To the Graduate Council:

I am submitting herewith a thesis written by Vijay T. Patel entitled "Synthesis of Anion Exchange Resins for Selective Complexation of Pertechnetate Ion." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

Spiro D. Alexandratos, Major Professor

We have read this thesis
and recommend its acceptance:

Accepted for the Council:

Associate Vice Chancellor and
Dean of the Graduate School

SYNTHESIS OF ANION EXCHANGE RESINS FOR SELECTIVE COMPLEXATION OF PERTECHNETATE ION

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville.

Vijay T. Patel

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To my family

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ABSTRACT

Anion exchange resins were synthesized by functionalizing polymer supports with different crosslink densities. A variety of amines, including trialkylamines, with different alkyl-chain lengths were used as the ligands in the synthesis of monofunctional and bifunctional resins. The resins were characterized by total anion exchange capacities (TAEC), percent solids of the resins, chlorine and nitrogen elemental analyses. The results show that as the alkyl-chain length of the trialkylamine increases, the degree of functionalization decreases. An increase in alkyl-chain length also contributes to an increase in hydrophobicity, resulting in slow accessibility. Bifunctional resins were synthesized with two different trialkylamines on a 5% crosslinked poly(vinylbenzyl chloride) polymer support in a two step reaction. Each step is similar to the monofunctionalization reaction.

Metal-ion studies of the resins were performed with a simulated ground water solution consisting of pertechnetate and other potentially interfering anions. The distribution coefficients were determined by batch processes with varying equilibrium time. The results indicate selectivity of the resin toward pertechnetate increases with an increase in alkyl-chain length and varies with the microenvironment. The increase in alkyl-chain length, however, increases the time needed to reach equilibrium. Optimum selectivity was achieved using tripropyl and tributyl ammonium groups on a crosslinked poly(vinylbenzyl chloride) polymer support. Copolymers incorporating methyl methacrylate show poor selectivity for pertechnetate. Styrene copolymers show remarkable selectivity over those with methyl methacrylate and butyl methacrylate. These results indicate the microenvironmental effect plays an important role in the selectivity of the resins.

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INTRODUCTION

The phenomenon of ion-exchange has been known for many years. In ancient times, Moses succeeded in preparing drinking water from brackish water by what is believed to be an ion-exchange phenomenon. About a thousand years later, Aristotle stated that sea water loses part of its salt content when percolating through a sand filter [1]. The first scientific study of ion-exchange was undertaken in the middle of the 18th century by Thompson and Spence. Spence, a New York based analyst engaged by English landowner H. S. Thompson to investigate the loss of ammonia from manure heaps, discovered that when a solution of ammonium sulfate was percolated through a column of soil, all of the ammonium ion was removed and was replaced by calcium [2]. This was a surprise because at that time, the dissociation of salt in water was not known. Soon after that, J. T. Way, an agricultural chemist, further studied the phenomenon [3,4], and confirmed Spence's work which had been presented to the Royal Agricultural Society in 1850. Zeolites were later determined to be responsible for the ion-exchange properties of soils [5].

Since that time many other natural compounds which undergo ion-exchange processes have been found. Some of these compounds include: silicates, humic acids, wool, cellulose, hair and certain seaweed components (e.g. agar and carrageen [6]). The first practical use of ion-exchange compounds was by Gans, who used both natural as well as synthetic zeolites in the treatment of water and of sugar solutions [7]. However, the evolution began in 1935 with the discovery by two English chemists, Adams and Holmes, that crushed phonograph records exhibit ion-exchange properties. This remarkable effect led them to produce the first

synthetic ion-exchange resin, a sulfonated phenol-formaldehyde condensation polymer [8]. After that, in 1944, G. F. D'Aleio at General Electric's Pittsfield Laboratories, synthesized the first polystyrene-based ion-exchange resin [9].

Ion-exchange resins, by common definition, are insoluble solid materials which carry exchangeable cations or anions [10]. These ions can be exchanged for a stoichiometrically equivalent amount of other ions of the same sign when the ion-exchanger is in contact with an electrolyte solution. Carriers of exchangeable cations are called cation exchangers and carriers of exchangeable anions, anion exchangers. By convention those resins (ion-exchangers) containing $-SO_3^-$, $-COO^-$, $-PO_2^-$, $-PO_3^{2-}$, or $-AsO_3^{2-}$ functional groups are cation-exchange resins, and those containing $-NH_3^+$, $>NH_2^+$, $>N<$, or $-S^+<$ are anion exchange resins [10]. So far, cation exchange resins have received more attention compared to anion-exchangers due to studies involving the recovery of precious metal cations. Relatively little work has been done on anion-exchange resins. Organic anion-exchangers were among the earliest ion-exchange resins. As with the cation-exchange resins [11], Adams and Holmes were the first who patented anion-exchange resins with weak-base amino groups [12].

Later, resins with strong-base quaternary ammonium groups were prepared [13-17]. Recent anion-exchangers include resins with other quaternary-phosphonium [18,19] and tertiary sulfonium groups. However, amino-based resins are most versatile due to the availability of a variety of amines, which contribute to the selectivity of the resin. In the past two decades, the selectivity of ion-exchange resins has been studied extensively. Uses for selective resins include the recovery of precious metals, radioactive metals and other environmentally hazardous ions.

The factor most associated with selectivity is the nature of the ligands. As a result,

many resins have been developed for selective recovery of cations as well as anions, including nitrate and gold cyanide.

Nitrate removal has received appreciable attention due to its toxicity. Ginocachio has found that high nitrate intake from drinking water can cause cyanosis in small children and can lead to gastric cancer in adults [20]. Thus, removal of nitrate ion from drinking water has become a major concern [21]. There are several anions present in drinking water along with nitrate which are not harmful, including sulfate, making their removal unnecessary. However, when a commercially available strong base resin (trimethylamine on styrene) was used, sulfate ion competed with nitrate in exchanging at the anionic sites thus reducing the capacity for nitrate.

McGarvey and Gonzalez [22] have studied the effect of ligand on nitrate selectivity over sulfate by using triethyl, tripropyl and tributylamine on crosslinked polystyrene. A separate study by Jackson and Bolto [23], using polyepichlorohydrin and polydiallylamine derivatives on polystyrene has also been carried out. Both studies have shown that the preference of an anion-exchange resin for nitrate over sulfate increases as the resin becomes more hydrophobic. Thus nitrate selective resins are those with a polystyrene backbone and large trialkyl substituents on the amino-nitrogen atom.

Another well known example for selective anion exchange involves the recovery of gold [24,25]. It has been reported that tris(2,6-dimethoxyphenyl)-phosphine [(2,6-MeOPh)$_3$P] and tris (2,4,6-trimethoxyphenyl)-phosphine [(2,4,6-MeOPh) P] ligands can complex $AuCl_4^-$ selectively. Matsushita and Fujiwara [25] have synthesized the anion-exchange resins by incorporating these ligands on a chloromethylated polystyrene backbone (Figure 1). These resins show high selectivity for gold over copper from acidic media such

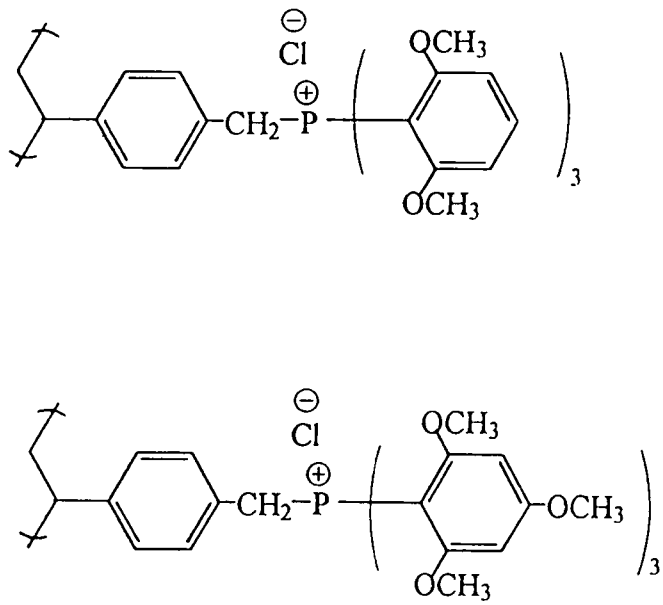


Figure 1 Tris(2,6-dimethoxyphenyl)-phosphine (Top) and Tris(2,4,6-trimethoxyphenyl)-phosphine (Bottom) on Chloromethylated Polystyrene Backbone.

as electroplating solutions. In the cyanide-leach process, where the solution is basic (pH 10-11), medium base polyamine ion-exchangers have shown remarkable selectivity for gold [26]. These resins were made by incorporation of 1,3-diaminopropane and 2,4-diamino-2-methylpentane on crosslinked polyvinylbenzylchloride.

Selectivity of the resin is of particular concern when the ion of interest exists in low solution concentrations along with other ions. Resin selectivity is thus critical to minimizing cost associated with many applications, including the purification of groundwater, contaminated with radioactive ions. One of the most dangerous radioactive pollutants found in the groundwater near nuclear fission plants is technetium-99. Because of its nuclear instability, technetium is not found naturally on earth. However, it has been produced in kilogram quantities from other elements by nuclear reaction, processes in which nuclei are transformed into different nuclei.

Technetium (from Greek "tekhnetos", meaning "artificial") was the first new element produced in the laboratory from another. It was discovered in 1937 by Carlo Perrier and Emilo Segre when the element molybdenum was bombarded with deuterons. Later, technetium was found to be a product of the fission or splitting of uranium nuclei. Thus, technetium is produced in nuclear fission reactors used to generate electricity. Technetium-99, one of the isotopes of technetium has a half-life 2.14×10^5 yr. It is formed in high yield (about 6% of the total fission product) in the thermal-neutron fission of uranium. Typical low-enrichment light water nuclear-power reactors may yield ~ 27.5 kg of Technetium-99 per 1000 MW/yr of electric energy produced [27].

Technetium-99 from the nuclear fuel cycle may enter the environment as a result of disposal of aqueous waste or during the separation and recovery of spent nuclear fuels[28].

The predominant form of technetium under oxygenated conditions is the pertechnetate (TcO_4^-) anion [29], which is highly soluble in water and of particular concern because of its persistence (Tc-99 undergoes radioactive decay by low-energy, 0.29 MeV, beta emission with a half-life of 2.14×10^5 yrs) and mobility [27,28,30]. Because of its great mobility and accidental releases Tc-99 (as the pertechnetate ion) ion has been detected in the groundwater samples taken from some monitoring wells around former nuclear-fuel recycling facilities and uranium enrichment plants [31]. Such a scenario violated the repository requirement established by the Environmental Protection Agency. Thus, both civilian and defense related nuclear waste must be treated using a strategy that deals with technetium.

Two important technologies of separation and isolation of pertechnetate ion have been known: solid-phase ion exchanger[32] and liquid-based solvent extraction [33]. Both of these techniques use ion-pair formation between the pertechnetate anion and an amine cation. However, solid-phase ion-exchange has been preferred in the case of groundwater treatment due to the ease of product separation and disposal.

The use of ion-exchange resins to separate radioactive ions from solution is well documented [32,34-36]. Many commercially available anion exchange resins are capable of removing TcO_4^- ion along with typical anions found in groundwater. Another scheme has been proposed for the removal of Tc from groundwater involving reduction of Tc to a lower oxidation state that is insoluble or that precipitates from solution [37]. This method may not be effective if oxygen in the aquifer or from other sources can oxidize the Tc back to the soluble TcO_4^- ion. Thus, the use of anion exchange resins to complex the pertechnetate anion will have advantages over reductive schemes if the resin can be made selective. The pertechnetate anion has a high affinity for strong base anion exchange resins such as those

made from quaternary amines. Most commercially available strong base resins do not have as high a selectivity for TcO_4^- over chloride, sulfate, or nitrate ion as is desirable. These latter anions can be present in the groundwater at a concentration of 10^6 times greater than pertechnetate.

Until recently, it has been known that the nature of the ligand has the most influence on the selectivity. Recent developments have shown that ionic selectivity can also be influence by what has been termed the microenvironmental effect . This is the effect in which the ligand-substrate interaction is affected by the microenvironment surrounding the polymer-supported ligand (Figure 2). Alexandratos and Beauvais [38] have studied the effect of the microenvironment surrounding a ligand within a polymer using ion complexing IPNs (interpenetrating polymer networks). The IPNs in this study were prepared by polymerizing a solution of N-vinylimidazole and ethyl acrylate in different ratios, within a polystyrene network. The imidazole ligand is capable of complexing Cu (II) and Co (II) ions and this

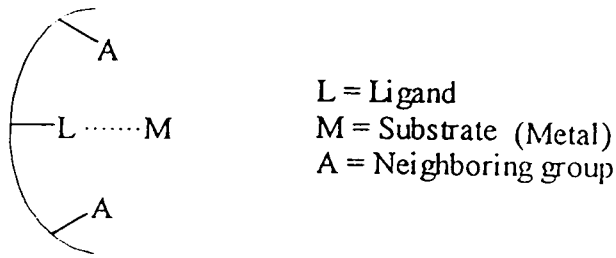


Figure 2 Microenvironmental Effect on Ligand Substrate Interaction.

ability has been studied as a function of the ligand's microenvironment. The strength of the imidazole-ion interaction is sensitive to the polymer microenvironment: as the imidazole/ester ratio decreases along the series 1/0, 0.77/0.23, 0.53/0.47, 0.27/0.73, and 0/1, the Cu (II) binding constants [39,40] are 3130, 4134, 8203, 3108, and 0 N^{-1}, respectively, and Co (II) binding constants are 294, 270, 86, 129 and 0 N^{-1}.

The goal of this research is to synthesize and study anion exchange resins which selectively remove pertechnetate ion from groundwater in the presence of potentially interfering anions. This work involves not only the nature of the ligands but also the influence of the microenvironmental effect. The question of whether the microenvironmental effect at the exchange sites within an ion exchange resin can play a major role in anionic selectivity will be addressed.

CHAPTER 1

SYNTHESIS OF ANION EXCHANGE RESINS

INTRODUCTION

Synthetic organic ion exchange resins have been made by three methods: (1) polymerization of functionalized monomers, (2)functionalization during polymerization, and (3) post-functionalization of the polymer support. Method two has not received more attention due to the difficulty in controlling the crosslink density. Use of method one is limited because several functional groups can act as inhibitors or retarders in the polymerization. Post-functionalization (method three) is the most convenient way to synthesize ion-exchange resins. This method allows for control of the crosslink density as well as flexibility in the selection of functional groups.

The post-functionalization method was used to prepare anion-exchange resins in this research. Chloromethylated polystyrene is a known polymer support for many ion exchange resins prepared by post-functionalization. Control over crosslink density, stability of the network and ease of functionalization are prominent features of this polymer support. Poly(divinylbenzene-co-vinylbenzyl chloride) (DVB/VBC copolymer) with varying crosslink density were used as polymer supports in this research, which gives essentially the same polymer support as the chloromethylated styrene. The use of DVB/VBC copolymer eliminates the highly toxic chloromethylation step in the laboratory and provides better control on the degree of functionalization. One of the ways to control the degree of functionalization is the incorporation of groups that are inert to the functionalization conditions. These groups are units present in the polymers which in general, do not take part

in the functionalization reaction, but act only to decrease steric interactions between the sites. Some polymer supports were synthesized using methyl methacrylate (MMA) and styrene groups in the studies.

Divinylbenzene (DVB) was used as a crosslinking agent due to its compatibility with vinylbenzyl chloride (VBC). VBC is the polymeric group on which functionalization takes place. Crosslink density is a function of the amount of divinylbenzene used. Thus, a 10% crosslinked polymer support is made with 10% DVB relative to the total monomer weight.

Polymer supports were synthesized by suspension polymerization in the form of beads. Beads can be either gels or macroporous (MRs). Gel beads have micro-channels and are prepared without diluent. MR beads have macro channels with approximate diameter of 500Å. To create macroporosity in the beads, inert diluent is added to the monomeric mixture prior to the polymerization. After polymerization, the diluent is distilled off, which leaves macropores in the beads. All the MR copolymers were synthesized with 50 weight % of the diluent relative to the total weight of the organic phase (chapter 4). 4-methyl-2-pentanol (4M2P), which is a good solvent for monomers like styrene, DVB and VBC, but a poor solvent for the polymer which forms, was used as a diluent. Both MRs and gels were Soxhlet-extracted with toluene to remove residual 4M2P (for the MR), monomers and oligomers. Before functionalization, the oven-dried copolymer was sieved by American Standard Testing sieves into different mesh sizes. For consistency, a -40 +60 mesh size was used for all resins, unless otherwise indicated. A -40 +60 size indicates that beads passed through the 40 mesh screen but were retained by the 60 mesh screen. Table 1 lists the bead sizes in both ASTM mesh and microns (μ).

Table 1

Comparison of Bead Sizes in Mesh and Microns (μ).

Mesh size	16	20	30	40	60	80	100	200	325
Bead diameter (μ)	1180	850	600	425	250	180	150	75	45

The size distribution of the beads depends on the design and speed of the stir paddle. The higher the stir speed, the smaller the bead size. A typical -40 +60 mesh size [425-250μ] was predominant at 240 rpm.

Crosslinking is required so that beads do not dissolve and retain a desirable strength. A typical gel polymer support was made with 2% crosslinking. However, higher crosslinking is required for the MR beads to prevent the collapse of the macro channels. Higher crosslink density provides high strength to the beads but restricts the accessibility of the functional groups. Polymer supports with 5%, 10%, 15%, 25%, and 40% crosslink density (MR) were synthesized for the accessibility study. For consistency, a 10% crosslinked polymer support was used for all resins which are compared, unless otherwise stated.

