%), BPO (1 wt%) and 4-methyl-2-pentanol (50 wt%) and the finish-off period of the polymerization was a 6-h distillation to remove 4-methyl-2-pentanol.

6.1.4 Synthesis poly(VBC-co-methyl methyacrylate) gel beads crosslinked with 2 % DVB

Copolymer beads of VBC, methyl methyacrylate (MMA) and 2 % DVB were prepared by suspension polymerization similar to the polyVBC gel beads. The molar ratios of VBC to MMA were 80/20, 50/50 and 20/80.

6.1.5 Synthesis of polyVBC-bound TMMA

TMMA (9.5 g, 60 mmol) was dissolved in 100 mL of 1-methyl-2-pyrrolidone (NMP) and NaH (2.3 g, 57 mmol, 60% dispersion) was added in portions. The reaction mixture was stirred to 60 °C for 2 h before 2.0 g of polyVBC beads, swelled in 50 mL for 2 h, were added. The reaction was stirred at 80 °C for 17 h. The resulting beads were recovered and washed with 100 mL NMP (once) and 100 mL water (three times).

6.1.6 Synthesis of poly(VBC-co-MMA)-bound TMMA

TMMA was dissolved in 100 mL of NMP and NaH (60% dispersion) was added in portions. The amount of each reactant was calculated to ensure a ratio of –CH_2Cl, NaH and TMMA of 1:5:5 (Table 6.1). The reaction mixture was stirred to 60 °C for 2 h before 2.0 g of polyVBC beads, swelled in 50 mL for 2 h, were added. The reaction was stirred at 80 °C for 17 h. The resulting beads were recovered and washed with 100 mL NMP (once) and 100 mL water (three times).

Table 6.1 Poly(VBC-co-MMA)-bound TMMA Resin Formula

Run	VBC/MMA (mol/mol)	$M_{VBC\ beads}$ (g)	M_{NaH} (g)	M_{TMMA} (g)
1	80/20	2.5	2.3	9.5
2	50/50	1.0	0.7	2.75
3	20/80	1.9	0.43	1.7

6.1.7 Synthesis of polyVBC-bound amide

The amide resin was prepared by amidation of the acylchloride made by chlorination of the oxidation product of polystrene-bound aldehyde with nitric acid and 30% hydrogen peroxide. The aldehyde resin was obtained by the reaction of polyVBC and dimethyl sulfoxide (DMSO) in the presence of sodium bicarbonate.

To obtain the aldehyde resin, 10 g of polyVBC beads were added to a reaction flask containing 30 g $NaHCO_3$ and 150 mL DMSO. The reaction mixture was refluxed for 20 h. After washing with ethanol for three times, the beads were contacted with 60 mL of dioxane for 1h, refluxed for 24 h after the addition of 130 mL of 3 M HNO_3, washed with water three times, dried and contacted with 60 mL of dioxane for 17 h followed by a 24-h reflux after the addition of 130 mL 30% H_2O_2.

The amidation reaction was carried out by refluxing 2.0 g of vacuum-dried carboxylic acid resin in 100 mL of $SOCl_2$ for 48 h, followed by addition of 30 mL of 2 M solution of dimethylamine in tetrahydrogenfuran (THF) after removing excess $SOCl_2$ with a Pipette. The mixture was kept at 45 °C for 17 h. The beads were recovered and washed with 100 mL THF and 100 mL water(three times).

6.1.8 Synthesis of primary amine resin

8.0 g of VBC resin were swelled in 50 mL NMP for 2 h before mixing with 40.0 g potassium phthalimide and 200 mL NMP. The mixture was stirred at 80 °C for 17 h. The beads were recovered and washed with 50mL NMP, 100 mL water and 100 mL MeOH (three times) sequentially. 100mL MeOH and 10 mL water and 50 mL hydrazine monohydrate were added to the reaction flask containing the recovered beads. The mixture was stirred at 65 °C for 17 h. The beads were recovered and washed with MeOH and water three times.

6.1.9 Synthesis of ethylenediamine (EDA) resin and diethylentriamine (DETA) resin

5.0 g of VBC resin were swelled in 100 mL NMP for 2 h before mixed with 50 mL EDA (or DETA). The mixture was stirred at 80 °C for 17 h. The beads were recovered and washed with 50mL NMP, 100 mL water and 100 mL MeOH (three times) sequentially.

6.1.10 Synthesis of urea resin

2.0 g of amine resin were mixed with 40 mL concentrated HCl at room temperature for 1h. The HCl was removed and the beads were washed with 100 mL water twice. 20 mL Potassium cyanate (KNCO) aqueous solution (20% w/w) was added to the beads. The reaction was stirred at room temperature for 17 h. The beads were recovered and washed with saturated sodium bicarbonate and water.

6.1.11 Synthesis of polyVBC-bound DETA monoamide of malonate ester

2.0 g of VBC resin was swelled 50 mL diethylenetriamine (DETA) for 2 h. The mixture was stirred at 110 °C for 17 h. The beads were recovered and washed with 50mL NMP, 100 mL water and 100 mL MeOH (three times) sequentially.

6.1.12 Synthesis of polyVBC-bound DETA amide of monocarboxylic acid

The DETA amide of monocarboxylic acid (DETA-AMA) resin was prepared by the amidation reaction of carboxylic acid resin similar to the polyVBC–supported carboxylic acid manoamide resin.

6.2 Resin treatment and characterization procedures

The functionalized resins were conditioned sequence of 1 L each of H_2O, 1 M NaOH, H_2O, 1 M HCl, and H_2O until neutral to pH paper at a rate of 1 L per h. After conditioning, all resins were kept under water at room temperature.

6.2.1 Büchner dried resin

All conditioned resins were stored in water and the excess water was removed by vacuum filtration with a Büchner funnel before using for characterization and metal ion contact studies. To get the Büchner-dried resin, approximately 1 g of resin was placed in a Büchner funnel, covered with a piece of latex and suction applied for 5 min at 710 mm Hg .

6.2.2 Percent solids determination

A 20 mL vial was weighed on an analytical balance after being dried in an over at 110 °C for 17 h. About 1.0 g of Büchner-dried resin was weighed in the vial and total mass was accurately recorded. The sample was then dried at 110 °C for 17 h. After cooling in a desiccator to room temperature, the mass of the oven-dried resin was determined. The percent solids was calculated with the following equation.

% Solids =[(Weight of oven-dried resin)/(Weight of Büchner-dried resin)] × 100%

6.2.3 Acid capacity determination

About 0.5 g of Büchner-dried resin were accurately weighed with an analytical balance into a 250 mL Erlenmeyer flask. To the same Erlenmeyer flask, 50 mL of astandardized 0.1 N NaOH containing 5 wt.% NaCl was added. The flask was shaken at a speed of 200 rpm for 17 h on a DS 500 Orbital Shaker after being covered with parafilm. Two 10 mL aliquots of the contacted NaOH were titrated with standardized 0.1 N HCl using phenolphthalein as the indicator. The acid capacity in mequiv/g was calculated with the following equation.

$$\text{Acid capacity} = (V_{NaOH}N_{NaOH} - 4 \times V_{HCl}N_{HCl})/[(g_{\text{Büchner-dried resin}})(\%\ \text{solids})]$$

where V_{NaOH} is the volume of NaOH, N_{NaOH} is the concentration of NaOH, V_{HCl} is the volume of HCl, N_{HCl} is the concentration of HCl, $g_{\text{Büchner-dried resin}}$ is the mass of Büchner-dried resin and % solids is percent solids of the resin.

6.2.4 Chlorine elemental analysis

A Parr bomb was used in the chlorine elemental analysis and care should be taken at all times. Nanopure water was used throughout the entire procedure due to a detectable amount of chlorine in distilled water. All the inner surfaces of a Parr bomb were rinsed thoroughly with nanopure water prior to use and 5 mL of 5 wt.% Na_2CO_3 was added.