All the polymer supports mentioned above were post-functionalized with different amines, mainly trialkylamines. For convenience, these resins are categorized into two main groups: (I) monofunctional resins, and (II) bifunctional resins. Monofunctional resins are further categorized based on the kind of polymer support (copolymer) used in the resin. They are resins based on: (A) VBC/MMA/DVB copolymer, (B) VBC/styrene/DVB copolymer, and (C) VBC/DVB copolymer.

1.I MONOFUNCTIONAL RESINS

As the name implies, only one kind of functional group was present in each resin.

1.I.A Resins derived from VBC/MMA/DVB copolymers

The copolymers (Table 2) were sieved into the range 425-250 μ (-40 +60 mesh) and allowed to react with different amines at reflux condition (details in Chapter 4). Typical amines used as ligands were trimethyl, triethyl, tripropyl, pyridine, trihexyl and triethanolamine. All of the resins made from the above copolymer were strong base ion exchangers, except the resins with pyridine as the functional group. From the polymer supports in Table 2, VP-01-134 has the appearance of a gel copolymer. 4-methyl-2-pentanol (4M2P) is a good solvent for MMA, but also a moderately good solvent for polymethyl methacrylate (PMMA). Hence, as the MMA composition in the copolymer increases, macroporosity of the beads decreases. This was supported with the percent solids (Chapter 4), which decreases with an increase in the MMA composition of the resins (Table 3). The general amination reaction with trialkylamines on VBC/DVB/MMA copolymers is described in Figure 3.

Table 2

Copolymers Code Associated with Different VBC/MMA Ratios.

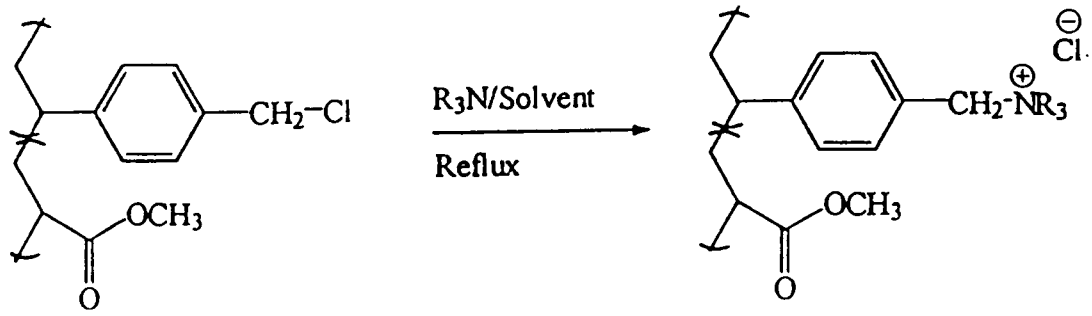
VBC:MMA ratio (mole %)	18:82 VBC:MMA	40:60 VBC:MMA	75:25 VBC:MMA
Copolymer code	VP-01-134	VP-01-137	VP-01-149

Note: All the polymer supports in the table are 10% crosslinked.

Table 3

Decrease in Percent Solids with Decrease in MMA Composition for Trimethylamine Resins Made from VBC/MMA Copolymers.

Resin code	Copolymer composition (mole %)	Percent solids
VP-01-157	18:82 (VBC:MMA)	54.12
VP-01-145	40:60 (VBC:MMA)	33.71
VP-01-152	75:25 (VBC:MMA)	26.75



R = $-CH_3$, $-CH_2CH_3$ $-(CH_2)_2CH_3$, $-(CH_2)_5CH_3$

$-CH_2CH_2OH$

Figure 3 General Amination Reaction with Trialkylamines on VBC/DVB/MMA Copolymers.

Prior to the amination reaction, copolymers were allowed to swell in a solvent used to expand the copolymer matrix (details in Chapter 4). This facilitates complete functionalization into the matrix. After the amination reaction, the beads were washed and conditioned with appropriate solvents and/or solutions (noted in Chapter 4). The conditioning of the resin was required to obtain reproducible values in the characterizations. Aminated resins were then characterized (details of characterization will be discussed in Chapters 2 and 4) by total anion exchange capacities (TAEC), chlorine, and nitrogen elemental analysis (shown in Table 4).

It can be seen from Table 4 that as the length of the alkyl chain increases, the percent solids decreases. This is an indication of decrease in hydrophilicity of the resins with increase in alkyl chain length. As the bulkiness of the trialkylamine increases, degree of functionalization decreases. Table 5 shows the degree of functionalization of the resins derived from copolymer VP-01-137 (40:60; VBC:MMA).

Table 4

Characterization of Resins Derived from VBC/MMA/DVB Copolymer.

Resin code	Functional group	Percent solids	TAEC (mequiv/g)	Cl - elemental (mequiv/g)	N - elemental (mequiv/g)
Copolymer VP-01-134 (18:82/VBC:MMA)					
VP-01-040	trimethylamine	37.31	1.10	1.19	1.10
VP-01-057	triethylamine	37.92	1.18	1.55	0.97
VP-01-173	tripropylamine	43.39	0.76	1.07	0.41
VP-01-187	pyridine	42.78	1.05	0.81	0.94
VP-01-210	trihexylamine	50.74	0.38	1.14	0.44
VP-01-229	triethanolamine	44.88	0.80	1.15	1.13
Copolymer VP-01-137 (40:60 / VBC:MMA)					
VP-01-145	trimethylamine	33.71	2.15	2.5	1.94
VP-01-162	triethylamine	32.81	1.71	2.14	1.73
VP-01-178	tripropylamine	39.30	1.29	1.74	1.56
VP-01-199	pyridine	37.38	1.31	1.62	1.44
VP-01-214	trihexylamine	37.58	0.52	1.98	0.66
VP-01-232	triethanolamine	41.21	1.52	1.76	1.63
Copolymer VP-01-149 (75:25 / VBC:MMA)					
VP-01-152	trimethylamine	26.78	3.29	4.29	2.94
VP-01-239	triethylamine	27.50	2.84	4.43	2.48
VP-01-181	tripropylamine	29.89	1.99	3.01	1.64
VP-01-202	pyridine	30.29	1.97	1.97	1.86
VP-01-223	trihexylamine	38.66	0.79	2.81	0.87
VP-01-242	triethanolamine	33.50	2.54	2.37	2.12

Table 5

Degree of Functionalization of VBC/MMA/DVB Resins.

Resin code	Functional group	N-elemental capacity (mequiv/g)	Theoretical capacity (mequiv/g)	Degree of functionalization (%)
VP-01-145	timethylamine	1.94	2.30	84.3
VP-01-162	triethylamine	1.73	2.09	82.8
VP-01-178	tripropylamine	1.56	1.92	81.2
VP-01-199	pyridine	1.44	2.19	65.7
VP-01-214	trihexylamine	0.66	1.55	42.6
VP-01-232	triethanolamine	1.63	2.09	78.0

1.I.B Resins derived from VBC/styrene/DVB copolymers

Three copolymers were synthesized with different VBC:styrene ratios, keeping the DVB composition constant (Table 6). Each copolymer in Table 6 was post-functionalized with trimethyl, triethyl, tripropyl, pyridine, trihexyl, and triethanolamine. The particle size used for all the resins was 425-250 μ (-40 +60 mesh), except for VP-02-255 which was 250-75 μ (-60 +200 mesh). Crosslink density for all of the resins was 10%. The general reaction of VBC/styrene copolymer with different amines is shown in Figure 4.

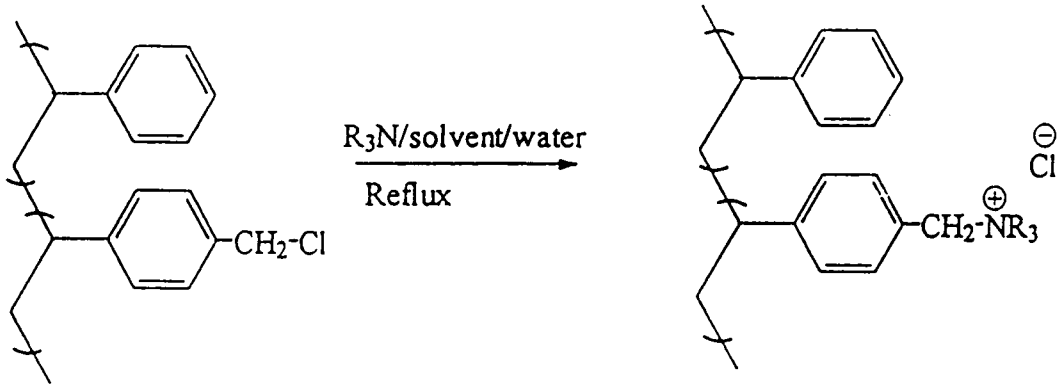
Before the amination reaction, the polymer supports were allowed to swell in an appropriate solvent for the same reason mentioned earlier. The presence of water was required in the reaction mixture to hydrate the product, a quaternary ammonium group. Aminated resins were washed and conditioned prior to characterization (Table 7). It can be seen from Table 8 that as the bulkiness of the trialkylamine increases, the degree of functionalization decreases.

Experimental conditions were varied in order to see whether the degree of functionalization could be improved. Tripropylamine was selected as a model functional group with different amounts of solvent and water (Table 9). Water is required for greater functionalization. The higher functionalization of VP-02-036 compared to VP-02-026 was due to stabilization of quaternary ammonium salt by excess amine molucules in the reaction mixture.

Table 6

Copolymer Codes Associated with Different VBC/Styrene Ratios.

VBC : Styrene (mole %)	25: 75 (VBC:Sty)	50:50 (VBC:Sty)	75:25 (VBC:Sty)
Copolymer code	VP-01-249	VP-01-251	VP-01-253



R = $-CH_3$, $-CH_2CH_3$ $-(CH_2)_2CH_3$, $-(CH_2)_5CH_3$

$-CH_2CH_2OH$ and NR_3 = Pyridine

Figure 4. General Reaction of VBC/Styrene Copolymer with Different Amines.

Table 7
Characterization of Resins Derived from VBC/Styrene/DVB Copolymers

Resin code	Functional group	Percent solids	TAEC (mequiv/g)	Cl-elemental (mequiv/g)	N-elemental (mequiv/g)
Copolymer VP-01-249 (25:75 / VBC:Sty)					
VP-01-255	trimethyl	28.14	1.84	1.89	1.22
VP-02-236	tripropyl	27.84	1.10	1.18	0.76
VP-02-248	trihexyl	31.89	0.47	--	--
VP-02-255	trihexyl∘	30.83	0.83	--	--
Copolymer VP-01-251 (50:50 / VBC:Sty)					
VP-01-258	trimethyl	27.08	2.70	2.50	2.42
VP-01-283	triethyl	27.99	2.03	2.02	2.08
VP-01-286	tripropyl	32.48	1.35	1.41	1.65
VP-01-292	pyridine	31.23	1.47	1.33	2.22
VP-02-011	trihexyl	39.78	0.46	2.38	0.89
VP-02-016	triethanol	33.56	1.66	1.96	1.78
VP-02-026	tripropyl †	36.01	0.75	2.49	1.31
VP-02-036	tripropyl ‡	36.23	1.05	1.95	1.88
Copolymer VP-01-253 (75:25 / VBC:Sty)					
VP-01-280	trimethyl	25.9	3.25	3.17	3.02
VP-02-033	triethyl	26.4	2.55	2.41	2.43
VP-02-039	tripropyl	33.74	1.58	2.36	1.79
VP-02-042	pyridine	26.86	1.97	1.87	1.92
VP-02-048	triethanol	31.18	2.11	2.27	2.17
VP-02-051	trihexyl †	37.36	0.46	3.44	0.76
VP-02-054	pyridine *	27.70	3.00	2.99	2.28

* resin was conditioned with water and 4% HCl.
† no water was used.
‡ no water and no solvent were used.
∘ -60 +200 mesh size

Table 8

Comparison of Degree of Functionalization with

Size of Amine in VBC/Styrene/DVB Resins

Resin code	Functional group	N-elemental (mequiv/g)	Theoretical (mequiv/g)	Degree of functionalization
VP-01-258	trimethyl	2.42	2.66	91
VP-01-283	triethyl	2.08	2.39	87
VP-01-286	tripropyl	1.65	2.17	76
VP-01-292	pyridine	2.22	2.53	88
VP-02-011	trihexyl	0.89	1.71	52
VP-02-016	triethanol	1.78	2.15	83

Table 9

Effect of Solvent/Water on Functionalization of VBC/Styrene/DVB Resins.

Resin code	Tripropylamine with:	Percent solids	TAEC (mequiv/g)	Cl-elemental (mequiv/g)	N-elemental (mequiv/g)
VP-01-286	dioxane /water	32.48	1.35	1.41	1.65
VP-02-026	dioxane	36.01	0.75	2.49	1.31
VP-02-036	No water No dioxane	36.23	1.05	1.95	1.88

1.I.C Resins derived from VBC/DVB copolymers

VBC/DVB polymer supports were synthesized with varying crosslink densities. Resins derived from VBC/DVB (10% Crosslinked; MR) copolymer were compared with the resins derived from VBC/MMA/DVB (MR) and VBC/Styrene/DVB copolymers (MR). The effect of incorporated MMA and Styrene groups on the complexation of pertechnetate will be addressed in Chapter 3. N,N-dimethyldodecylamine, tributylamine, imidazole, ethylenediamine, and guanidine were used as functional groups in addition to the amines mentioned earlier. In order to increase the degree of functionalization, different particle sizes and times were tried. Characterization of macroporous resins derived from VBC/DVB (10% Crosslinked) copolymer is given in Table 10.

Accessibility of the functional groups into the copolymer matrix was studied with 5%, 10%, 15%, 25%, and 40% crosslinked VBC/DVB copolymers. These copolymers were functionalized with tripropylamine , trimethylamine, and trihexylamine. The results are given in Table 11. It can be seen from Table 11 that as the crosslink density increases, the degree of functionalization decreases. However, the trimethylamine group reacted almost to completion on the 40% Crosslinked MR due to its smaller size. Groups larger than tripropylamine did not penetrate into the 40% crosslinked matrix (Table 12; VP-02-078; VP-02-089; VP-02-095). The general reaction of VBC/DVB copolymers with different amines is shown in Figure 5

Table 10

Characterization of Resins Derived from VBC/DVB (10% Crosslinked), MR,Copolymers.

Resin code	Functional group	Percent solids	TAEC (mequiv/g)	Cl-elemental (mequiv/g)	N-elemental (mequiv/g)	Remark
VP-01-165	trimethyl	26.53	3.77	5.64	3.51	
VP-01-168	triethyl	27.5	2.84	4.43	2.48	
VP-01-184	tripropyl	29.98	1.73	3.25	1.70	
VP-01-207	pyridine	29.54	2.59	2.68	2.93	
VP-01-226	trihexyl	40.23	0.79	3.44	1.06	
VP-01-245	triethanol	34.79	2.71	2.91	2.41	
VP-02-060	trihexyl	38.24	0.33	3.96	0.56	no water
VP-02-066	trihexyl	40.54	0.35	3.85	0.44	48 h
VP-02-083	tributyl	32.41	1.66	2.04	1.40	
VP-02-086	trihexyl	38.19	0.76	3.68	0.65	repeat
VP-02-102	trihexyl	38.76	0.63	3.18	0.47	59 h
VP-02-228	guanidine	52.43	0.65	--	2.13	
VP-02-225	guanidine	52.25	--	--	1.14	
VP-02-142	trihexyl	35.57	0.81	3.45	0.59	150-75 μ
VP-02-145	dodecyl*	30.32	2.16	2.16	1.90	
VP-02-174	ethylene-diamine	29.95	3.18	3.13	5.95	quaterniz-ed w/MeI
VP-02-152	tripropyl	26.17	2.33	2.37	1.37	
VP-02-155	dodecyl	32.61	2.08	2.25	1.99	
VP-02-181	imidazole	30.92	1.86	1.83	5.30	
VP-02-185	imidazole	31.3	1.60	1.72	5.54	
VP-02-190	imidazole	30.53	2.68	2.49	4.98	quaterniz-ed w/ MeI

* N,N-dimethyldodecyl amine.

Table 11

Characterization of Resins Derived from Differently

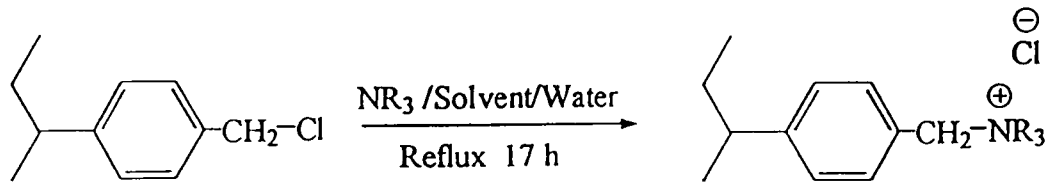
Crosslinked VBC/DVB Copolymer and Tripropylamine.

Resin code	Percent DVB	Percent solids	TAEC (mequiv/g)	Cl-elemental (mequiv/g)	N-elemental (mequiv/g)
VP-02-131	5%	34.73	2.58	2.24	1.99
VP-01-184	10%	29.98	1.73	3.25	1.70
VP-02-138	15%	28.96	1.58	2.21	1.40
VP-02-072	25%	30.05	1.32	2.23	1.28
VP-02-089	40%	30.29	0.48	1.35	0.46

Table 12

Characterization of Resins Derived from 40% Crosslinked, MR; VBC/DVB Copolymer.

Resin code	Functional group	Percent solids	TAEC (mequiv/g)	Cl-elemental (mequiv/g)	N-elemental (mequiv/g)	Theoretical capacity (mequiv/g)
VP-02-078	tripropyl	30.73	0.36	1.34	0.39	1.40
VP-02-089	tripropyl	30.29	0.48	1.35	0.46	1.40
VP-02-095	trimethyl	27.39	1.48	1.29	1.01	1.59



R = $-CH_3$, $-CH_2CH_3$, $-(CH_2)_2CH_3$, $-(CH_2)_3CH_3$, $-(CH_2)_5CH_3$

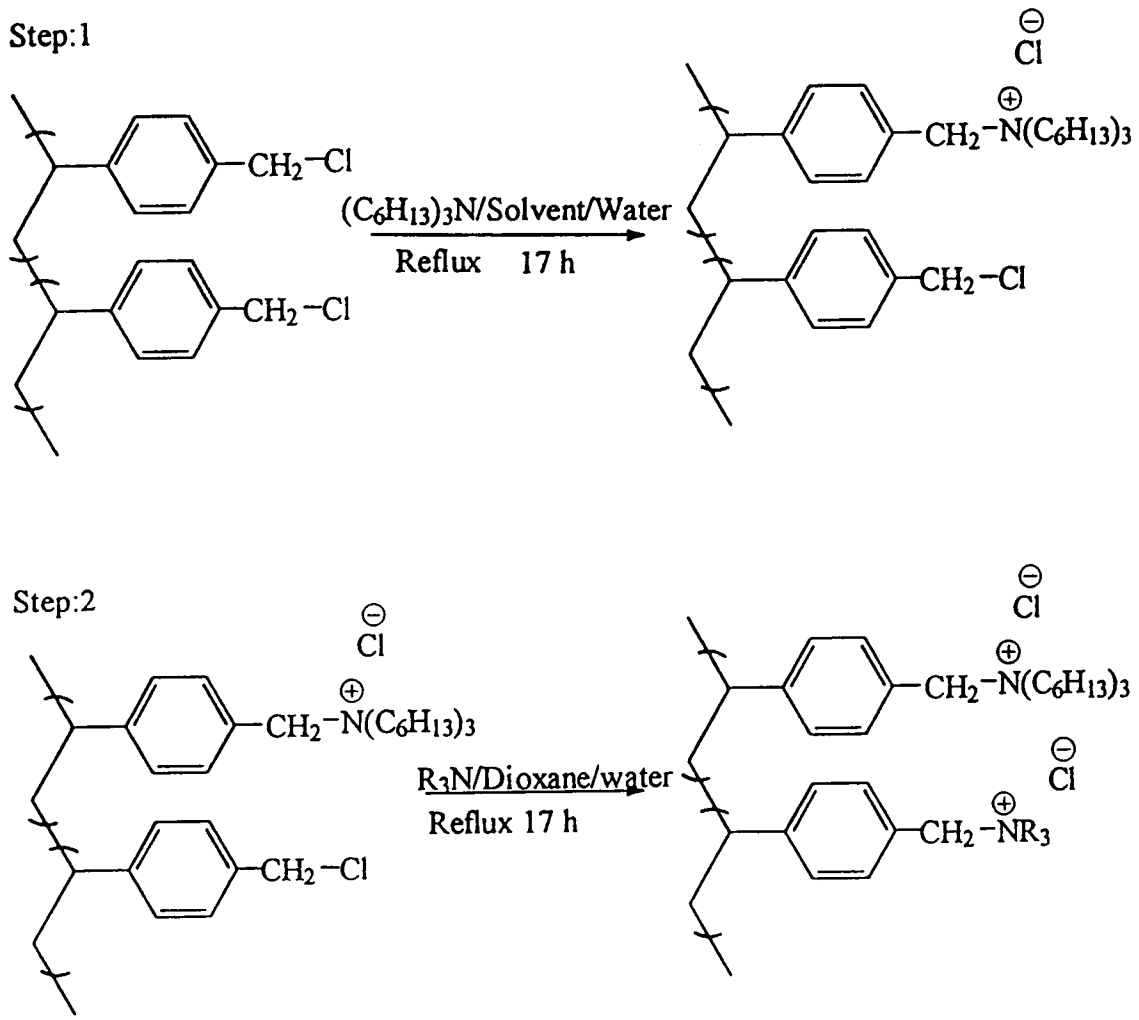
NR_3 = Pyridine, Imidazole, Guanidine, N,N-Dimethyldodecylamine, Ethylenediamine

Figure 5 General Reaction of VBC/DVB Copolymer with Different Amines.

1.II BIFUNCTIONAL RESINS

Bifunctional resins were derived from 5% DVB MR VBC/DVB (VP-02-105) copolymer. The reason for using a 5% DVB MR copolymer was to obtain a higher functionality (see Table 13). This copolymer support was functionalized first with trihexylamine following the process described earlier (and in Chapter 4). The resin was washed and conditioned before further functionalization with a second amine. Steric hindrance of the bulky trihexylamine does not allow a degree of functionalization above 45%. Thus, vinylbenzyl chloride groups remain unreacted. The unreacted vinylbenzyl chloride groups were further reacted with comparatively small trialkylamines. Trimethyl, triethyl, tripropyl, and tributylamine were used as a second functional group (see Chapter 4). The general reaction involved in the bifunctional resins is given in Figure 6.

The effect of one functional group on the other will be discussed in Chapter 3. -40 +60 mesh size [425-250μ] beads were used in all the bifunctional reactions, unless otherwise indicated. Characterization of the bifunctional resins is given in Table 13.



R = $-CH_3$, $-CH_2CH_3$, $-(CH_2)_2CH_3$, $-(CH_2)_3CH_3$

Figure 6. General Reaction Involved in Bifunctional Resins.

Table 13

Characterization of Bifunctional Resins.

Resin code	Functional groups	Percent solids	TAEC (mequiv/ g)	Cl- elemental (mequiv/g)	N- elemental (mequiv/g)
VP-02-092	trihexyl / trimethyl	29.31	3.25	2.93	2.80
VP-02-122	trihexyl / tripropyl	46.37	1.76	1.90	1.59
VP-02-165	trihexyl / tripropyl*	40.60	2.13	2.16	1.30
VP-02-217	trihexyl / tripropyl**	37.81	2.06	1.97	1.47
VP-02-245	tri-isoctyl / tripropyl	43.77	1.97	1.96	1.79
VP-02-258	trihexyl / triethyl	40.71	2.36	2.31	2.09
VP-02-261	trihexy / tributyl	46.30	1.76	1.84	1.36

* Larger batch.
** -200 + 325 mesh size beads were used (75-45 μ)

CHAPTER 2

CHARACTERIZATION

When a functional group is bound to a polymer support it is immobilized. The diffusion of a targeted ion within the support network depends on the distance between two charges and the complexing ability of the functional group. Important variables include the chemical structures of the bound functional groups, ionic accessibility into the network and the extent of functionalization. Characterization of anion exchange resins requires measurements of the total anion exchange capacity (TAEC), nitrogen elemental analysis, chlorine elemental analysis and infra-red spectroscopy.

2.I TAEC

The TAEC quantifies the number of exchange sites per gram of resin. The experimental procedure is discussed in Chapter 4. Prior to characterization, the resins are in the chloride form. In determining the TAEC, the chloride ion on the resin is displaced by nitrate using 1M $NaNO_3$ solution. The displaced chloride, as NaCl, is determined via Mohr titration. The ion-exchange reaction for the TAEC determination is given below.

$$R^+ Cl^- + NaNO_3 \leftrightarrows R^+ NO_3^- + NaCl$$

R = quaternary ammonium site on the resin.

2.II ELEMENTAL ANALYSIS

Elemental analysis is an important adjunct to the TAEC determination. The degree of functionalization is determined by N-elemental analysis (experimental procedure in chapter 4) of the trialkylamine resins. If the resin matrix is fully accessible, the N-elemental value should match the TAEC within experimental error. If the resin matrix is not fully accessible, as in the case of VP-02-112 (trihexylamine ligand on 2% DVB gel copolymer), the TAEC will be lower than the N-elemental value (Table 14). The results in Table 14 indicate that resin VP-02-112 has functional groups that are not available for ion-exchange, probably due to a lower ionic accessibility into the matrix. The hydrophobicity of the trihexylamine ligand also limits accessibility.

The Cl-elemental analysis confirms the extent of functionalization: if the resin is not fully functionalized, the chlorine capacity will be greater than the theoretical capacity. At 100% functionalization, the TAEC, N-elemental and Cl-elemental analysis of a fully functionalized quaternary amine resin should be identical (within 0.2 mequiv/g) (Table 15). The lower Cl-elemental capacities in VP-02-207 and VP-01-245 relative to the theoretical capacities suggests either oxidation and/or internal-crosslinking, though the later possibility can be ignored due to similar TAEC and N-elemental capacities.

2.III IR ANALYSIS

Infra-red spectra of selected resins were taken on a Bio-Rad Digilab FTS-7 FT-IR spectrometer. Samples were ground with KBr and pressed into pellets. It was found that

Table 14

Comparison of Resins Derived from Gel and MR; VBC/DVB Copolymers.

Resin code	Functional group	Percent solids	TAEC (mequiv/g)	N-elemental (mequiv/g)
VP-02-112 (2% gel)	trihexylamine	76.23	0.72	1.31
VP-02-086 (10% MR)	trihexylamine	38.19	0.76	0.65

Table 15

Comparison of Capacities of 100/VBC; 10% Crosslinked MR Resins.

Resin code	Functional group	Percent solids	TAEC (mequiv/g)	Cl-elemental (mequiv/g)	N-elemental (mequiv/g)	Theoretical capacity (mequiv/g)
VP-01-165	trimethyl	26.53	3.77	5.64	3.51	4.04
VP-01-168	triethyl	27.50	2.84	4.43	2.48	3.46
VP-01-184	tripropyl	29.98	1.73	3.25	1.70	3.02
VP-01-207	pyridine	29.54	2.59	2.68	2.93	3.74
VP-02-086	trihexyl	38.19	0.76	3.68	0.65	2.19
VP-01-245	triethanol-amine	34.79	2.71	2.91	2.41	3.44

5%, 10% (Figure 7), and 15% crosslinked VBC/DVB, MR copolymers have the same IR spectra. The characteristic absorbance of the -CH_2Cl group in the VBC/DVB copolymers is at 1270 cm^{-1} and 706 cm^{-1}. When a VBC/DVB copolymer is fully fucntionalized with the trialkylamine, the peak at 1270 cm^{-1} disappears and the peak at 706 cm^{-1} decreases in strength but does not disappear or shift. Figures 8 and 9 compare the IR spectra of trihexyl and tripropyl resins with the copolymer used for their preparation. Since trialkyl ammonium salts do not have a characteristic peak, it is difficult to determine the type of functionalization from IR spectra. However, the relative decrease in peak intensity at 1270 cm^{-1} suggests appreciable functionalization in the tripropylamine resin (VP-01-184) and low functionalization in the trihexylamine resin (VP-01-226) (Figures 10,11 and 12). An unexpected absorbance in the range of 1720-1750 cm^{-1}, which is a characteristic of the carbonyl group, was observed in almost all resins. It is suggested that some of the methylene chloride groups may have been oxidized to carbonyl groups during functionalization.

Figures 13 to 15 show the spectra of bifunctional resins. The spectrum of the bifunctional resin is compared with a mixed-resin-analogue, prepared by mixing two monofunctional resins with identical groups as the bifunctional resin. If an inter-ligand interaction occurs, it is possible that some peaks in the bifunctional spectrum may shift compared to the mixed-analogue. Since no characteristic peak is observed for the trialkylammonium $(-NR_3)^+$ group, it is difficult to conclude whether any such interaction is present.

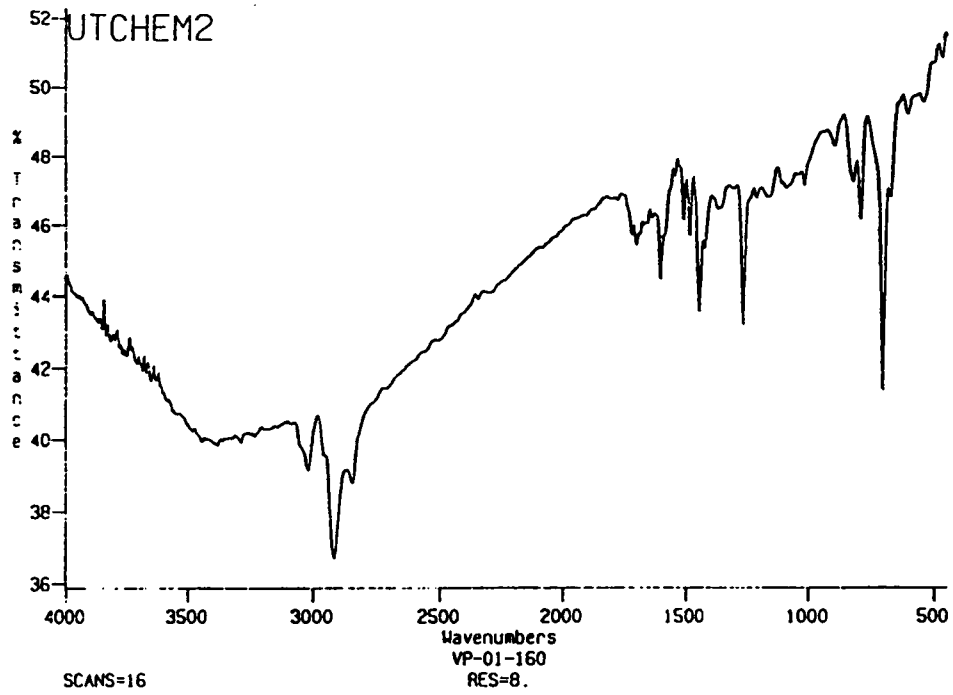


Figure 7. IR Spectrum of copolymer VP-01-160 (10% crosslinked VBC/DVB, MR)

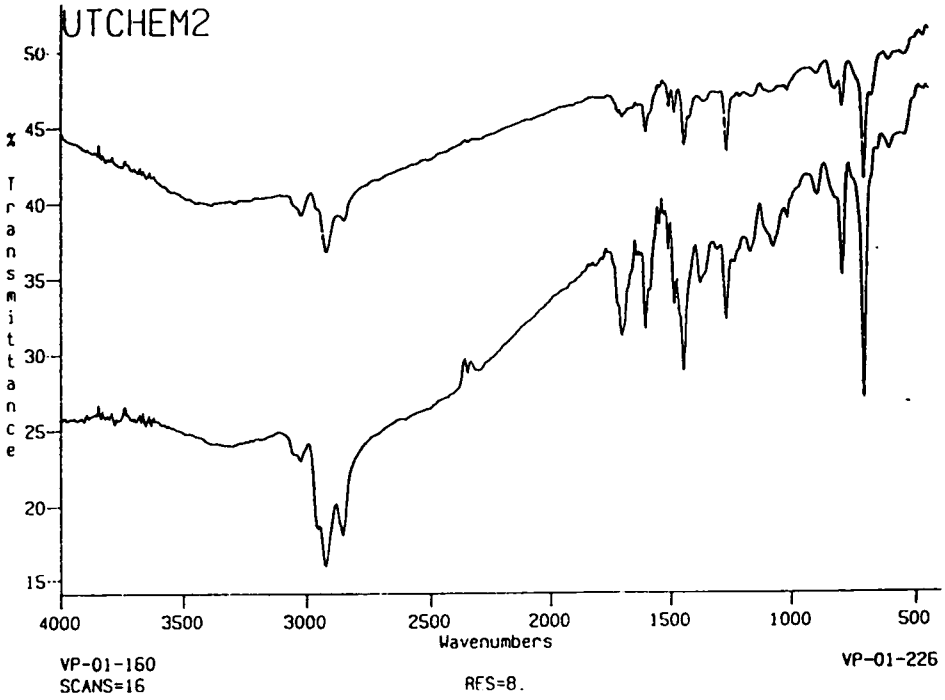


Figure 8. IR Spectra of Trihexylamine Resin (VP-01-226) (Bottom) and copolymer (VP-01-160)(Top).

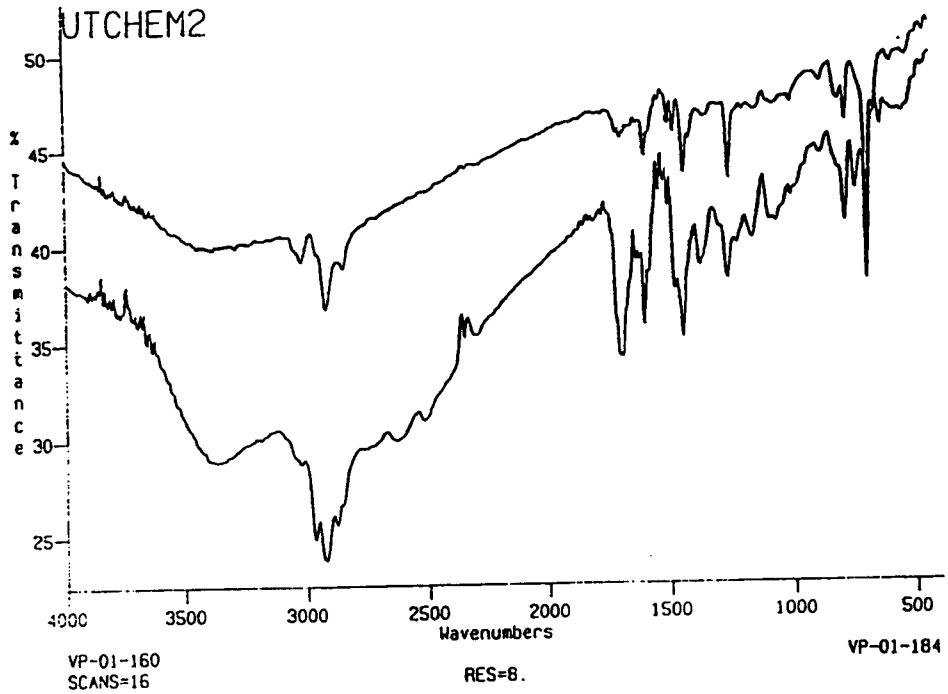


Figure 9. IR Spectra of Tripropylamine Resin (VP-01-184) (Bottom) and Copolymer (VP-01-160) (Top).