About 1.0 g of oven-dried resin and 0.7 g of mineral oil were accurately weighed into a stainless steel capsule. After the capsule was placed securely in the holder, 10 cm of nickel alloy fuse wire was threaded through the bomb stem holes and secured so that the wire did not touch the metal of the capsule and hovered just over the oil/resin mixture. The bomb was capped and purged with 30 atm oxygen twice. On the third purge of oxygen, the gas was left in the bomb. The wire leads were attached to the bomb ignition unit and the bomb was submerged in a water bath followed by ignition. After 3 to 5 min in the water bath, the pressure inside the bomb was released slowly and the contents of the bomb were carefully rinsed into a 500 mL beaker. The solution was transferred into a 250 mL volumetric flask and diluted to the mark.

Two 25 mL aliquots were pipetted into separate 125 mL Erlenmeyer flasks in which about 2 mL of 2 N HNO_3 solution was added to remove the carbonate. 10 mL of 0.05 N $AgNO_3$ was added into the above flasks and the samples were heated until boiling on a hot plate and then were allowed to cool in a dark place to room temperature. The samples were filtered with pre-folded filter paper into clean 125 mL Erlenmeyer flasks and washed with 1 to 2 small pipettes of 0.01 N HNO_3. The samples were titrated with 0.05 N NH_4SCN to a faint orange end-point using 3 mL of $FeNH_4(SO_4)_2$ as the indicator. Two controls containing 10 mL of 0.05 N $AgNO_3$ were also titrated in the same manner. The chlorine capacity in mequiv/g was calculated with the following equation.

$$\text{Cl capacity} = [(V_{NH4SCN}\ \text{control} - V_{NH4SCN}\ \text{sample}) \times 10 \times N_{NH4SCN}]/g_{\text{oven-dried resin}}$$

where V_{NH4SCN} control is the volume of NH_4SCN consumed in the titration of the control; V_{NH4SCN} sample is the volume of NH_4SCN consumed in the titration of the sample; N_{NH4SCN} is the concentration of NH_4SCN solution; $g_{\text{oven-dried resin}}$ is the mass of the oven-dried resin.

6.2.5 Nitrogen elemental analysis

About 0.2 g of oven-dried resin was accurately weighted into a 500 mL three-neck round-bottom flask in which 0.25 g $CuSO_4$, 10 f K_2SO_4, 25 mL of concentrated

H_2SO_4 and a few boiling chips were added. A standard water jacket condenser was placed in the center joint of the flask and the other two joints were stoppered with glass stoppers. The mixture was gently heated with a heating mantle for 45 min followed by vigorously heating for about 8 h until the beads disappeared and the solution turned clear or had a faint blue/green color.

After cooling to room temperature, the condenser and two stoppers were carefully rinsed down into the flask and then removed. Approximately 100 mL of distilled water and a magnetic stir bar were added to the flask. A distillation condenser with a plastic funnel attached by a piece of Tygon tubing was placed in the center neck of the flask and one of the side joints was connected to a 150 mL addition funnel with a pressure equalization arm containing 150 mL of 6 N NaOH. Exactly 50 mL of standardized 0.1 N HCl was pipetted into a 600 mL beaker in which the plastic funnel was submerged in the acid but not completely flat against the bottom of the beaker. The NaOH was allowed to drip into the round-bottom flask over a 5 min period while the mixture was stirred. The solution in the flask should turn dark brown when all of NaOH was added. The brown mixture was distilled until the distillate was neutral. It usually took 40 to 45 min and the pH of the distillate was checked for neutrality using pH paper.

The acid solution was quantitatively transferred into a 250 mL volumetric flask and diluted to marked with distilled water. Two 25 mL aliquots of the acid solution were titrated with standardized 0.1 N NaOH using about 10 drops bromocresol green as the indicator. The nitrogen capacity in mequiv/g was calculated with the following equation.

$$\text{N capacity} = [(V_{HCl}N_{HCl}) - 10 \times (V_{NaOH}N_{NaOH})]/g_{\text{oven-dried resin}}$$

where , V_{HCl} is the volume of HCl, N_{HCl} is the concentration of HCl, V_{NaOH} is the volume of NaOH, N_{NaOH} is the concentration of NaOH, $g_{oven\text{-}dried\ resin}$ is the mass of oven-dried resin.

6.2.6 FTIR spectroscopy

All the resins were studied by FTIR (Bomem (MB Series); Hartmann-Braun) using KBr pellets which were prepared with 0.01 g of resin and 0.100 g of KBr followed by grinding and compression into pellets.

6.3 Contact studies

6.3.1 Metal ion contact solution preparation

All metal ion solutions were prepared with nanopure water along with reagent grade metal salts and acids. Stock solutions of the metal ions were prepared in concentration of 10^{-2} N in 100 mL volumetric flasks. Contact solutions were prepared by subsequent dilutions of the stock solutions in volumetric flasks to 10^{-4} N using acid solution with an appropriate acidity.

6.3.2 Metal ion contact study experiment

About 0.1 g of Büchner-dried resin was accurately weighted into a 20 mL polyethylene terephthalte (PET) scintillation vial. The resin was pre-equilibrated with approximately 10 mL of the background solution with the same acidity for 15 min and the solution was removed with a Pasteur pipette. The procedure was repeated three more times.

After the removal of the last exchange solution, 5 mL of the contact solution was added into the vial and the mixture was shaken on a DS500 Orbital Shaker for 17 h. The contact solution was removed from the resin to a clean PET vial using a clean pipette and analyzed by inductively coupled plasma–atomic emission spectrometer (Spectra Analytical Instruments, Spectroflame M120E). The appropriate wavelength used for each metal ion studied is listed in Table 6.2.

The results of contact study were expressed as percent metal ion complexed (%M^{n+} complexed) and distribution coefficient (D), defined below:

$$\%M^{n+} \text{ complexed} = \{([M^{n+}]_i - [M^{n+}]_{eq}) / [M^{n+}]_i\} \times 100$$

$$D = (\text{mmol } M^{n+} \text{ per gram of resin}) / (\text{mmol } M^{n+} \text{ per mL of solution})$$

Table 6.2 Selected wavelengths for metal ions studied

Metal ion	Wavelength (nm)
La	333.749
Ce	394.275
Nd	386.340
Sm	359.260
Eu	381.970
Gd	303.284
Tb	332.440
Dy	339.898
Ho	353.170
Er	337.271
Tm	313.126
Yb	211.667
Lu	261.542
Fe	259.940
Hg	184.950
Co	238.892
Ni	221.647
Cu	224.700
Zn	213.856
Cd	220.353

6.4 References

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7 Appendix A

Results of the complexation of transition metal ions with poly(vinylbenzyl chloride)-bounded *N, N, N', N'*-tetramethylamlonamide (TMMA)

7.1 Effect of HCl concentration

The complexation of TMMA resin with 10^{-4} N solution of Fe(III), Hg(II), Cd(II), Cu(II), Zn(II), Co(II) and Ni(II) was examined under acidic conditions 0.001 M to 8 M.

The effect of HCl concentration on complexation of those transition metal ions is depicted in Fig. 7.1. Fe(III) complexation increases as the HCl concentration increases and 95% Fe(III) is complexed on the resin from 6 M and 8 M HCl (log$D$ > 3). The extraction of Hg(II) by TMMA resin peaks in 0.1 M HCl but declines in both higher and lower acidities. Cd(II) and Zn(II) behave similarly under different acidities—the complexations are low in 0.001 M to 0.1 M HCl, then remain moderate as the acidity increases to 8 M. The TMMA resin has low affinity for Cu(II), Co(II) and Ni(II) over all acidities.

The differences in the complexation of transition metals by the TMMA resin may be attributed to the tendency to form MCl_4^- and MCl_4^{2-} ions under different acidities.

Spectrophotometric investigation of the extraction of Fe(III), Co(II), Cu(II), and Ni(II) by tertiary amines in toluene from HCl solution showed excellent agreement between the spectra observed from the organic phase and those of the MCl_4^- and MCl_4^{2-} ions, indicating that the extracted species are four-coordinate complex ions.[1] The complexed anion species by an anion exchange resin AG MP-1 in 12 M HCl was reported to be $CuCl_4^{2-}$ ions based on the results of an extended X-ray absorption fine structure (EXAFS) study in combination with Raman spectroscopy.[2]

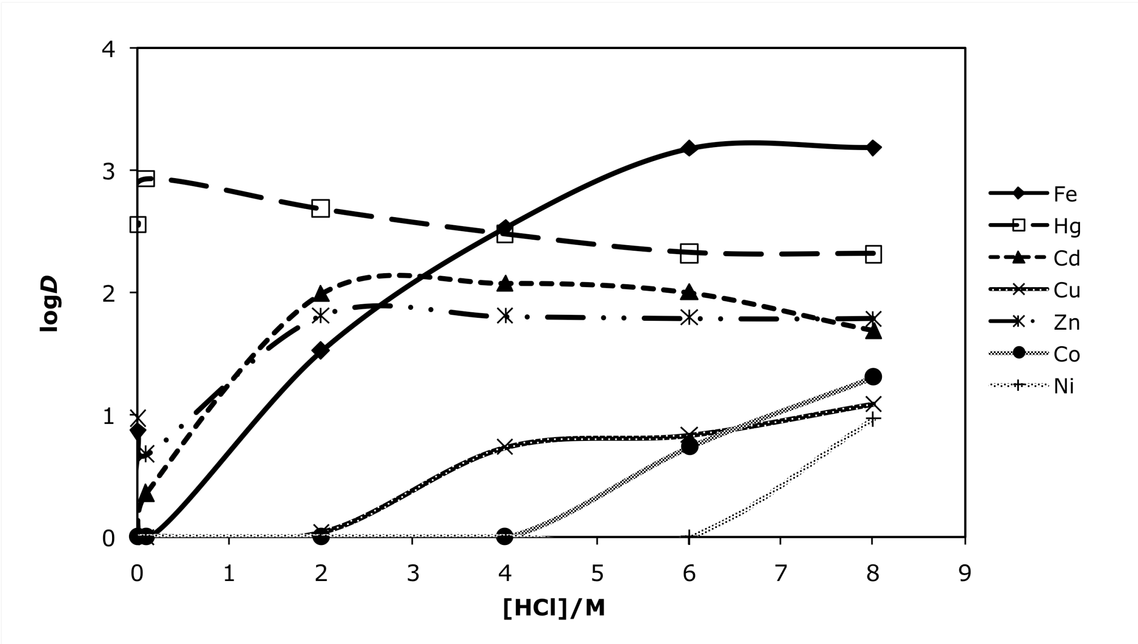

Figure 7.1 Complexation of transition metal ions as a function of HCl concentration

In the complexation of TMMA resin with Fe(III), the protonation of the TMMA and formation of iminum moiety take place when the concentration of HCl reaches 6 M and ion exchange then operates by exchanging the chloride ion with the anionic ferric complex. The HCl concentration dependency for Fe(III) is consistent with soluble *N,N'*-tetrasubstituted malonamides.[3, 4, 5] $FeCl_4^-$ is the predominant species when the HCl concentration is greater than 4 M.[6, 7] It has also been detected by UV-visible spectroscopy as the extracted species by malonamide complexants in 8 M HCl. In a study of the complexation of Fe(III) by malonamides to confirm the ion exchang mechanism involved with $FeCl_4^-$ formation, HCl was replaced by LiCl or NaCl for a total chloride concentration of 8 M. The metal ion is, however, complexed by the ligand only from lithium chloride solutions due to the bigger size of sodium which does not allow it to act as lithium to form $Li^{+}FeCl_4^{-}$ complex in a similar way to a proton.[8]

Mercury (II) exists as tetrachloromercury(II) complex ($HgCl_4^{2-}$) in acidic solutions[9] and the tetrachloro complex becomes the predominant solution species as [Cl^{-}] > 0.1 M.[10] Consistent with that, the complexation of Hg(II) by TMMA resin achieved a maximum at 0.1 M HCl. The subsequence decrease of affinity is probably due to the competition by the high chloride ion concentration.

In the case of Zn(II), it is suggested that in 12 M HCl 87.9% zinc forms the anionic complexes $ZnCl_4^{2-}$[11] and consequently a moderate affinity is observed. Similar to Zn, Cadmium shows a modest distribution coefficient.

The low affinities towards Co(II), Ni(II) and Cu(II), as evidenced by low sorption over the entire HCl concentration range, may be ascribed to unfavorable formation of anionic complexes. In 0.001 M to 8 M HCl solutions, Co(II) and Cu(II) are not present predominately as anionic complexes although they form four-coordinated $CoCl_4^{2-}$ and $CuCl_4^{2-}$ in more concentrated HCl (12 M). Only 28.8% copper forms $CuCl_4^{2-}$ compared to 51.5% forms $CuCl_3^{-}$. The average coordination number of Cl around Cu is 2.4, 3.1, and 3.3 in 3 M, 7 M and 12 M HCl solutions, respectively, indicating that the dominant species in 7 M HCl is $CuCl_3^{-}$ rather than $CuCl_4^{2-}$. On the other hand, Ni(II) does not form $NiCl_4^{2-}$ complex ions in HCl and they exist as $Ni(OH)_6^{2+}$ instead.

7.2 Affinity Sequence in 8 M HCl

Affinity sequence of Fe(III), Hg(II), Zn(II), Cd(II), Co(II) and Cu(II) by the TMMA resin in 8 M HCl is Fe(III) > Hg(II) > Zn(II) > Cd(II) > Co(II) > Cu(II) > Ni(II) (Fig. 7.2). The metal affinity is affected by the metal's tendency to form chloro complexes in 8 M HCl. Fe(III) has the greatest affinity whereas Ni(II) exhibits the lowest affinity due to its inability of forming $NiCl_4^{2-}$ complex.[12]

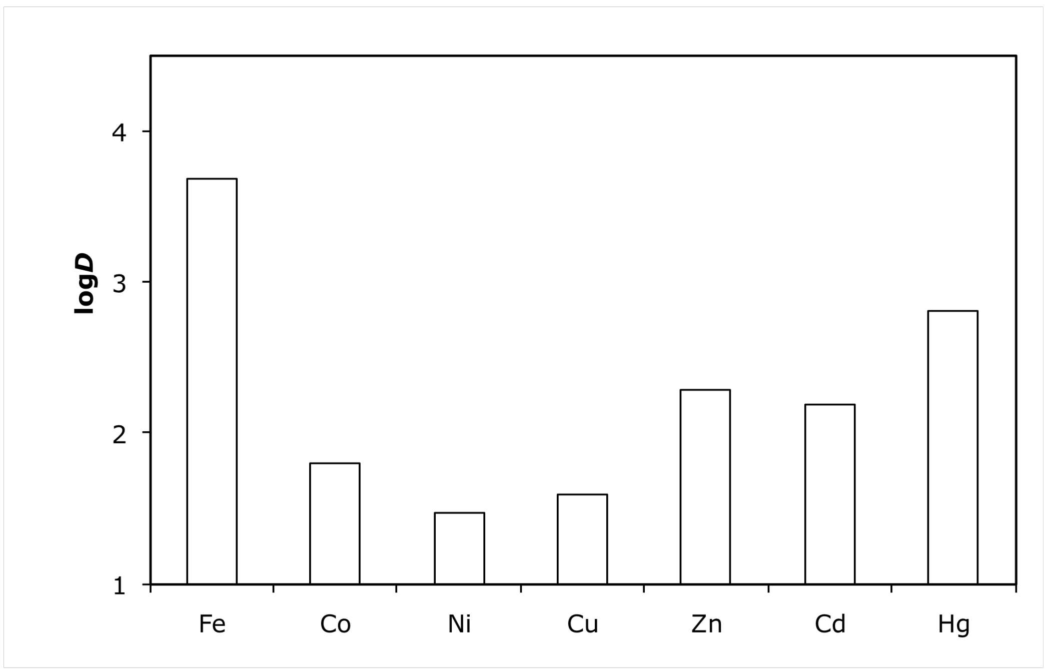

Figure 7.2 Metal ion sorption from 8 M HCl by the TMMA resin

7.3 Effect of HNO_3 concentration

The effect of nitric acid concentration on the complexation of Fe(III), Hg(II), Cd(II), and Zn(II) by the TMMA resin is shown in Fig. 7.3. The level of complexation towards Hg(II), Cd(II), and Zn(II) decreases substantially (Fig. 7.4). The high level of iron sorption is in contrast with what has been found by the substituted malonamide complexants which showed no complexation of Fe(III) in concentrated HNO_3.[12, 13] The low sorption of other transition meal ions may be ascribed to the unfavorable formation of anionic nitrate complexes. The affinity of Fe(III) in nitric acid increases with the increasing acid concentration up to 6 M and then decreases as the acidity further increases, which might be attributed to the formation of less extractable $Fe(NO_3)_5^{2-}$ complex and the extraction of acid.