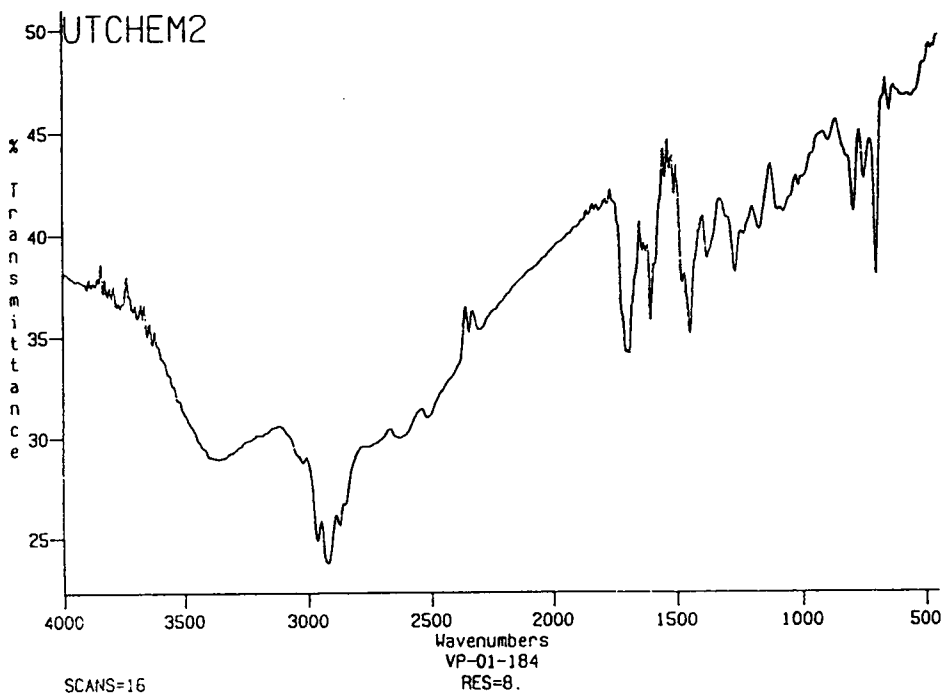


Figure 10. IR Spectrum of Tripropylamine Resin (VP-01-184).

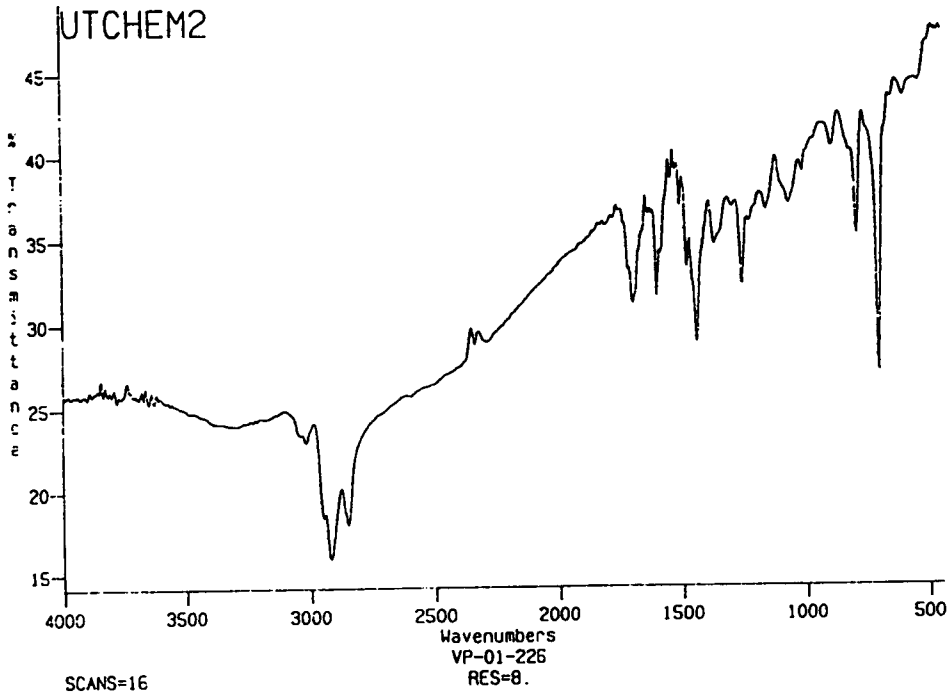


Figure 11. IR Spectrum of Trihexylamine Resin (VP-01-226).

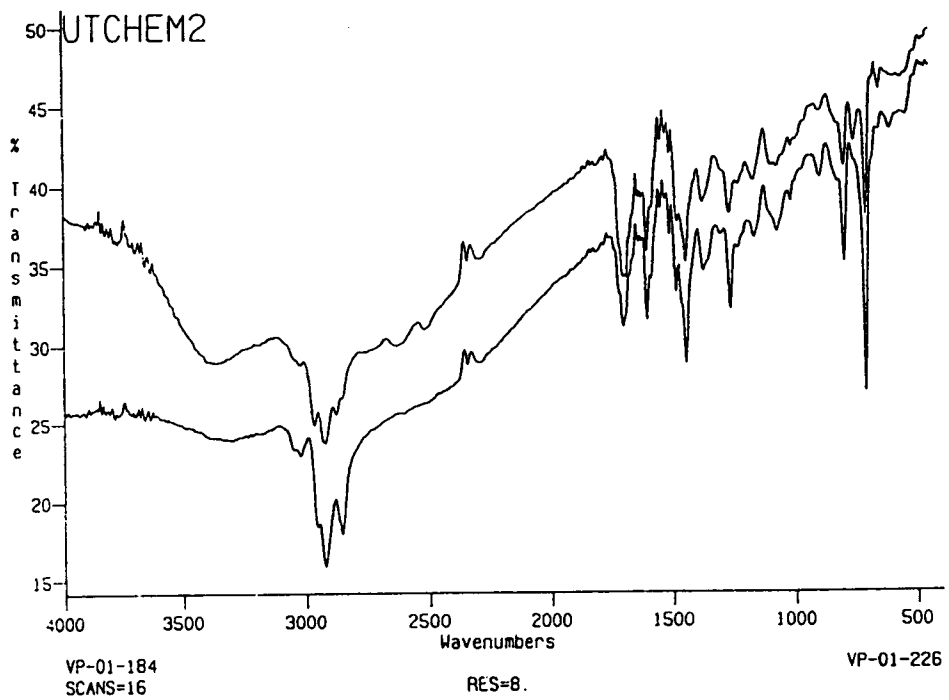


Figure 12. Comparision of IR Spectra of Trihexyl (Bottom) and Tripropyl (Top) Resins.

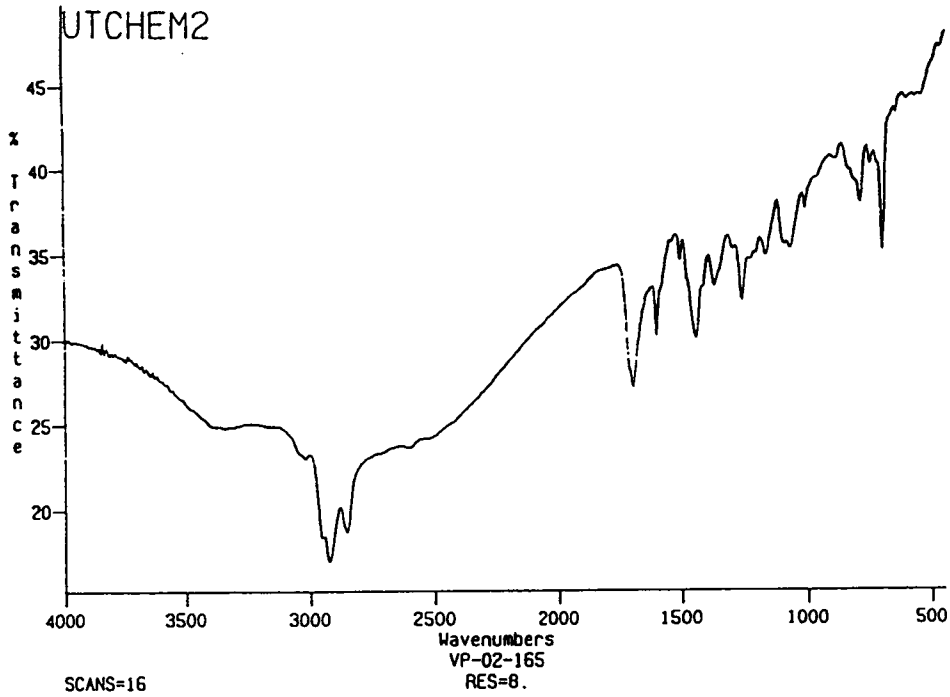


Figure 13. IR Spectrum of Bifunctional Resin (VP-02-165).

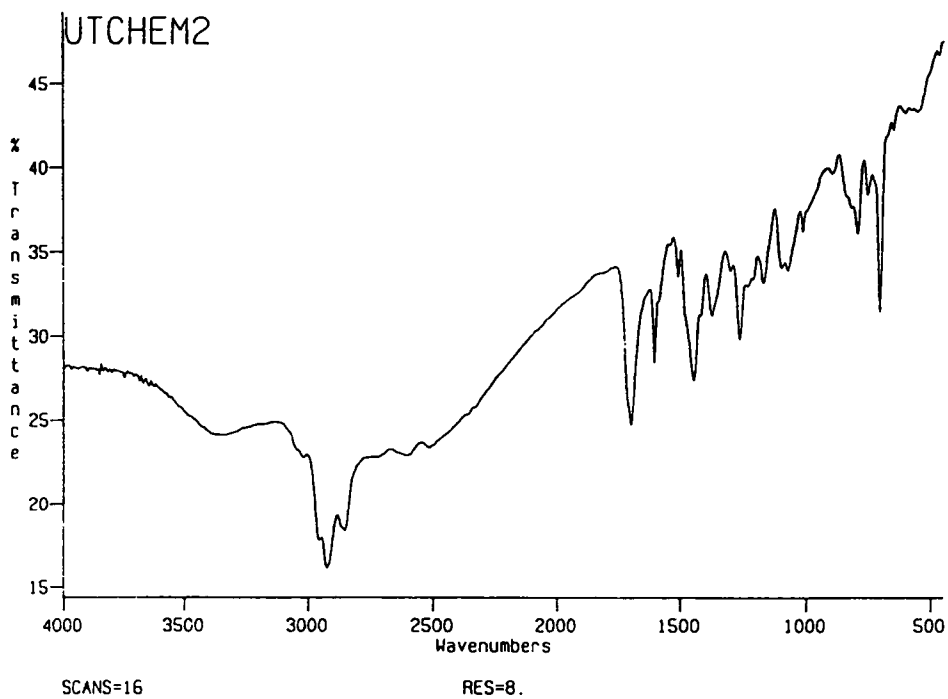


Figure 14. IR Spectrum of Mixed-Resin-Analogue (Mixture of Two Monofunctional Resins; VP-02-131 and VP-02-109).

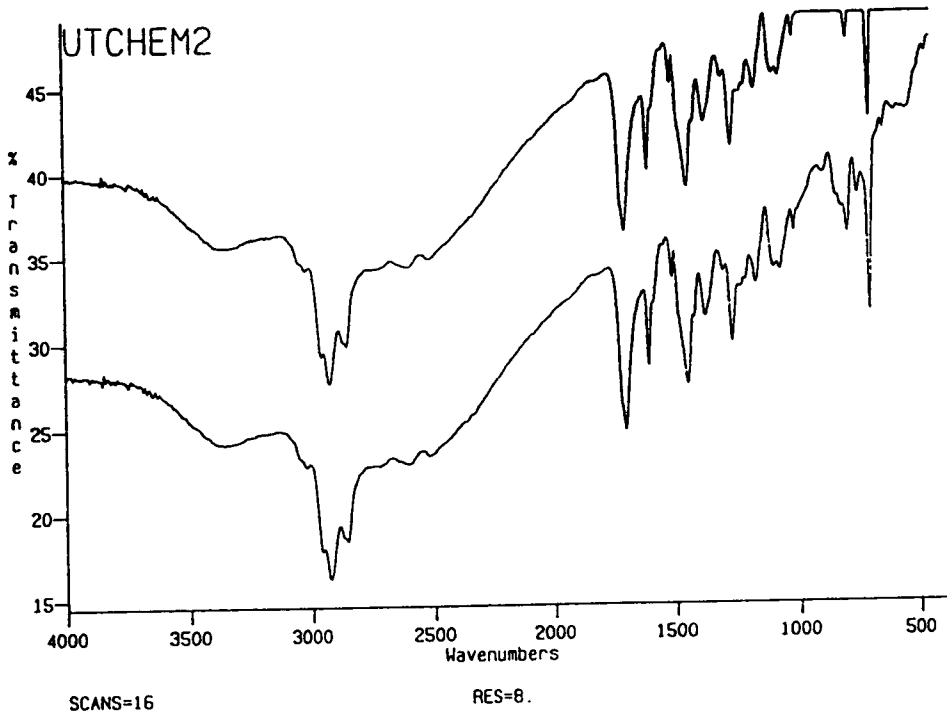


Figure 15. Comparision of Spectra; Bifunctional Resin (VP-02-165) (Top) Vs Mixed-Resin-Analogue (Bottom).

CHAPTER 3

METAL-ION STUDIES WITH PERTECHNETATE

INTRODUCTION

Groundwater at the Department of Energy (DOE) sites in Paducah (KY) and Portsmouth (OH) has been contaminated by radionuclides. Technetium is the principal radioactive metal-ion contaminant to be removed. In groundwater, technetium exists in a stable oxidized form as pertechnetate anion (TcO_4^-). The high mobility of TcO_4^- in water along with its half life of 2.14×10^5 yr has made it a priority concern for the DOE. Tc-99 entered the gaseous diffusion enrichment plants as an impurity in uranium oxide recovered from spent fuels generated in atomic reactors. The multi-step conversion of the oxide to uranium hexafluoride (UF_6) also produced a volatile technetium fluoride [41]. UF_6 was subsequently fed to the enrichment cascades where the Tc-99 remained absorbed on surfaces. Decontamination of gaseous diffusion plants at Paducah and Portsmouth has been achieved with nitric acid, which solubilizes uranium and Tc-99 residues. The uranium is then recovered by solvent extraction, with the majority of the Tc-99 remaining in the aqueous waste. Composition of the waste stream is varied, but is generally characterized by toxic heavy metals, high concentration of nitric acid, and relatively low levels of radioactivity. The treatment of the waste stream consist of the following steps : (I) dilution of waste with equal amount of water and pH adjustment to about 8.5 to precipitate the hydrolyzable heavy metals; (II) filtration of the precipitation slurry to remove the heavy metal hydroxides; (III) processing of the filtrate with a strong-base anion exchange resin to remove the soluble pertechnetate ion; (IV) biodenitrification and (V) sewage disposal [42].

Because of the high mobility of the pertechnetate ion and poor selectivity of the ion exchange resin, Tc-99 has been detected in groundwater samples taken from monitoring wells around uranium enrichment plants. Analysis of groundwater from well-66 at Paducah is shown in Table 16 [31].

Many methods have been deployed for the absorption of pertechnetate ion from groundwater. Some inorganic ion-exchange materials and naturally occurring minerals, including CrO_2 and Al_2O_3 were studied [43]. A mixture of sulfide and iron dust as an inexpensive material was also studied [44]. Ease of handling and regeneration makes organic anion-exchange resins more practical for the complexation of pertechnetate ion. Several anion-exchange resins have been synthesized and studied for selective complexation and over a period of time some have been commercialized. The best commercial resins known to the date are: Reillex™HPQ [45-48], Amberlite™ IRA-900, IRA-904, Purolite™ A-520E and Sybron Ionac™ SR-6.

All the commercial resins are patented, thus exact information was not available in the literature. Reillex™-HPQ, (Reilly Industries Indianapolis, IN) is a co-polymer of divinylbenzene (25%) and 4-vinylpyridine, subsequently methylated (~75%) at the pyridine nitrogen to give pyridinium strong base sites. Ionac™ SR-6, a product of Sybron Chemical Inc, is a tributyl-quaternary-amine styrene divinylbenzene copolymer; crosslink density is not specified. Purolite A-520E™, a product of Purolite Industries (Bala Cynwyd, PA), is a triethyl ammonium salt on cross linked polystyrene. Amberlite IRA-900 and IRA-904, trademarks of Rohm and Haas (Philadelphia, PA), consist of trimethyl ammonium salt on cross linked polystyrene with the crosslink densities of 5% and 20%, respectively.

Table 16

Analysis of Ground Water from Paducah (well # 66)

Species	Range	Average	Units
calcium	27.0-38.0	33.0	mg/L
sodium	17.7-22.2	20.5	mg/L
magnesium	6.9-10.6	8.8	mg/L
chloride	20.0-30.0	26.0	mg/L
sulfate	10.0-25.0	11.0	mg/L
nitrate	2.3-9.0	6.3	mg/L
Tc-99	544-3670	2803	pCi/L
uranium	---	< 0.001	mg/L

This research was focused on creating a microenvironment which favors absorption of pertechnetate ion over other anions. Alkylamines with different chain lengths were the ligands used in this study. Hydrophobicity and hydrophilicity of the ligands were the variables used to alter the microenvironment. All the resins were tested at ORNL with standard pertechnetate solutions. The best commercial resins for pertechnetate recovery were also studied with the same testing conditions and compared with resins synthesized in the laboratory.

3.I METAL-ION STUDIES

Metal-ion studies of the resins were done at ORNL by Dr. Peter V. Bonnesen and colleagues. The studies consist of (A) complexation of pertechnetate ion on the resin and (B) removal of pertechnetate from the resin.

3.I.A Complexation of pertechnetate ion on the resins:

The uptake studies involve batch, kinetic and column studies.

3.I.A(a). Batch study

Twenty-four hour batch studies for all resins and one week batch studies for selected resins were performed at ORNL. The analysis of contaminated ground water from well-66 (Paducah) revealed the concentration of technetium to be in the range of 0.3 to 2.2 nanomolar compared to a concentration of the most abundant anions chloride, nitrate, and sulfate in the range of 0.56 - 0.90, 0.04 - 0.15 and 0.10 - 0.26 millimolar, respectively. In order to simulate the performance on a large scale, the concentration of each of these ions was kept approximately 10^5 times higher than their concentration in actual ground water (Table 17).

Table 17

Concentrations of Sodium, Chloride, Sulfate, Nitrate, and Tc-99 in Both the Groundwater Test Solution, and Paducah Well # 66 (average values cited in Table 16), Along with the Ratio of Each Ion to Tc-99.

Species	Molarity in groundwater test solution	Ratio of [Species] to [Tc-99]	Molarity in Paducah Well # 66	Ratio of [Species] to [Tc-99]
Sodium	1.8×10^{-1}	3.0×10^{4}	8.9×10^{-4}	5.2×10^{5}
Chloride	6.0×10^{-2}	1.0×10^{4}	7.3×10^{-4}	4.3×10^{5}
Nitrate	6.0×10^{-2}	1.0×10^{4}	1.0×10^{-4}	5.9×10^{4}
Sulfate	6.0×10^{-2}	1.0×10^{4}	1.2×10^{-4}	7.1×10^{4}
Tc-99	6.0×10^{-6}	1	1.7×10^{-9}	1

Technetium-99 was obtained from Isotope Products Laboratories (Burbank, CA), in the form of NH_4TcO_4 solution with a concentration of 1.023 mCi, in a flame-sealed ampoule. A 3.006×10^{-3} M 99-TcO_4 (1.120×10^7 DPM/mL) working stock solution was prepared by transferring 4.9506 g of the solution in the ampoule to a 200 mL volumetric flask, and diluting to the mark with distilled water. The appropriate volume from this working stock solution was added to the solution containing sodium chloride, sodium nitrate and sodium sulfate (0.06 M in each) to make a Tc-99 concentration of 6 micromolar.

Prior to the complexation experiment, each resin (in the chloride form) was equilibrated with the "Ground water test solution matrix" (test solution without Tc-99). The resins were then Buchner-dried and 200 mg (on a dry weight basis) placed in 250 mL Teflon® FEP bottles. 100 mL of the test solution was added to each bottle and shaken for either 24 h or 168 h. After the given contact time, beads were filtered out and the solution was tested for Tc-99 activity. Activity of Tc-99 was tested on Packard Tricarb (model 4530) or Tricarb (model 2700 TR) counter and Packard Ultima Gold XR cocktail using the standard liquid scintillation method. The amount of Tc absorbed on to the resin was determined by subtracting the Tc activity in the equilibrium solution from the total Tc activity in the starting solution. The distribution ratio K'_d in mL/g was determined by equations 3-1,3-2, and 3-3, described by Ashley et al. [45]

$$K'_d = \frac{\dfrac{[(\text{Tc-99 dpm})_{initial} - (\text{Tc-99 dpm})_{solution}]}{\text{g resin}}}{\dfrac{(\text{Tc-99 dpm})_{solution}}{\text{mL solution}}} \qquad \text{eq. 3-1}$$

$$K'_d = \frac{\dfrac{\text{m mol } TcO_4^-}{\text{1 g of dry resin}}}{\dfrac{\text{m mol } TcO_4^-}{\text{1 mL of solution}}} \qquad \text{eq. 3-2}$$

K'_d(eq) in mL/mequiv is an alternative distribution ratio per equivalent site which was determined by dividing K'_d by the TAEC value of the particular resin. The K'_d value provides a measure of the pertechnetate absorption ability per gram of resin, and K'_d(eq) provides a measure of the relative technetium affinity per exchange site.

$$K'_d(\text{eq}) = \frac{\dfrac{\text{m mol } TcO_4^-}{\text{1 g of dry resin}}}{\dfrac{\text{m mol } TcO_4^-}{\text{1 mL of solution}}} \times \frac{1}{\text{TAEC of resin}} \qquad \text{eq. 3-3}$$

3.I.A(b) Kinetic study

Kinetic studies were carried out on selected resins which performed well in the batch studies. The ground water test solution was prepared as in the case of batch study. The general procedure described earlier was followed with the exception of the contact time. At various times the contact solution was removed and tested for the Tc-99 activity. Typical time periods varied from 9 minutes to 14 days. (see Figures 16, 17 and 18).

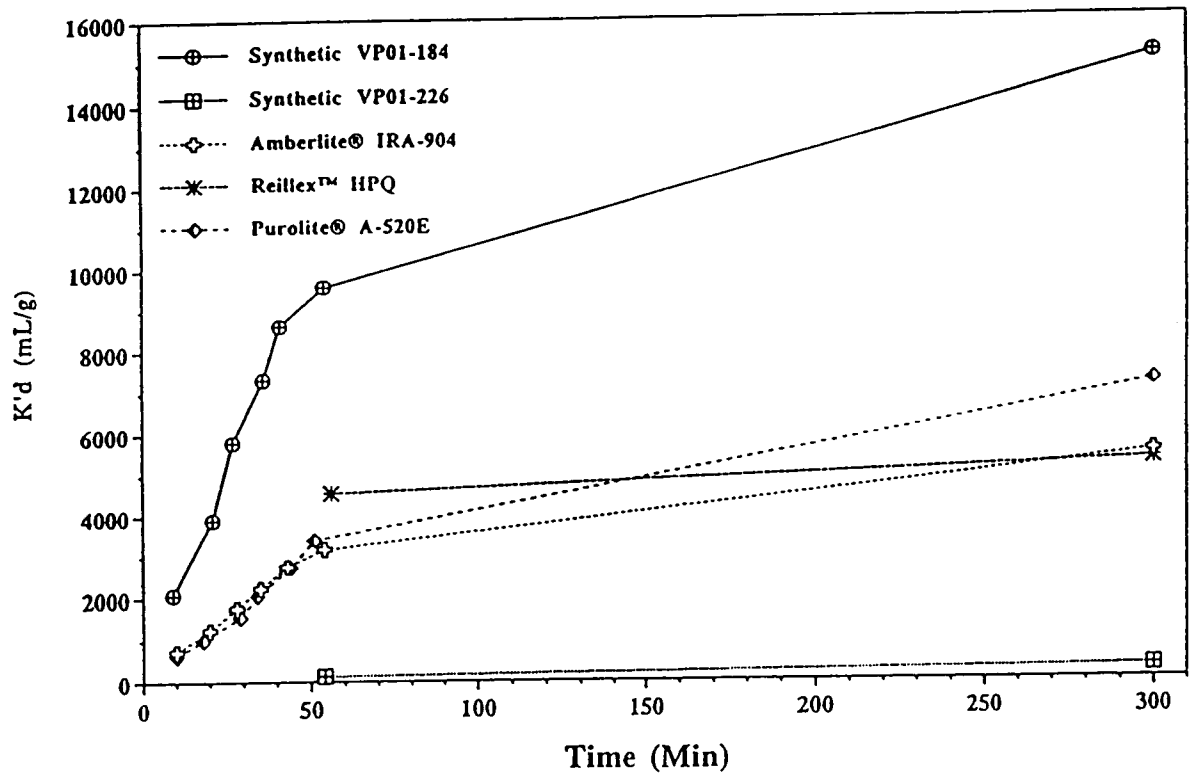


Figure 16. Short Term Batch Equilibrium Tc-99 Complexation Study of Selected Resins.

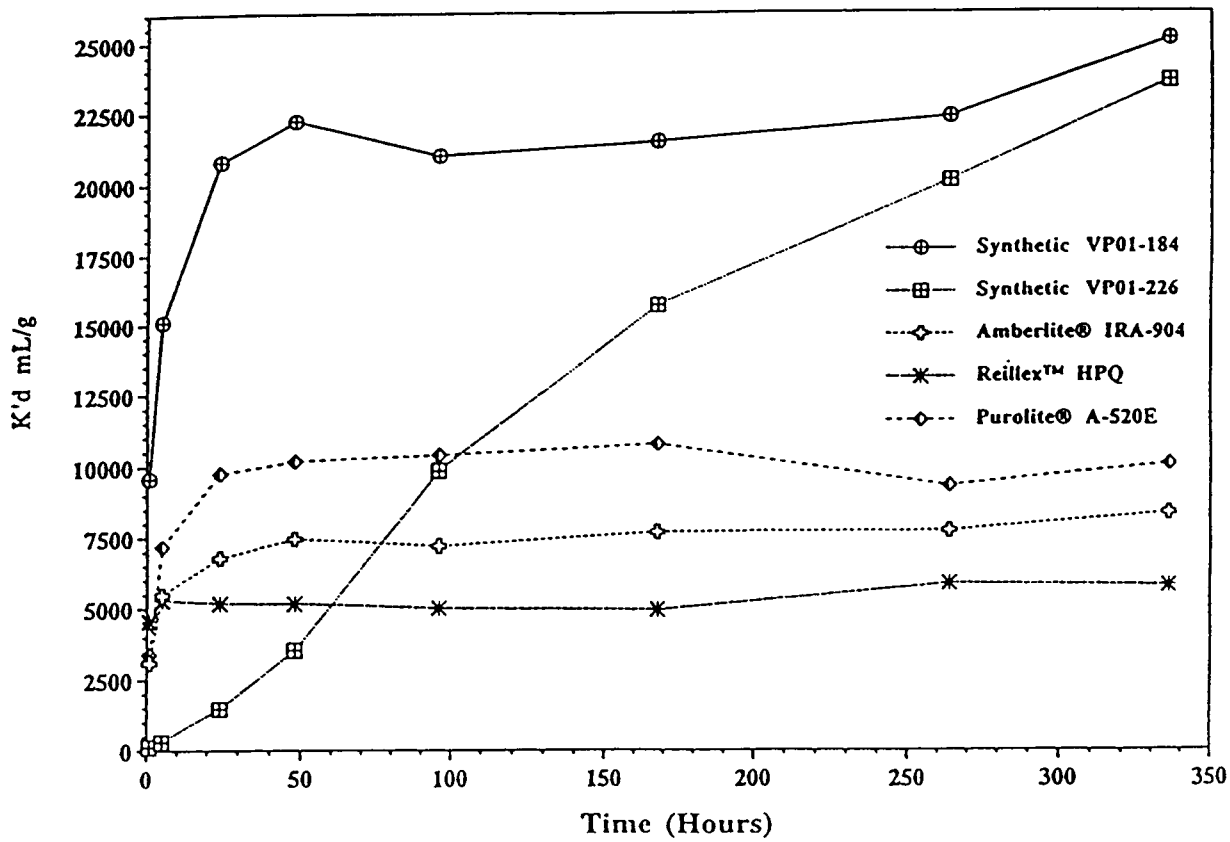


Figure 17 Long Term Batch Equilibrium Tc-99 Complexation (K'd) Study of Selected Resins.

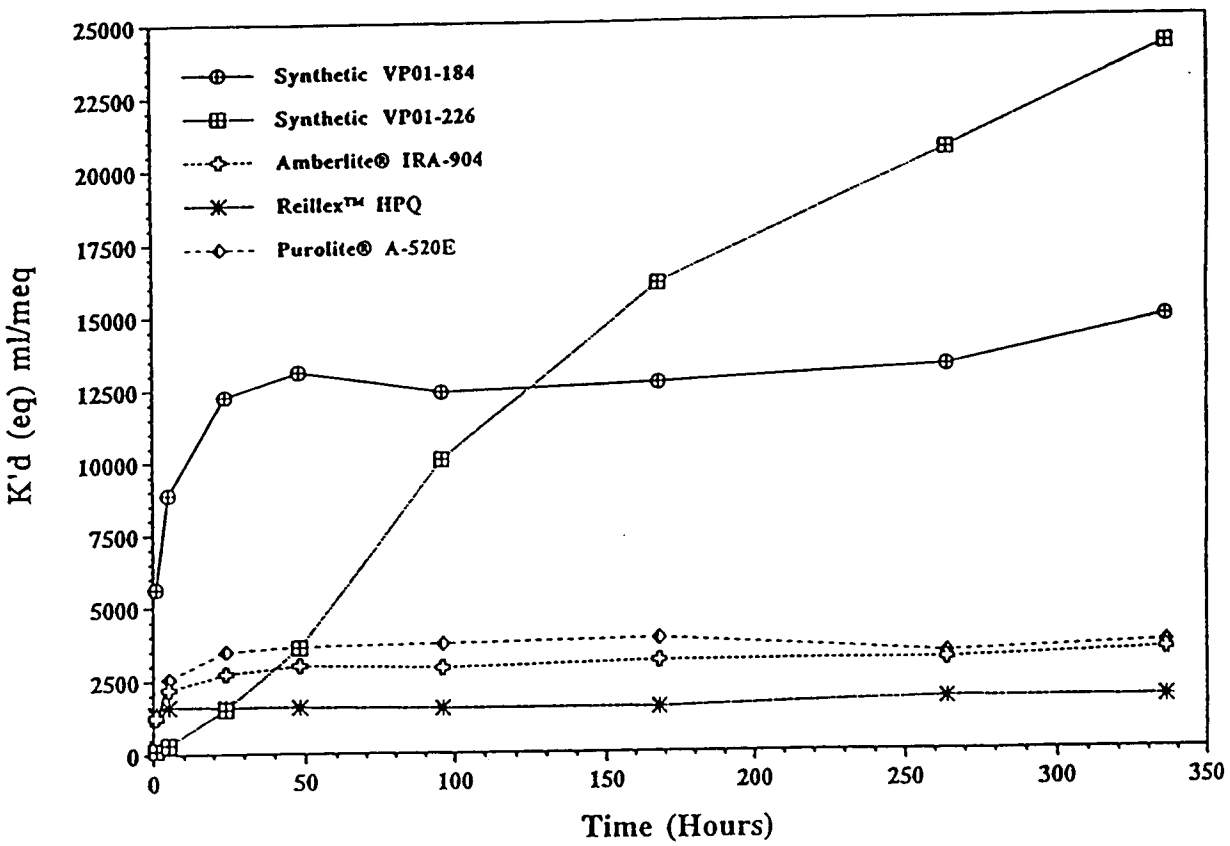


Figure 18 Pertechnetate Complexation Per Exchange Site (K'd(eq)) from Groundwater Test Solution for Selected Resins as a Function of Time.

3.I.A(c) Column study

Column studies were done for those resins which performed very well in the batch studies. Standard ground water test solution was prepared as described in the procedure for the batch study. The ground water test solution was dripped through the columns containing 3.0 mL of resin (bed volume). The rate of the solution throughput was roughly constant for individual resins, i.e. 3.5 BV/ min. The fractions of the eluent were collected every 200 mL (1st fraction at 100 mL) for Tc-99 activity. Tc-99 activity was determined following the standard liquid scintillation method described in the case of the batch study. Breakthrough at 0.1%, 1.0%, and 10.0% are shown in Table 18 and Figure 19 and 20. The best commercially available resins were also tested along with the synthetic resins made for this study. A comparison of selected synthetic resins with the best commercial resins were made (Figure 19 and 20).

3.I.B Removal of Pertechnetate from the resin

Removal of pertechnetate from the resin was performed using the method described by Schroeder [49]. This method involves reducing TcO_4 to TcO_2^+ using stannous ion in the presence of a water soluble ligand (ethylenediamine) to complex and solubilize the TcO_2^+. A solution consisting of stannous chloride (0.01 M), ethylenediamine (0.10 M), and NaOH (1.0 M) was prepared. The aliquots were passed through a Knotes 10.0 x 1.0 cm column, containing 200 mg of equilibrated Buchner-dried resin. The aliquots of the solution were passed through the resin at ~1 mL/min, and collected for the activity count.

Table 18

Results of Column Study for Bifunctional Resins.

resin code	function-ality	mesh size	24 h K'd mL/g	Bed volume for breakthrough			flow rate BV/min
				0.1%	1%	10%	
VP-02-261	But/Hex	-40 +60	39180	40	240	1370	3.40
VP-02-165	Pr/Hex	-40 +60	43260	66	400	1950	3.89
VP-02-258	Et/Hex	-40 +60	37320	140	800	*	3.42
VP-02-217	Pr/Hex	-60+200	48310	400	1250	**	3.52

* 10% breakthrough was not reached by 1800 BV. 4% breakthrough achieved at 1730 BV.