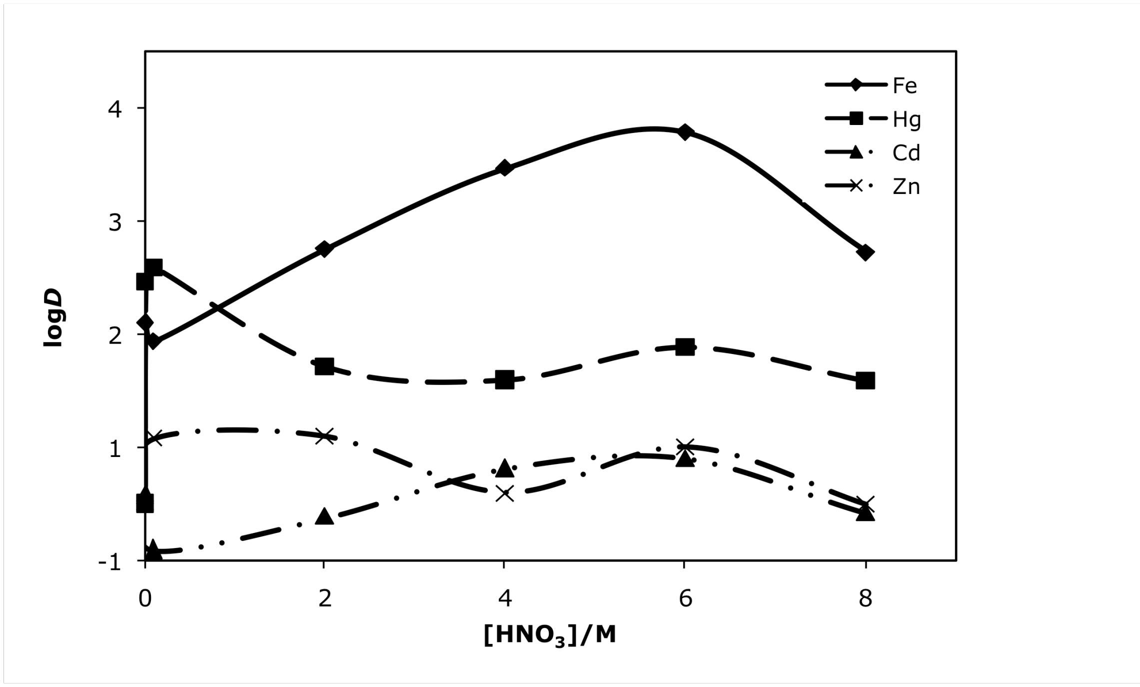

Figure 7.3 Complexation of transition metal ions as a function of HNO_3 concentration

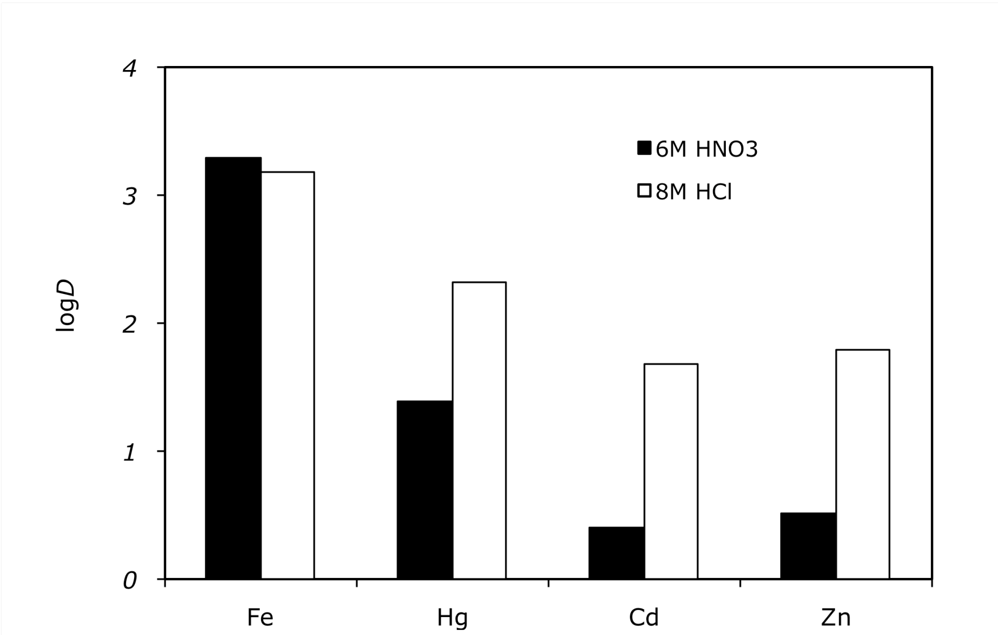

Figure 7.4 Comparison of Fe(III), Hg(II), Cd(II) and Zn(II) complexation by TMMA resin from 6 M HNO_3 and 8M HCl

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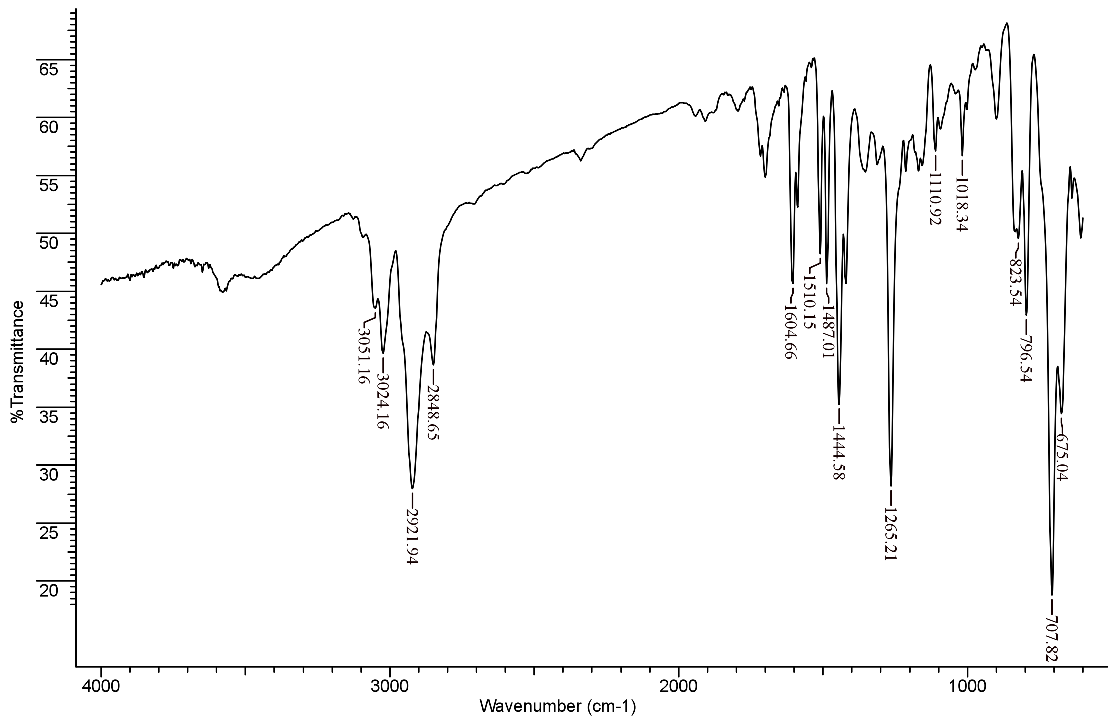
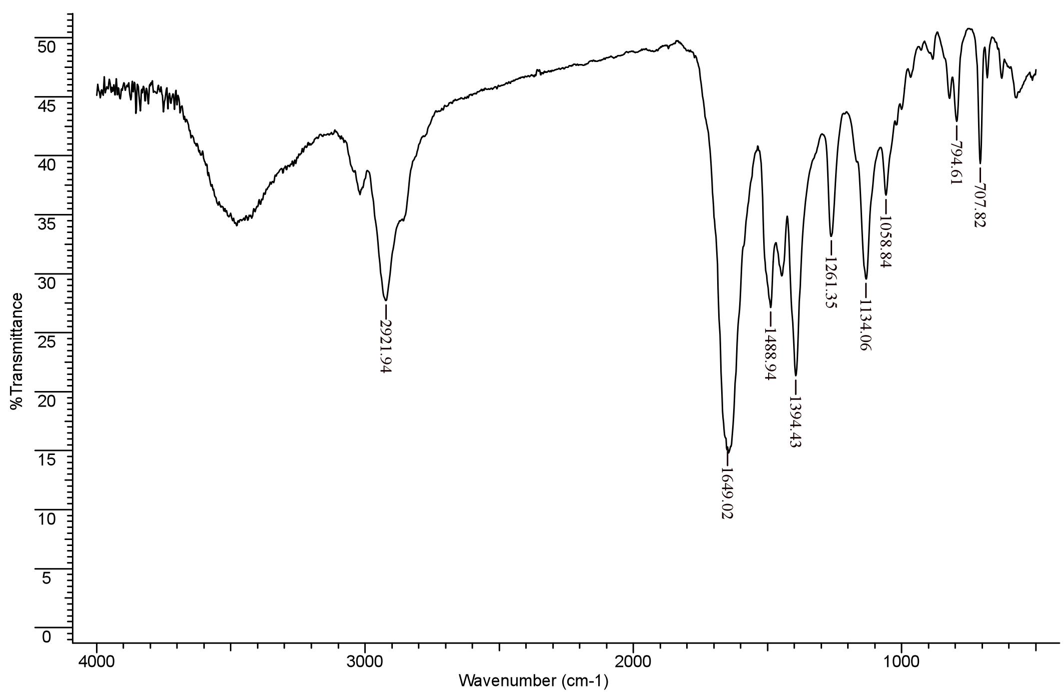
8 Appendix B