** 10% breakthrough was not reached by 2500 BV. 4% breakthrough achieved at 2440 BV.

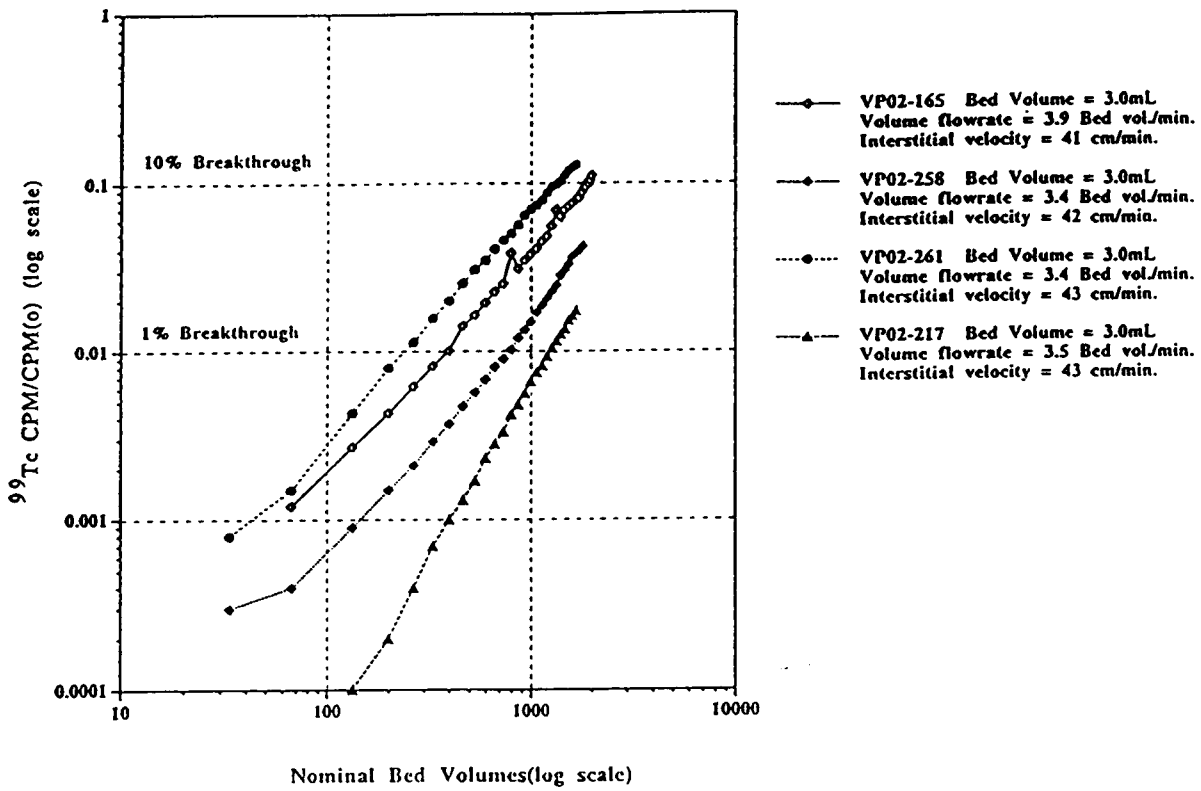


Figure 19 Technetium Breakthrough for VP-02-165, VP-02-217, VP-02-258, and VP-02-261 (in Column) Using Groundwater Test Solution.

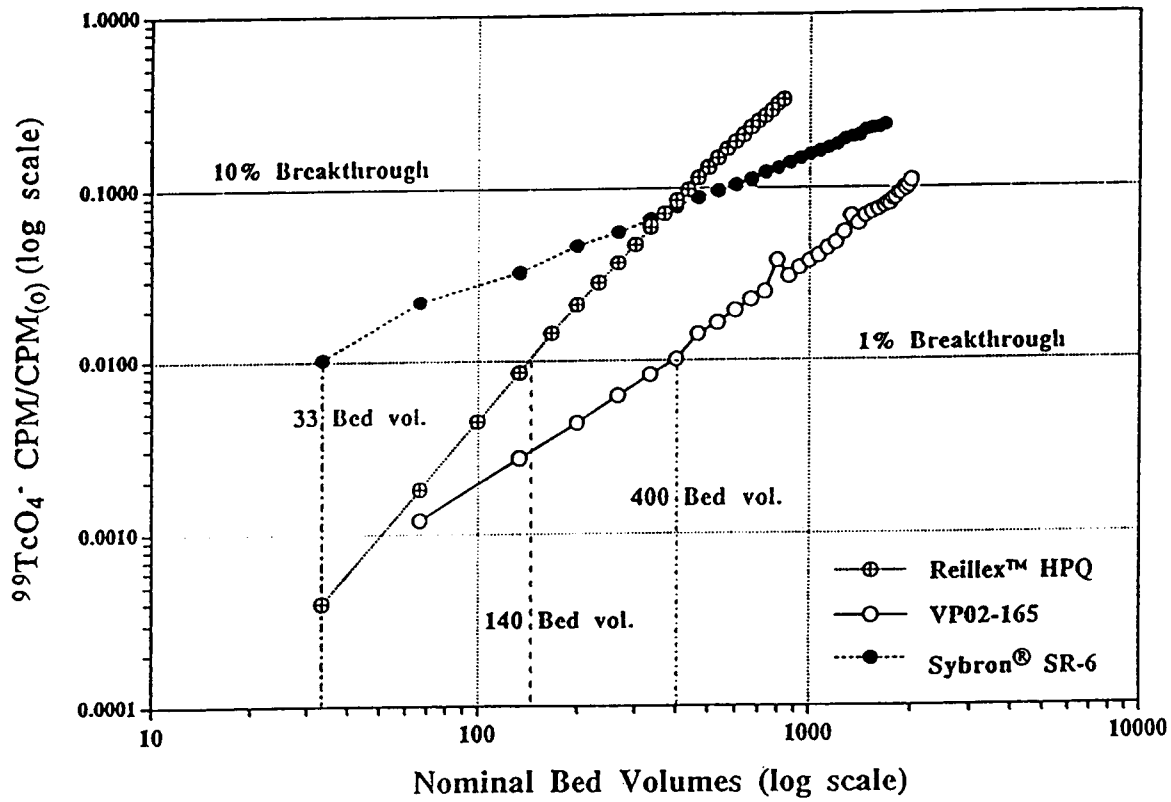


Figure 20 Comparision of VP-02-165 with Reillex™ HPQ and Sybron® SR-6 in the Column Study.

3.II DISCUSSION

Based on the metal ion studies, several conclusions were made concerning the effect of crosslink density, spacers and the presence of other functional groups.

The effect of crosslink density on complexation of pertechnetate was studied using resins functionalized with tripropylamine. The purpose of the study was to determine an optimum crosslink density which provides higher K'_d and K'_d (eq) values along with reasonable resin strength. As the crosslink density increases from 15% DVB, K'_d and K'_d(eq) decrease, due to lower functionalization per gram of resin as well as a decreased accessibility (Table 19). Functionalization can be increased by lowering the crosslink density at the cost of the strength of the resin. It was observed that below a certain crosslink density, K'_d and K'_d(eq) did not increase as expected. The poorer performance of VP-02-138 (15% DVB) and VP-02-072 (25% DVB) is due to the lower capacity of the resins and decreased accessibility. No significant difference in K'_d and K'_d(eq) for the same resin, at 24 h and 96 h was observed. This eliminates the possibility of slow kinetics.

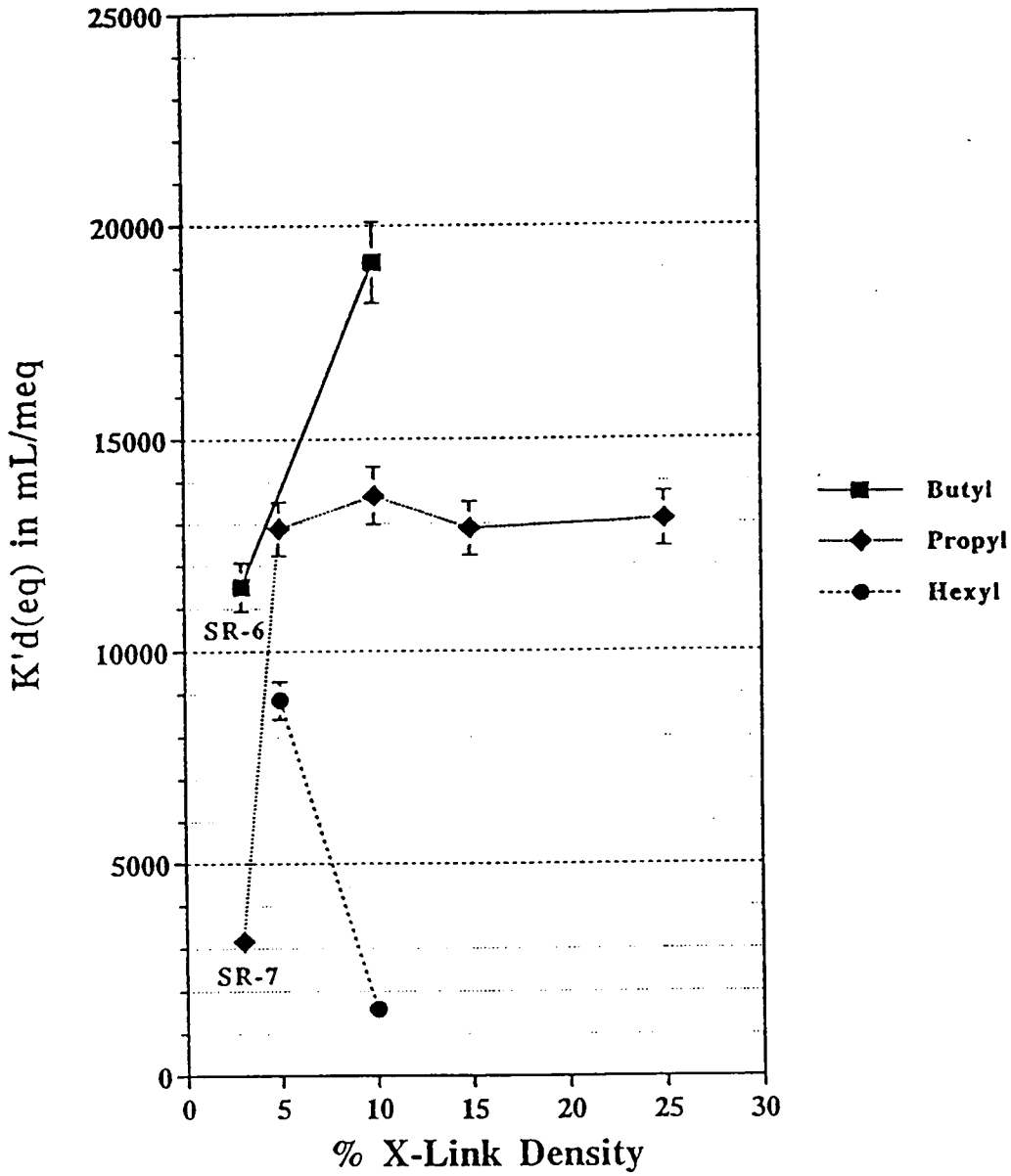
From the results of Table 19, 10% DVB turned out to be an optimum crosslink density. Even though this was optimum, 5% DVB was used for the bifunctional resins in order to improve functionalization with the bulky trihexylamine group. Distribution ratios per exchange site, K'_d (eq), as a function of crosslink density for VBC based resins functionalized with various trialkylamines are shown in Figure 21.

The length of the alkyl chain in the trialkylamine ligands determined the selectivity of the resins. As the alkyl chain length increases, the distribution coefficient per exchange site (K'_d(eq)) increases. Less hydrophilic ligands are required for selective complexation of pertechnetate, a soft base, in the presence of the more hydrophilic nitrate and sulfate.

Table 19

Effect of Crosslink Density on Distribution Coefficients.

Resin code	Functional group (100% VBC)	24 h, K'_d (K'_d (eq))	96 h,K'_d (K'_d (eq))
VP-02-131	$(Pr)_3N$ w/ 5% x-link	20274 (7858)	21710 (8414)
VP-01-184	$(Pr)_3N$ w/ 10% x-link	23217 (13657)	
VP-02-138	$(Pr)_3N$ w/ 15% x-link	20348 (12878)	21633 (13692)
VP-02-072	$(Pr)_3N$ w/ 25% x-link	16889 (12795)	16796 (12860)



Note: The SR resins are synthetic. Cross-linking above 3% is via divinyl benzene.

Uncertainty is ± 5%.

Figure 21 Distribution Coefficient per Exchange Site (K'd (eq)) Vs Crosslink- Densities (Alkyl group = Propyl, Butyl, and Hexyl)

However, the time needed to reach equilibrium increases with the decrease in hydrophilicity; i.e. selectivity is increased at the expense of kinetics. Distribution coefficients K'_d and K'_d(eq) at 24 h as a function of the size of the functional group are given in Figure 22.

Contact studies have shown that the monofunctional tripropylamine resin (VP-01-184) has the highest K'_d. It provides the optimum hydrophilicity along with the fastest kinetics. Trihexylamine resin (VP-01-226), on the other hand, did not perform well at 24 hours, but performed well with a longer contact time. These two resins are compared with the best commercial resins in Figures 16, 17, and 18.

For practical applications, kinetics is an important factor. There is a trade off between selectivity and kinetics. Based on the results of these contact studies, research was focused on tripropyl and trihexylamine ligands. It is interesting to note that, upon standing in water, recent experiments revealed the highest K'_d and K'_d(eq) for the tributylamine resin (VP-02-083). The distribution ratios for other resins still remain within experimental error (±5%). Sybron Ionac SR-6, a commercial resin with tributylamine ligands, has also shown noticeable increases in the K'_ds after the resin is stored in distilled water for several months. The reason for the increase in the distribution ratios for the tributylamine resins after being kept in water for a long period of time is not understood. For high selectivity the trihexylamine group was kept as the principal ligand and combined with trimethyl, triethyl, tripropyl or tributylamine in bifunctional resins. Contact studies at 24 h show the highest K'_d values for the combination of tripropyl and trihexylamine ligands (VP-02-165 and VP-02-217), (Table 18), due probably to an optimum balance of hydrophilicity and hydrophobicity

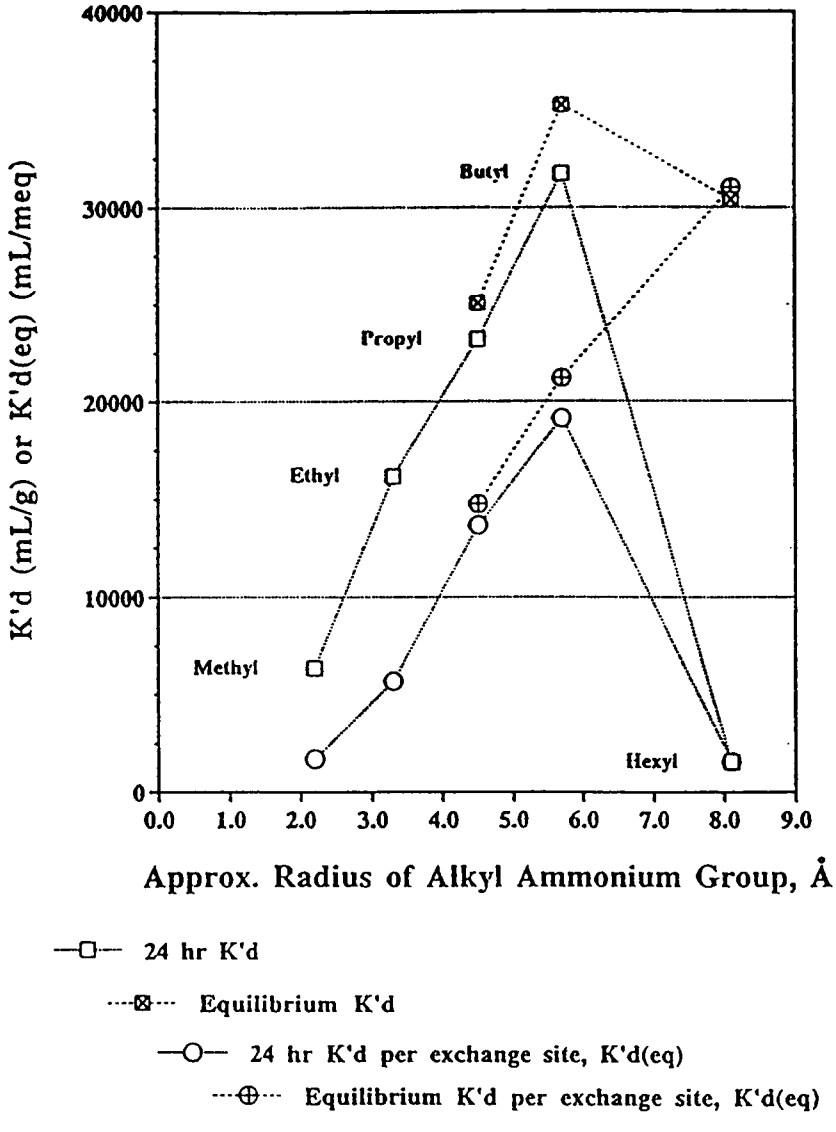


Figure 22. Distribution Coefficients K'd and K'd(eq) Vs Size of Alkyl Ammonium Group.

for the complexation of pertechnetate. Even though the tributylamine resin (VP-02-083) has shown higher K'_d in the monofunctional category, a lower K'_d value was observed with the combination of tributyl and trihexyl amine resin (VP-02-261) in the bifunctional category.

A decrease in the degree of functionalization has played an important role in creating the most appropriate microenvironment for pertechnetate complexation. It can be seen (Table 20) that MMA copolymers have lower K'_d values compared to resins with the same functional group and styrene units in the backbone. Resins with low functionality in 100% VBC/DVB copolymers have shown higher K'_d values due to the unreacted VBC group, which acts to increase the resin hydrophobicity. Butyl methacrylate gives higher K'_d values than MMA , but very low K'_d values compared to styrene copolymers. Higher K'_d values with styrene copolymers is probably due to the hydrophobic nature of styrene.

Table 20

Effect of Incorporated Styrene and MMA Monomeric Units on Distribution Ratios.

Functional group	75:25 / VBC:MMA		75:25 / VBC:Styrene	
	Resin code	K'_d (K'_d(eq))	Resin code	K'_d (K'_d(eq))
trimethylamine	VP-01-152	3551 (1079)	VP-01-280	5693 (1752)
triethylamine	VP-01-239	10102 (3798)	VP-02-033	17451 (6844)
tripropylamine	VP-01-181	17811 (8950)	VP-02-039	15004 (9497)
pyridine	VP-01-202	3273 (1661)	VP-02-042	5694 (2890)
triethanolamine	VP-01-242	1411 (556)	VP-02-048	1760 (834)

CHAPTER 4

EXPERIMENTAL

4.I COPOLYMERIZATION

4.I.A. Copolymerization of VBC/DVB/Inert Comonomer*.

The suspension copolymerization was conducted in a 1000 mL three-neck round bottom flask equipped with an overhead stirrer, a condenser and a Therm-o-watch® (a temperature control device from 'Instrument for Research and Industry', Cheltenham, PA). The system was purged with N_2 for 2 hours before and throughout the reaction. The reaction mixture consists of an aqueous phase and an organic phase.

The composition of the aqueous phase was the same for both gel and macroporous (MR) copolymers, but was different for the polyvinylimidazole/styrene copolymer. With gel and MR copolymers, 0.92 g pharmagel is dissolved in 100.0 g water at 50 °C. In a separate beaker, 12.90 g of poly (diallydimethylammonium chloride), (PADMAC, Calgon Corp) and 6.35 g of boric acid (Aldrich) were added to 216.45 g of water. This solution was combined with the PADMAC solution and 50% NaOH was added to adjust the pH to 10.3. The aqueous solution was added to the three-neck round bottom flask. The stirrer speed was set to the desired value before the organic phase was added. The organic phase was prepared in a separate flask. Monomers and initiator were added to give the different polymer supports. A typical MR copolymer contains DVB (55.4% pure, Aldrich), VBC (Aldrich), benzoyl peroxide initiator and 4-methyl-2-pentanol (4M2P). Fifty percent of the total organic phase consists of 4M2P added as diluent. In the gel copolymers, diluent is not used.

* Inert to functionalization (amination) reaction.

The composition of the organic phase varies depending on the kind of copolymers that are made, as shown in Tables 21 and 22. After the organic phase was prepared, it was added to the round-bottom flask. The reaction mixture was stirred at room temperature for 2 min, then stopped for 1 min. This was repeated three times, to check whether the suspension was stable. The reaction mixture was then stirred continuously at the desired speed. The temperature was raised to 80 °C at the rate of 7 °C/15 min and was held at 80° C for 10 h. After 10 h, approximately 200 mL of distilled water was added into the mixture and a finish off procedure was carried out, which differs for both gels and MRs.

For the MR copolymer system, the diluent (4M2P) was removed by steam distillation with the use of a Dean-Stark trap. A typical MR copolymerization required about 6 h to remove the 4M2P. The beads were washed by water adjusted to pH 4 with HCl, then with distilled water.

For the gel copolymer, the reaction mixture was heated at 100 °C for an additional 2 h. The mixture was washed with water adjusted to pH 4 with HCl and then with distilled water several times. After the finish off procedure (for both MRs and gels), the beads were washed with acetone and dried in a Buchner funnel. Buchner-dried beads were kept in a glass tray for about 15 min and transferred to a thimble for soxhlet extraction in toluene for 17 h to remove residual monomers and uncrosslinked oligomers.

4.I.B Copolymerization of Vinylimidazole/Styrene

Suspension copolymerization of vinylimidazole (VIm) and styrene was conducted in a 500mL three-neck round bottom flask with the same equipment used above.

The aqueous phase was prepared by adding 26.66 g Na_2SO_4 and 0.86 g

Table 21

Composition of Organic Phase in Copolymers Without Inert Comonomer.

Crosslink density	VBC (g)	DVB (g)	BPO (g)	4M2P (g)
2% (gel)	193.16	7.31	2.03	0.0
5% (MR)	134.96	13.54	1.50	150.0
10% (MR)	121.50	27.00	1.50	150.0
15% (MR)	53.94	20.31	0.75	75.0
25% (MR)	81.86	67.69	1.50	150.0
40% (MR)	108.30	40.13	1.50	150.0

Table 22

Composition of Organic Phase in 10% Crosslinked

MR Copolymers with Inert Comonomer.

	VBC (g)	DVB (g)	BPO (g)	Styrene (g)	MMA (g)	4M2P (g)
VBC/MMA (18/82)	30.37	27.0	1.50	0.0	91.12	150.0
VBC/MMA (40/60)	60.75	27.0	1.50	0.0	60.75	150.0
VBC/MMA (75/25)	99.70	27.0	1.50	0.0	21.78	150.0
VBC/Sty (25/75)	39.87	27.0	1.50	81.63	0.0	150.0
VBC/Sty (50/50)	72.23	27.0	1.50	49.27	0.0	150.0
VBC/Sty (75/25)	99.00	27.0	1.50	22.51	0.0	150.0
VBC/BMA (50/50)	62.90	27.0	1.50	0.0	58.59*	150.0

* BMA was used instead of MMA.

poly(acrylamide-acrylic acid, sodium salt) (MW 200,000 from Polysciences, Inc. Warrington, PA) to a beaker containing 160 mL distilled water. The organic phase was prepared with 32.33 g vinylimidazole, 11.92 g styrene, 9.09 g technical grade DVB, 1.5 g asobisisobutyronitrile (AIBN) and 50 g toluene as diluent. The aqueous phase was added first to the round bottom flask and heated to 60°C. The organic phase was then added slowly to the round bottom flask, stirred for 2 min, and stopped to check the stability of monomer droplets. The reaction mixture was stirred continuously at 450 RPM with the temperature at 60 °C for 1 h, 70 °C for 1 h and 80 °C for 10 h. The copolymer was then washed with 1 L H_2O followed by soxhlet extraction with methanol. This copolymer was stored in water.

4.II AMINATION REACTIONS

4.II.A Trimethylamine

A given amount of copolymer (Table 23) was allowed to swell in the appropriate amount trimethylamine (25% wt. in water, Aldrich) in a 500mL round bottom flask overnight. The copolymers that were not allowed to swell overnight in trimethylamine are marked with an asterik in Table 23. Due to the low boiling point of trimethylamine, the round bottom flask was tightly closed with a rubber septum. After overnight swelling, the round bottom flask was equipped with a condenser, an overhead stirrer and sealed with a balloon. The reaction mixture was then refluxed for 17 h. The aminated beads were washed with water several times and then conditioned with successive elutions of water, 4% NaOH, water, 4% HCl, and water until the eluent became neutral, all at a rate of 1 L/h.

Table 23

Composition of Reactants in Trimethylamine Resins

Resin code	Copolymer composition	Weight of copolymer (g)	Reaction mixture: Trimethylamine (25% in water) (mL)
VP-01-140*	18:82/ VBC:MMA	5.0	200
VP-01-145*	40:60/ VBC:MMA	5.0	170
VP-01-152*	75:25/ VBC:MMA	6.0	200
VP-01-255	25:75/ VBC:Sty	6.0	200
VP-01-258	50:50/ VBC:Sty	6.0	200
VP-01-280	75:25/ VBC:Sty	6.0	200
VP-01-165	100/ VBC	6.0	200

* copolymers were not allowed to swell overnight in trimethylamine.

4.II.B Triethylamine

Copolymers in Table 24 were allowed to swell overnight in a 500 mL round bottom flask with 50 mL dioxane. Triethylamine (99% pure, Aldrich), water, and additional dioxane (see Table 24) were added to the round bottom flask. The flask was equipped with an overhead stirrer and a condenser. The reaction mixture was refluxed for 17 h. The resin was washed with water and conditioned as above.

4.II.C Tripropylamine

Copolymers (Table 25) were weighed into a 500 mL or 300 mL round bottom flask, depending on the size of the reaction mixture, with 50 mL dioxane and allowed to swell overnight. Additional dioxane (total amount inTable 25), water and tripropylamine (98%

Table 24

Composition of Reactants in Triethylamine Resins

Resin	Copolymer composition (%by mole)	Weight of copolymer (g)	Amount of reactants: dioxane : water : triethylamine (mL)
VP-01-157	18:82 / VBC:MMA	5.0	75 : 75 : 50
VP-01-162	40:60 / VBC:MMA	6.0	75 : 75 : 50
VP-01-239	75:25 / VBC:MMA	6.0	75 : 10 : 75
VP-01-168	100 / VBC	6.0	75 : 75 : 50
VP-01283	50:50 / VBC:Sty	6.0	100 : 25 : 75
VP-02-033	75:25 / VBC:Sty	7.0	100 : 25 : 75

Table 25

Amount of Reactant Used in Tripropylamine Resins

Resin code	Copolymer composition (% mol)	Weight of copolymer (g)	Reaction mixture dioxane : water : tripropylamine (mL)
VP-01-173	18:82 / VBC:MMA	6.0	125 : 10 : 50
VP-01-178	40:60 / VBC:MMA	6.0	125 : 10 : 50
VP-01-181	75:25 / VBC:MMA	6.0	125 : 10 : 50
VP-01-184	100 / VBC (10%MR)	6.0	125 : 10 : 50
VP-02-152	100 / VBC (10%MR)	15.0	375 : 30 : 150
VP-02-236	25:75 / VBC:Sty	5.0	100 : 10 : 50
VP-01-286	50:50 / VBC:Sty	6.0	125 : 5 : 70
VP-02-026	50:50 / VBC:Sty	6.0	125 : 00 : 75
VP-02-036	50:50 / VBC:Sty	6.0	00 : 00 : 200
VP-02-039	75:25 / VBC:Sty	7.0	50 : 00 : 150
VP-02-128	50:50 / VBC:BMA	7.0	140 : 5 : 60
VP-02-138	100 / VBC (15%MR)	6.0	140 : 5 : 60
VP-02-072	100 / VBC (25%MR)	7.0	130 : 10 : 60
VP-02-078	100 / VBC (40%MR)	7.0	130 : 10 : 60
VP-02-131	100 / VBC (5% MR)	6.0	140 : 5 : 60

pure, Aldrich) was added to the flask. The reaction mixture was refluxed for 17 h while stirring with an overhead stirrer. The experiments VP-01-173 and VP-01-178 were carried out with a balloon on the condenser. The aminated resin was then washed with dioxane, ethanol, ethanol/water (50/50), 2% HCl and water in that order. The resins were conditioned as noted above.

4.II.D Tributylamine

Only two amination reactions were carried out using tributylamine (Table 26). The given amount of copolymer or partially functionalized resin was weighed into a 300 mL round bottom flask and swelled in 50 mL dioxane. In the case of bifunctional resin, no swelling was required due to the swollen monofunctional precursor. Additional dioxane, water and tributylamine (Aldrich) were added to the round bottom flask equipped with an overhead stirrer and a condenser. The reaction mixture was refluxed for 17 h. The aminated resin was washed with dioxane, ethanol, ethanol/water (50/50 by vol.), 2% HCl and water in that order. Conditioning of the resins were as noted above.

Table 26

Amount of Reactant Used in Tributylamine Resins

Resin code	Copolymer composition (% mol)	Weight of copolymer (g)	Reaction mixture dioxane : water : tributylamine (mL)
VP-02-283	100 / VBC (10%MR)	7.0	130 : 10 : 130
VP-02-261	Bifunctional	7.7	100 : 5 : 50

4.II.E Pyridine

Six grams of the given copolymer (Table 27) was weighed into a 500 mL round bottom flask with the stated amount of dioxane, water and pyridine (98% pure, Aldrich). The beads were not allowed to swell overnight. The round bottom flask was equipped with an overhead stirrer and a condenser. Reaction mixture was refluxed for 17 h, then washed with water, 4% HCl, and water. All of the resins were conditioned as described above, except VP-02-054, which was conditioned with successive elutions of water, 4% HCl and water at a rate of 1 L/h.

Table 27

Amount of Reactants Used in Pyridine Resins

Resin code	Copolymer composition (% mol)	Weight of copolymer (g)	Reaction mixture Dioxane : water : Pyridine
VP-01-187	18 : 82 / VBC:MMA	6.0	00 : 00 : 150
VP-01-199	40:60 / VBC:MMA	6.0	00 : 50 : 150
VP-01-202	75:25 / VBC:MMA	6.0	00 : 50 : 150
VP-01-292	50:50 / VBC:Sty	6.0	00 : 25 : 175
VP-02-042	75:25 / VBC:Sty	6.0	50 : 00 : 150
VP-02-054*	75:25 / VBC:Sty	6.0	50 : 00 : 150
VP-01-207	100 / VBC (10%MR)	6.0	00 : 50 : 150

* Resin was conditioned only with water and 4% HCl (4% NaOH was not used).

4.II.F Trihexylamine

Trihexylamine (Aldrich) was used as an aminating agent with different copolymers, shown in Table 28. A given amount of copolymer was allowed to swell in 50 mL dioxane in a round bottom flask overnight. The remaining amount of dioxane, water and trihexylamine was added to the round bottom flask equipped with an overhead stirrer and a condenser, and refluxed for 17 h. Two aminations were refluxed for 48 h (VP-02-066) and 59 h (VP-02-102). After amination, the beads were washed with dioxane, ethanol, ethanol/water (50/50 by vol.), and water. The conditioning of this resin was similar to that for the trimethylamine resin except for an extra elution with 500 mL ethanol prior to the standard elution sequence: the beads float on the water in the frit unless the aqueous elutions are preceded with ethanol.

4.II.G N,N-dimethyldodecylamine

The given amount (Table 29) of copolymer, VP-02-107 (100% VBC; 10% MR), was allowed to swell in 50 mL dioxane in a 500 mL round bottom flask overnight, followed by an additional 110 mL dioxane, 40 mL N,N-dimethyldodecylamine and 3 mL water. The mixture is refluxed for 17 h with stirring. The aminated beads were washed with dioxane, ethanol, ethanol/water (50/50 by vol.), water/2% HCl (50/50 by vol.) and water. The beads were conditioned with the standard sequence; however, the last elution with water (1 L) was repeated 3 times to remove the last trace of HCl.

Table 28

Amount of Reactans Used in Trihexylamine Resins

Resin code	copolymer composition (% mol)	Weight of copolymer (g)	Amount of reactants dioxane : water : trihexylamine (mL)
VP-01-210	18:82 / VBC:MMA	6.0	116 : 04 : 30
VP-01-214	40:60 / VBC:MMA	6.0	116 : 04 : 30
VP-01-223	75:25 / VBC:MMA	6.0	116 : 04 : 30
VP-02-248	25:75 / VBC:Sty	5.0	100 : 04 : 40
VP-02-011	50:50 / VBC:Sty	6.0	130 : 02 : 40
VP-02-051	75:25 / VBC:Sty	7.0	150 : 00 : 50
VP-02-269	50:50 / VBC:BMA	5.0	100 : 06 : 30
VP-02-112	100/VBC (2% gel)	7.0	160 : 03 : 40
VP-02-109	100/VBC (5% MR)	5.0	160 : 03 : 40
VP-02-119	100/VBC (5% MR)	10.0	150 : 03 : 60
¤ VP-02-149	100/VBC (5% MR)	7.0	80 : 00 : 40
VP-01-226	100/VBC (10% MR)	6.0	130 : 04 : 35
VP-02-060	100/VBC (10%MR)	8.0	150 : 00 : 70
† VP-02-066	100/VBC (10%MR)	7.0	150 : 00 : 75
VP-02-086	100/VBC (10%MR)	7.0	160 : 03 : 40
▪ VP-02-102	100/VBC (10%MR)	5.0	160 : 02 : 40
‡ VP-02-142	100/VBC (10%MR)	4.2	120 : 02 : 30

¤ 80 mL toluene was used as a mixture to the solvent.
† refluxed for 48 h.
▪ refluxed for 59 h
‡ - 100 +200 mesh (150-75 μ) bead size

Table 29

Amount of Reactants Used in N,N-dimethyldodecylamine Resins

Resin code	Copolymer constitution (% mol)	Weight of copolymer (g)	Amount of reactants dioxane : water : N, N-dimethyl dodecylamine, (mL)
VP-02-145	100/VBC (10%MR)*	7.0	160 : 03 : 40
VP-02-155	100/VBC (10%MR)	6.0	160 : 03 :40

* bead size -60 +100 mesh.

4.II.H Ethylenediamine

In a round bottom flask, 6 g of VP-02-107 (100% VBC; 10% MR) was allowed to swell in 50 mL of dioxane. Ethylenediamine (Aldrich), (17 mL), and 40 mL dioxane were added to the round bottom flask and refluxed for 17 h. The aminated beads were first washed in the round bottom flask with water, followed by 2% HCl, and finally with water. After amination, the beads were not conditioned, instead, 4% NaOH solution was added to the round bottom flask and stirred overnight. The following day, the beads were washed twice with water, twice with acetone and once with dioxane (about 200 mL each). Quaternization of the aminated resin was done by adding 13 mL methyl iodide and 90 mL dioxane to the flask and refluxed for 17 h. The quaternized resin was conditioned by eluting with 2 L 2M NaCl solution and water until the eluent was free of chloride.

4.II.I Guanidine

Guanidine was received in the form of guanidine-hydrochloride from Aldrich. In a round bottom flask, 5 g copolymer, VP-02-105 (100%VBC, 5%MR), was allowed to swell in 50 mL dioxane. In another beaker 10 g guanidine-hydrochloride and 7.12g NaOH were dissolved in 30 mL water. The guanidine solution was then added to the copolymer beads and refluxed for 17 h. After the amination, the resin was conditioned with 4% NaOH solution, followed by water (4 times), each at 1 L/h.

A similar reaction (VP-02-228) was carried out using ethanol as the solvent instead of dioxane. The resin (VP-02-228) was conditioned by the standard conditioning sequence.

4.II.J Triisooctylamine

Seven grams of copolymer VP-02-105 was placed in a round bottom flask with 50 mL dioxane. A mixture of 50 mL dioxane, 40 mL triisooctylamine (Aldrich) and 5 mL water was added to the swollen beads in the flask, equipped with an overhead stirrer and condenser. The reaction mixture was refluxed for 17 h, and washed with dioxane, ethanol, ethanol/water (50/50 by vol.), 2% HCl , and water. Prior to the usual conditioning procedure, 0.5 L of acetone was eluted through the beads.