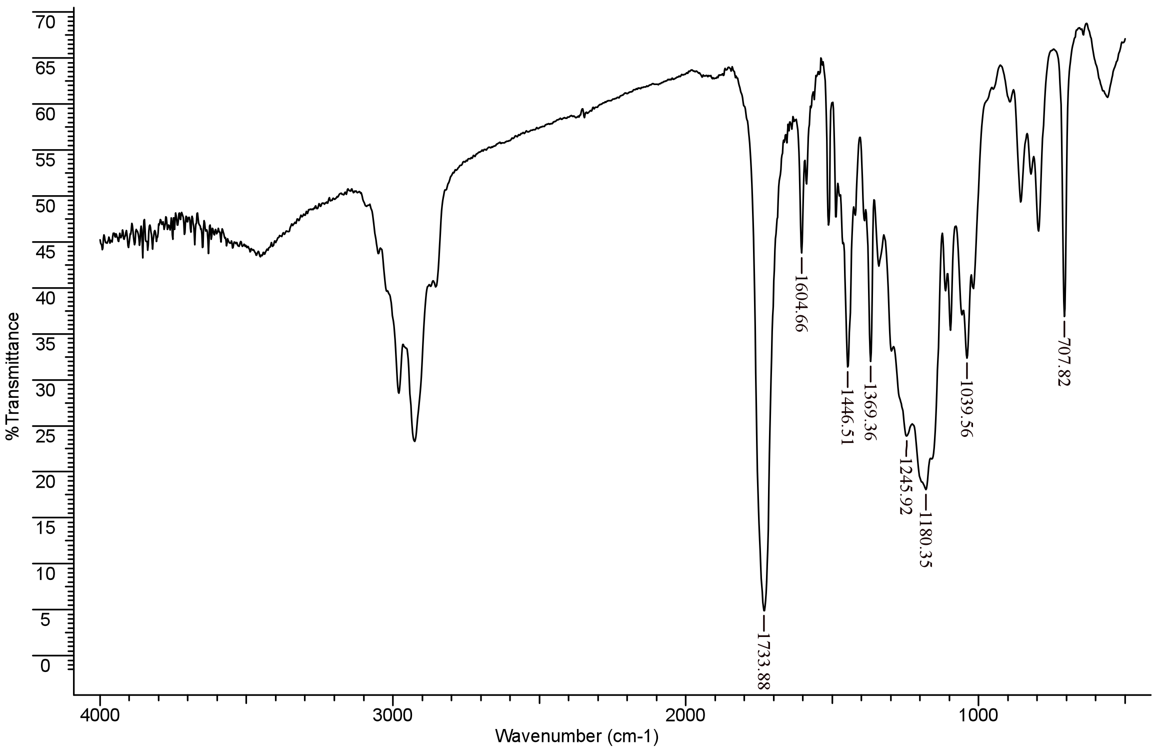
IR spectrum of poly(Vinylbenzyl chloride) gel resin



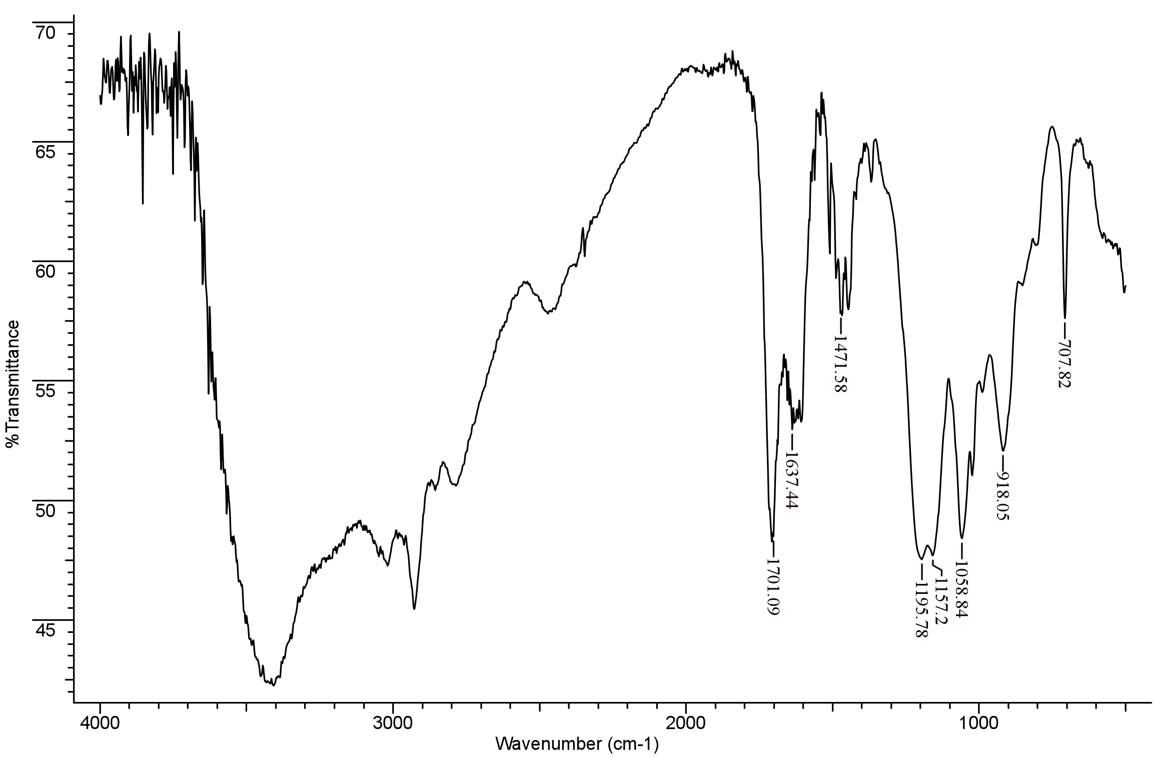
IR spectrum of polyVBC-supported TMMA gel resin



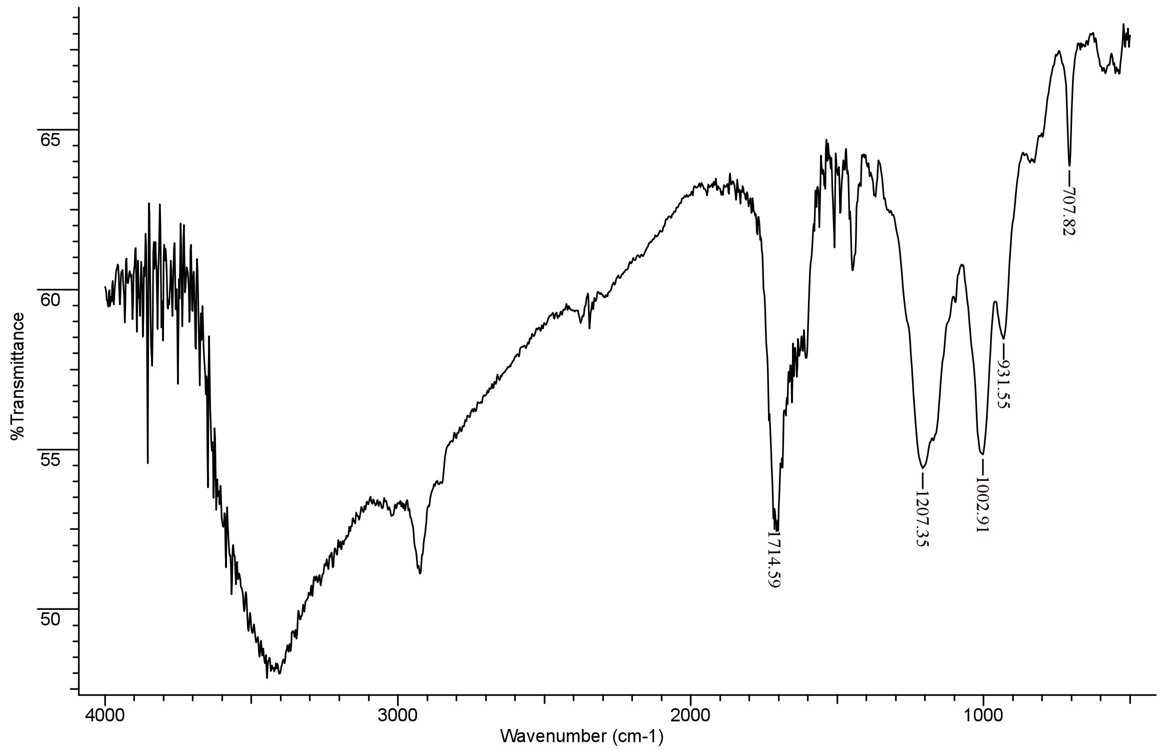
IR spectrum of polyVBC-supported malonate diester gel resin



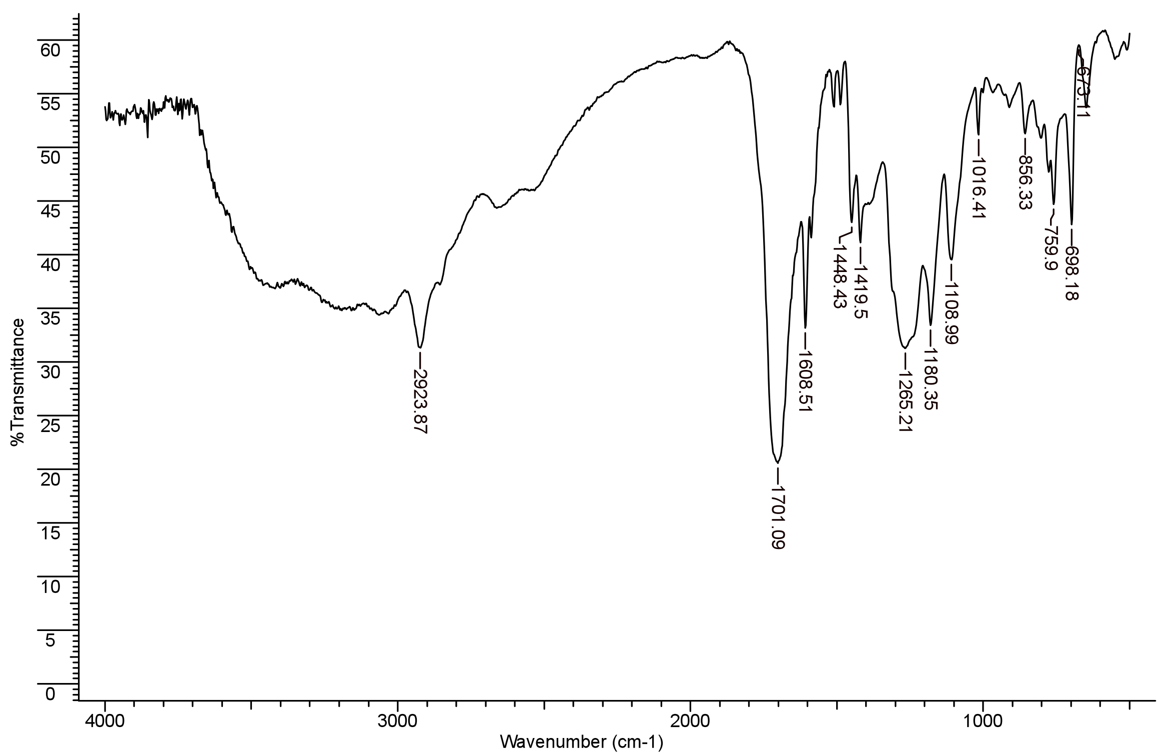
IR spectrum of polystyrene-supported monoamide gel resin



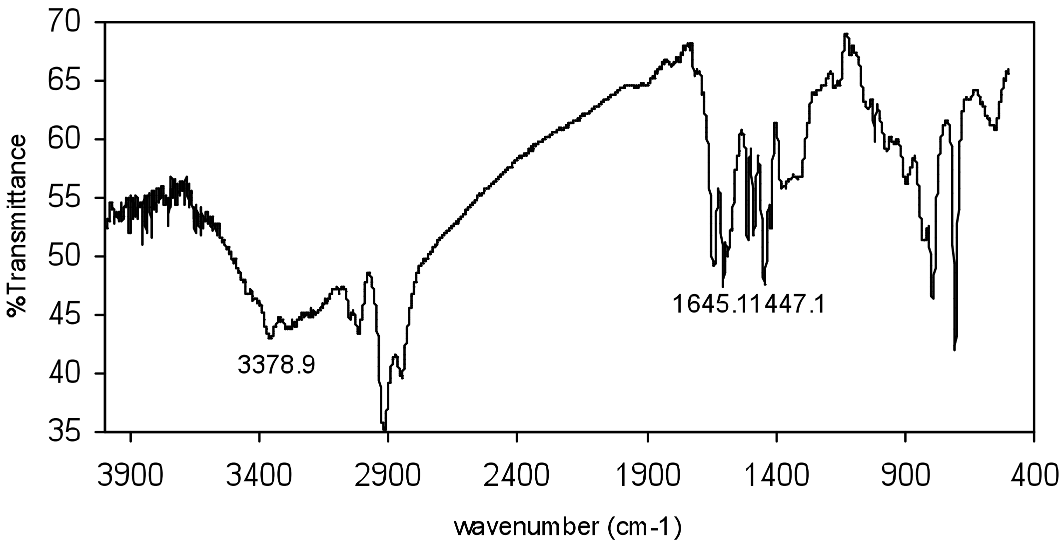
IR spectrum of polysytrene-supported malonic chloride gel resin



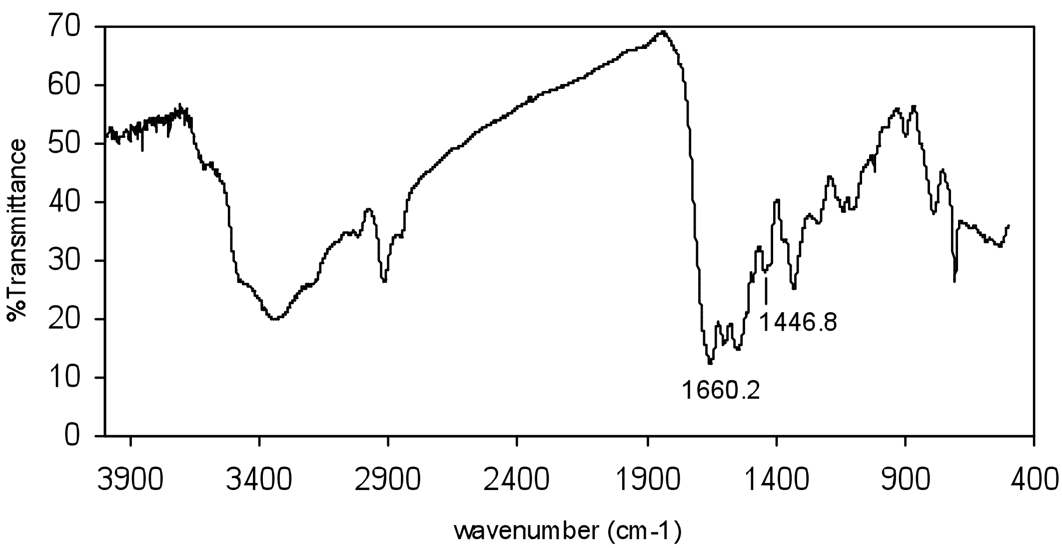
IR spectrum of polystyrene-supported malonic acid gel resin



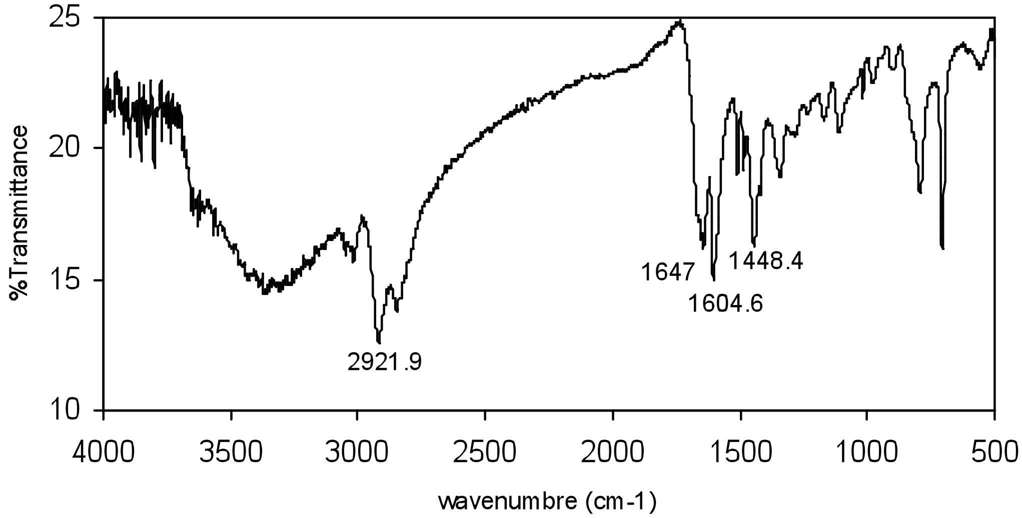
IR spectrum of polyVBC-supported primary amine gel resin



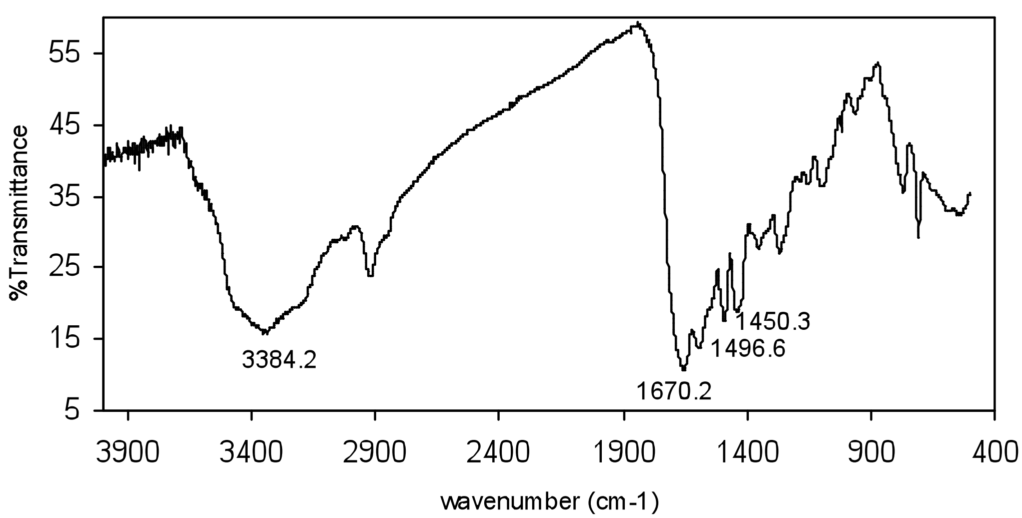
IR spectrum of polyVBC-supported Urea-1 gel resin



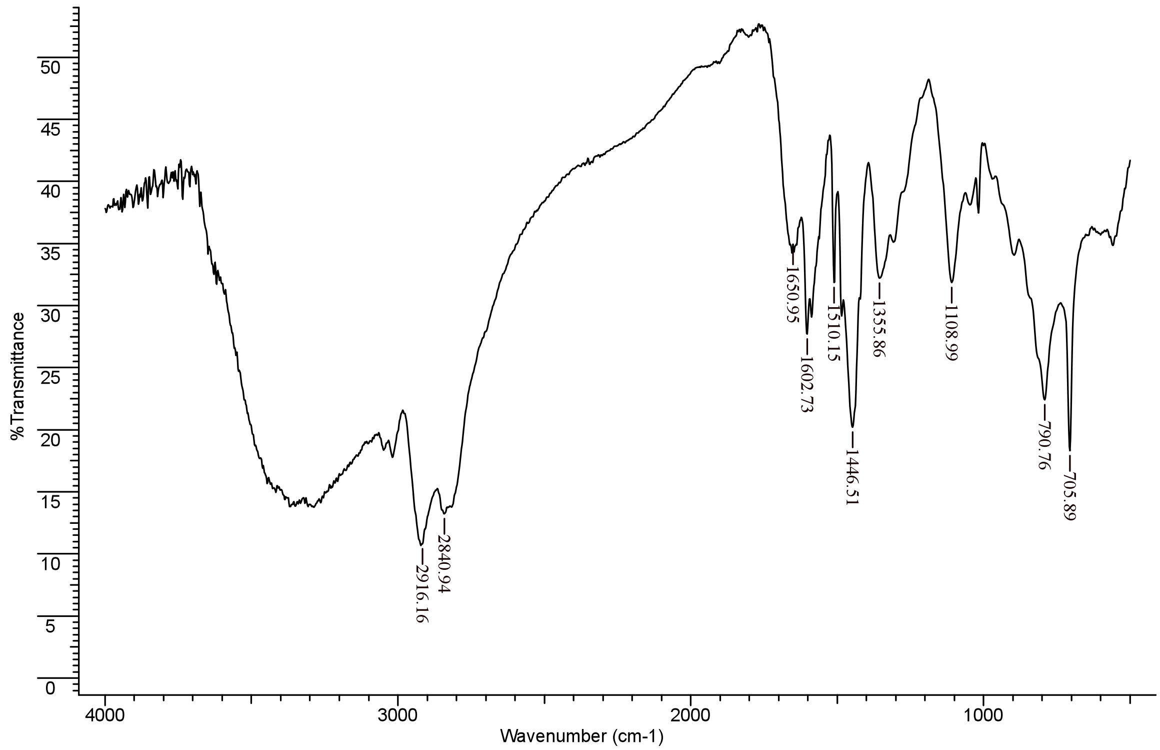
IR spectrum of polyVBC-supported EDA gel resin



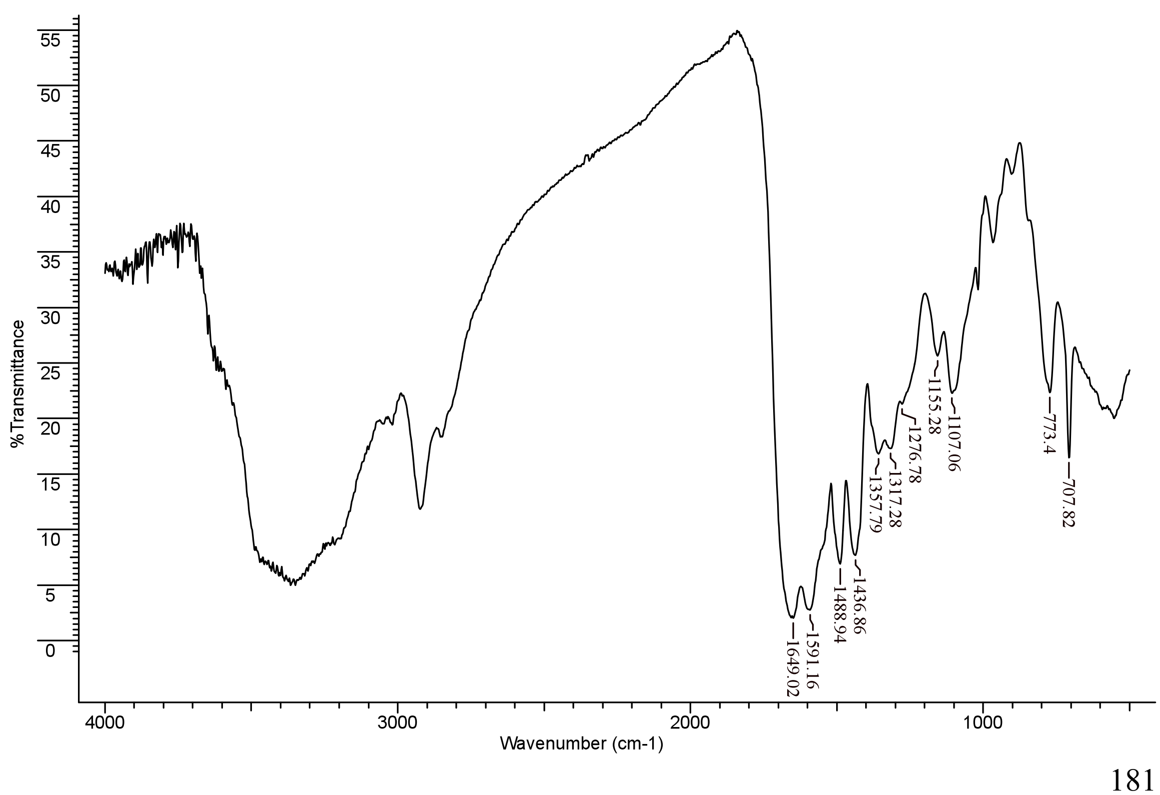
IR spectrum of polyVBC-supported Urea-2 gel resin



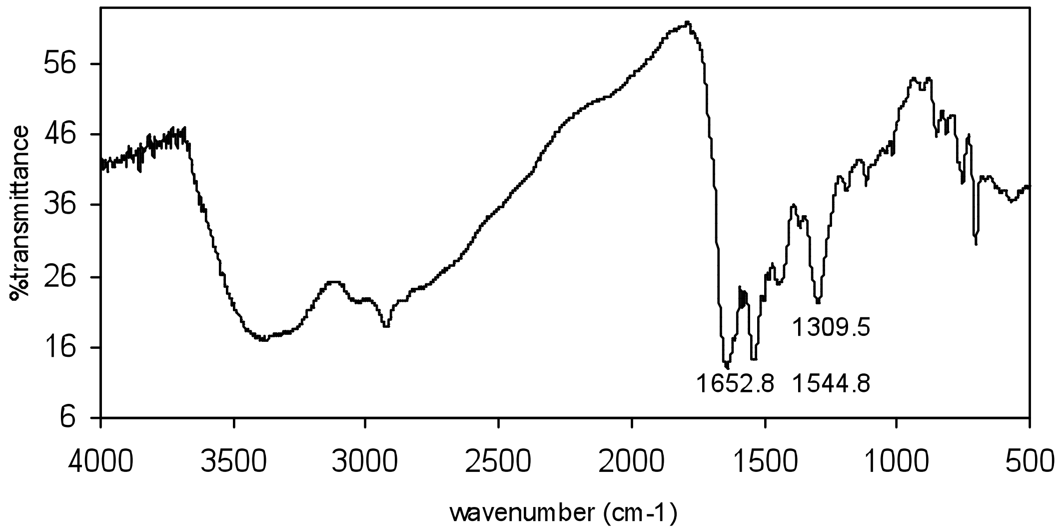
IR spectrum of polyVBC-supported DETA gel resin



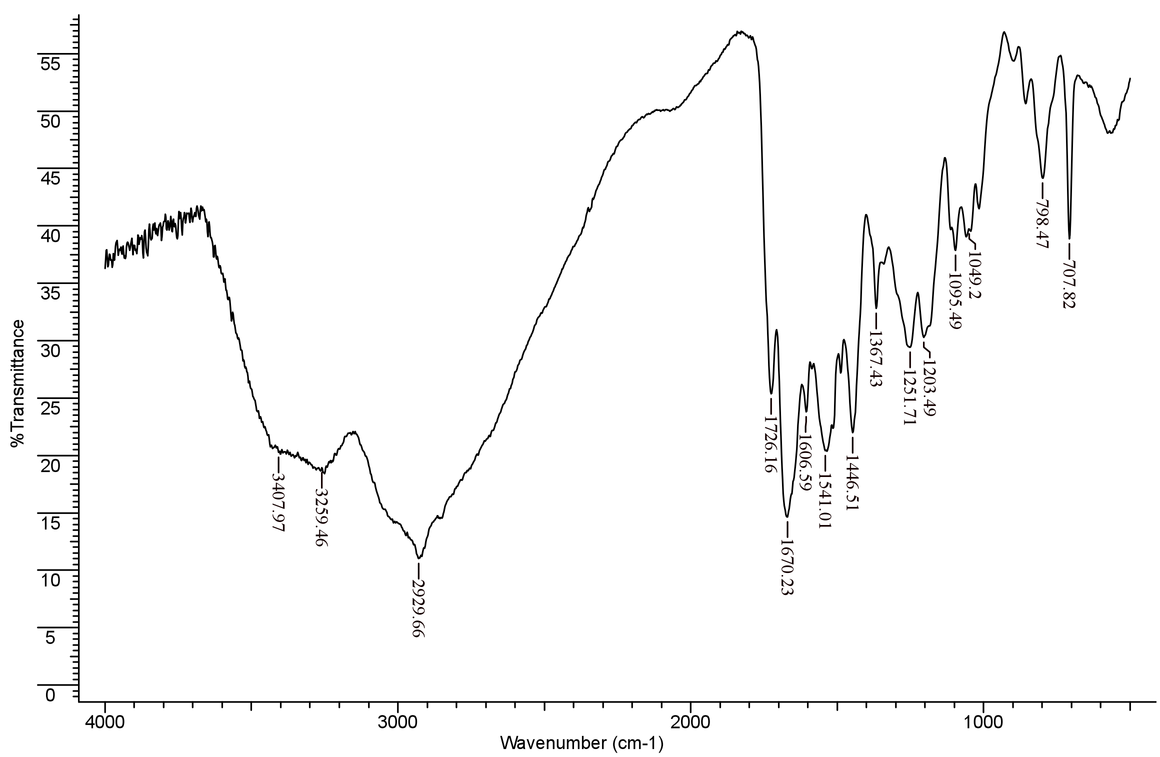
IR spectrum of polyVBC Urea-3 gel resin



IR spectrum of polyVBC-supported DETA-AMA gel resin



IR spectrum of polyVBC-supported DETA-MAM gel resin



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Chapter 3

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