4.II.K Imidazole

A given amount of copolymer (Table 30) was weighed into a round bottom flask with 50 mL of dioxane and allowed to swell overnight. A solution of imidazole was prepared by dissolving a given amount of imidazole (Aldrich; 99% pure) in a given amount

Table 30

Amount of Reactants Used in Imidazole Resins

Resin code	Copolymer compositon (% mol)	Weight of copolymer (g)	Reactants dioxane : water : imidazole (mL)
VP-02-181	100/VBC (10% MR)	5.0	80 : 30 : 20
VP-02-185	100/VBC (10% MR)	5.0	50 : 50 : 30
VP-02-204	100/VBC (10% MR)	7.0	80 : 40 : 30

water. The imidazole solution and the remaining dioxane was added to the round bottom flask and then the mixture was refluxed for 17 h. Resins VP-02-181 and VP-02-185 were washed with water. In the case of VP-02-204, washing was done with water, ethanol, ethanol/water (50/50 by vol.) and water. The conditioning of VP-02-181 and VP-02-185 was done as previously noted. VP-02-204 was conditioned by successive elutions of water, 4% NaOH (2 L) and water until neutral. The resin was then eluted with 2 M NaCl (1 L) solution followed by water until no chloride was detected. Finally, the resin was eluted with 1 M KI (2 L) followed by water until no iodide was present in the eluent.

Resins VP-02-185 and VP-02-204 were used in a subsequent reaction with methyl iodide (Aldrich),(see Table 31). A given amount of Buchner-dried resin was added to a given amount of reactants in a round bottom flask equipped with a stirrer and condenser. The reaction mixture was refluxed for 17 h and washed with dioxane, acetone, 2% HCl, ethanol and water. VP-02-190 was conditioned by eluting with water, 4% HCl and water until neutral. VP-02-209 was conditioned by eluting with water, NaCl solution (2 M) and water

Table 31

Amount of Reactant Used in Quaternization Reactions

Resin code (quaternized)	Precourser resin	Weight of precourser † (g)	Reactants metyliodide : dioxane (mL)
VP-02-190	VP-02-185*	15.26	20 : 100
VP-02-209	VP-02-204*	17.46	30 : 100

* resins are listed in the previous table.
† weight of Buchner dried resin

until the eluent was free of chloride.

4.III PERCENT SOLIDS OF RESIN

Wet resins were buchner dried at 720 mmHg for 5 min and accurately weighed (1-2 g) on a Mettler analytical balance into a vial. The vial was placed in an oven at 110^{0}C for 17 h and then reweighed. The difference in the amount of water present in the Buchner-dried and the oven dried resin gave percent solids of the resin

$$\% \text{ solid} = \frac{\text{weight of oven dried resin}}{\text{weight of buchner dried resin}} \times 100$$

4.IV TOTAL ANION EXCHANGE CAPACITY (TAEC)

Approximately 2-3 g of Buchner-dried amine resin (in the chloride form) was accurately weighed into a clean vial and transferred quantitatively to a fritted glass funnel with deionized water. The resin was then eluted with 1 L 1 M $NaNO_3$ solution for one hour and the eluent was collected in a 1 L volumetric flask. A 50 mL aliquot was titrated with 0.05 M $AgNO_3$ by Mohr titration. The total anion exchange capacity was calculated using equation:

$$TAEC = \frac{[\text{ M } AgNO_3] \text{ x } [\text{ mL } AgNO_3] \text{ x } 20}{\text{dry weight of resin (g)}}$$

4.V NITROGEN ELEMENTAL ANALYSIS

A sample of oven-dried resin (0.2-0.3g) was accurately weighed and transferred to a 500 mL three-neck round bottom flask equipped with a liebig condenser and two stoppers. To the flask, 0.30 g $CuSO_4$, 10.0 g K_2SO_4 and 25 mL concentrated H_2SO_4 were added to the round bottom flask. Carborundum chips were added to prevent bumping. The mixture was heated gently (variac at 50) with a heating mantle for two hours. The heat was increased (variac at 90) after two hours and kept there until the mixture became a transparent light-blue. The mixture was cooled and the condenser was rinsed into the flask with a small amount of H_2O. A stir bar was added and 100 mL H_2O was slowly added with stirring. The condenser was replaced with a distillation apparatus with a glass-funnel attached at the end. Exactly 50

mL of standardized HCl solution was added to a 600mL beaker. The glass-funnel from the distillation apparatus was placed into the HCl (in the beaker) in such a way that any gas coming off will have to bubble through the solution. One stopper of the round bottom flask was replaced with a 250 mL addition funnel containing 150 mL 6 N NaOH. After ensuring that the system was closed to the atmosphere, the NaOH solution was slowly added to the flask with stirring. After the addition was completed, the flask was heated and the liquid was allowed to distill into the standardized HCl which neutralized the ammonia in the distillate. The distillation was continued for an hour at which time the condensate was tested with pH paper. If the condensate was neutral to the pH paper, the distillation was stopped. The system was partially disassembled prior to turning off the heat to avoid aspiration of the HCl back into the distillation flask. The HCl solution was quantitatively transferred to a 250 mL volumetric flask and diluted to the mark with distilled water. A 50 mL aliquot was pipetted out and titrated with standardized NaOH solution using bromocresol green indicator. The nitrogen capacity was calculated using equation:

$$\text{N capacity} = \frac{[\text{Vol. HCl}]\,[\text{N HCl}] - 5\,[\text{vol. NaOH}]\,[\text{N NaOH}]}{\text{weight of dry resin (g)}}$$

4.VI CHLORINE ELEMENTAL ANALYSIS

A sample of oven dried resin (0.5-1.0 g) was accurately weighed in a metal capsule of the Parr-Bomb, and an amount of mineral oil (0.0-0.5 g) was added to the resin to make

a total of about one gram. The capsule was then placed in a capsule-holder. A 10 cm nickel alloy fuse wire was threaded through the bomb stem holes to make a loop. The bottom of the loop was allowed to touch the sample-oil mixture without touching the capsule. Five milliliters 5% Na2CO3was added to the cylinder. The cylinder was rotated to wet the entire inside surface. The capsule assembly was then placed into the cylinder while keeping the bleeder open (for oxygen). A security cap was then screwed on the cylinder (bomb). The bleeder was closed and attached to the oxygen tank with high pressure tubing. The bomb was then purged with oxygen (30 atm), and the pressure was released with the bleeder. This step was repeated twice to remove any trace of gases other than oxygen. Finally the bomb was filled with oxygen at 30 atm and connected to a bomb ignition unit. After the connection, the bomb was placed in a water bath to test for leaking. The sample in the bomb was then ignited using the ignition switch. The bomb was left in the water bath for at least 15 min to dissipate heat generated during the ignition. The bomb was removed from the water bath and the pressure of the bomb was released by opening the bleeder very slowly. After releasing the pressure, the bomb was dissembled and the capsule was placed in a clean 600 ml beaker. The inside wall of the cylinder was then washed with deionized water. The solution was transferred quantitatively to the 600 mL beaker. The washing was repeated three times. The solution in the beaker was then filtered into a 250 mL volumetric flask and diluted to the mark with deionized water. Two 25 mL aliquots of the solution were pipetted into 125 mL erlenmeyer flasks. Approximately 3 mL 3 M HNO_3 was added to neutralize the carbonate. Ten milliliters of 0.05 M $AgNO_3$ were added to the 125 mL flask and boiled on a hot plate to coagulate the precipitate. The precipitate was filtered and washed with 3 M HNO_3 and deionized water. The filtrate was titrated with standard NH_4SCN solution using

ferricammoniumsulfate indicator. The chlorine capacity was calculated in mequiv Cl/g dry resin by using equation:

$$\text{Cl capacity} = \frac{\{ [\text{M } AgNO_3] [\text{ml } AgNO_3] - [\text{M } NH_4SCN] [\text{mL } NH_4SCN] \} \times 10}{\text{weight of dry resin (g)}}$$

CONCLUSION

The selectivity of anion exchange resins depends on both the nature of the ligand and the microenvironment within the polymer. Large anions with low hydration energies prefer to associate with large, hydrophobic cations rather than small anions with high hydration energies. This will allow large, hydrophobic ligands to be selective toward anions of increasing size and decreasing hydration energies. Since the pertechnetate anion is larger than competing anions present in groundwater and has a low hydration energy, large hydrophobic ligands would be an appropriate choice for preparing a pertechnetate selective anion exchange resin.

As the size of the trialkylamine increases, the selectivity for the pertechnetate anion increases; however, the time needed to reach equilibrium also increases due to the increase in hydrophobicity. The highest distribution coefficients for twenty four hour metal ion studies of monofunctional resins are obtained with tripropyl- and tributylamine resins. These resins have adequate hydrophobicity along with fast kinetics. On the other hand, the more hydrophobic trihexylamine resin does not perform well at twenty four hours due to limited kinetics, but shows higher selectivity than other ligands with longer contact times. Thus, selectivity is increased at the expense of kinetics.

Resins using tripropyl- and trihexylammonium ligands show the highest distribution coefficients relative to any other bifunctional resin. The tripropylammonium group provides optimum selectivity for short reaction times. Trihexylammonium is more selective but less accessible due to its hydrophobic nature. Bifunctional resins consisting of both ligands show the highest selectivity with the fastest kinetics. In the presence of the tripropylammonium

group, the trihexylammonium group becomes more accessible to the pertechnetate ion. The distribution coefficients are not as high when the trimethylammonium group is used instead of the tripropylammonium group. This is probably because the trimethylammonium group prefers smaller anions (e.g. nitrate) over larger anions.

The microenvironmental effect plays an important role in the selectivity of the resins. Resins incorporating MMA monomeric units into the polymer backbone show lower selectivity than resins with styrene units. This is due to the hydrophobic nature of the styrene group which creates the right microenvironment for the pertechnetate ion. Partially functionalized VBC/DVB resins show high distribution coefficients due to the unreacted VBC groups which act to increase the resin hydrophobicity. Crosslink density is another variable that can alter the microenvironmernt. High crosslink density provides high strength along with high hydrophobicity. Both hydrophobicity and strength are important for high selectivity; however, accessibility becomes restricted above a certain level of crosslink density. The optimum crosslink densities for the monofunctional and bifunctional resins are ten percent and five percent respectively.

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APPENDIX

APPENDIX

General information about resins discussed in this work

#	Resin code	Backbone VBC= vinylbenzylchloride MMA= methylmethacrylate BMA= buttylmethacrylate ST= styrene	Functionality (all Cl form)	x-link % DVB	K'_d mL/g (24 h)	K'_d (eq) mL/mequiv (24 h)
1	Amberlite IRA-900	100 VBC	$(Methyl)_3N+$	5 (?)	2459	691
2	Amberlite IRA-904	100 VBC	$(Methyl)_3N+$	20	7590	3048
3	Purolite A-520E	100 VBC	$(Ethyl)_3N+$	5 (?)	12382	4422
4	Purolite A-520E	100 VBC	$(Ethyl)_3N+$	5 (?)	13628	4867
5	Sybron Ionac SR-3	100 VBC	thiouronium	3	141	83
6	Sybron Ionac SR-6	100 VBC	$(Butyl)_3N+$	3 (?)	20609	11449
7	Sybron Ionac SR-6	100 VBC	$(Butyl)_3N+$	3 (?)	20707	11504
8	Sybron Ionac SR-6	100 VBC	$(Butyl)_3N+$	3 (?)	25256	14031
9	Sybron Ionac SR-7	100 VBC	$(Propyl)_3N+$	3 (?)	6948	3158
10	VP-01-140	18 VBC / 82 MMA	$(Methyl)_3N+$	10	1336	1757
11	VP-01-145	40 VBC / 60 MMA	$(Methyl)_3N+$	10	1873	871
12	VP-01-152	75VBC / 25 MMA	$(Methyl)_3N+$	10	3551	1079
13	VP-01-157	18 VBC / 82 MMA	$(Ethyl)_3N+$	10	2775	4955
14	VP-01-162	40 VBC / 60 MMA	$(Ethyl)_3N+$	10	5044	2950
15	VP-01-165	100 VBC	$(Methyl)_3N+$	10	6354	1689
16	VP-01-168	100 VBC	$(Ethyl)_3N+$	10	16150	5688

#	Resin code	Backbone VBC= vinylbenzylchloride MMA= methylmethacrylate BMA= buttylmethacrylate ST= styrene	Functionality (all Cl form)	x-link % DVB	K'_d mL/g (24 h)	K'_d (eq) mL/mequiv (24 h)
17	VP-01-173	18 VBC / 82 MMA	$(Propyl)_3N+$	10	3169	4169
18	VP-01-178	40 VBC / 60 MMA	$(Propyl)_3N+$	10	6346	4919
19	VP-01-181	75 VBC / 25 MMA	$(Propyl)_3N+$	10	17811	8950
20	VP-01-184	100 VBC	$(Propyl)_3N+$	10	23217	13657
21	VP-01-187	18 VBC / 82 MMA	Pyridyl	10	1273	1213
22	VP-01-199	40 VBC / 60 MMA	Pyridyl	10	2014	1537
23	VP-01-202	75 VBC / 25 MMA	Pyridyl	10	3273	1661
24	VP-01-207	100 VBC	Pyridyl	10	5066	1956
25	VP-01-210	18 VBC / 82 MMA	$(Hexyl)_3N+$	10	2427	6386
26	VP-01-214	40 VBC / 60 MMA	$(Hexyl)_3N+$	10	7355	14144
27	VP-01-223	75 VBC / 25 MMA	$(Hexyl)_3N+$	10	3156	3996
28	VP-01-226	100 VBC	$(Hexyl)_3N+$	10	1535	1566
29	VP-01-229	18 VBC / 82 MMA	$(Ethanol)_3N+$	10	625	771
30	VP-01-232	40 VBC / 60 MMA	$(Ethanol)_3N+$	10	1008	663
31	VP-01-239	75 VBC / 25 MMA	$(Ethyl)_3N+$	10	10102	3798
32	VP-01-242	75 VBC / 25 MMA	$(Ethanol)_3N+$	10	1411	556
33	VP-01-245	100 VBC	$(Ethanol)_3N+$	10	1587	586
34	VP-01-258	50 VBC/ 50 ST	$(Methyl)_3N+$	10	5488	2033
35	VP-01-280	75 VBC / 25 ST	$(Methyl)_3N+$	10	5693	1752

#	Resin code	Backbone VBC= vinylbenzylchloride MMA= methylmethacrylate BMA= buttylmethacrylate ST= styrene	Functionality (all Cl form)	x-link % DVB	K'_d mL/g (24 h)	K'_d (eq) mL/mequiv (24 h)
36	VP-01-283	50 VBC/ 50 ST	$(Ethyl)_3N+$	10	13303	6553
37	VP-01-286	50 VBC/ 50 ST	$(Propyl)_3N+$	10	18819	13940
38	VP-01-292	50 VBC/ 50 ST	Pyridyl	10	4006	2725
39	VP-02-011	50 VBC/ 50 ST	$(Hexyl)_3N+$	10	247	537
40	VP-02-016	50 VBC/ 50 ST	$(Ethanol)_3N+$	10	1518	915
41	VP-02-033	75 VBC / 25 ST	$(Ethyl)_3N+$	10	17451	6844
42	VP-02-036	50 VBC/ 50 ST	$(Propyl)_3N+$	10	2479	2361
43	VP-02-039	75 VBC / 25 ST	$(Propyl)_3N+$	10	15004	9497
44	VP-02-042	75 VBC / 25 ST	Pyridyl	10	5694	2890
45	VP-02-048	75 VBC / 25 ST	$(Ethanol)_3N+$	10	1760	834
46	VP-02-072	100 VBC	$(Propyl)_3N+$	25	17282	13092
47	VP-02-083	100 VBC	$(Butyl)_3N+$	10	31750	19127
48	VP-02-092	100 VBC	Me_3N/Hex_3N Bifun.	5	13175	4117
49	VP-02-109	100 VBC	$(Hexyl)_3N+$	5	9031	8854
50	VP-02-122	100 VBC	Pr_3N/Hex_3N Bifun.	5	34461	19580
51	VP-02-128	50 VBC / 50 BMA	$(Propyl)_3N+$	10	13678	10132
52	VP-02-131	100 VBC	$(Propyl)_3N+$	5	20274	7858
53	VP-02-138	100 VBC	$(Propyl)_3N+$	15	20348	12878
54	VP-02-152	100 VBC	$(Propyl)_3N+$	10	22340	9588

#	Resin code	Backbone VBC= vinylbenzylchloride MMA= methylmethacrylate BMA= buttylmethacrylate ST= styrene	Functionality (all Cl form)	x-link % DVB	K'_d mL/g (24 h)	K'_d (eq) mL/mequiv (24 h)
55	VP-02-155	100 VBC	$(Me)_2(dodecyl)N+$	10	20309	9764
56	VP-02-165	100 VBC	Pr_3N/Hex_3N Bifun.	5	41733	19593
57	VP-02-174	100 VBC	Me Ethylenediamine	10	5185	1630
58	VP-02-181	poly N-vinylimidazole	(HCl salt)	10	5613	2118
59	VP-02-190	100 VBC	N-Me-imidazole	10	8422	3142
60	VP-02-198	poly N-vinylimidazole	Methylated	10	2773	640
61	VP-02-209	poly N-vinylimidazole		10	Not tested	
62	VP-02-217	100 VBC	Pr_3N/Hex_3N Bifun.	5	48314	23454
63	VP-02-228	100 VBC	guanidinium	10	117	180
64	VP-02-236	25 VBC / 75 ST	$(Propyl)_3N+$	10	16764	15240
65	VP-02-239	100 VBC	$(Isooctyl)_3N+$	10	942	1346
66	VP-02-245	100 VBC	$Pr_3N/i\text{-}oct_3N$ Bifun.	5	37766	19467
67	VP-02-248	25 VBC / 75 ST	$(Hexyl)_3N+$	10	5468	11634
68	VP-02-258	100 VBC	Et_3N/Hex_3N Bifun.	5	37322	15814
69	VP-02-261	100 VBC	Bu_3N/Hex_3N Bifun.	5	39184	22264

VITA

Vijay T. Patel was born in Gujarat, India on June 23, 1968. After graduating from High School in 1986, he joined Sardar Patel University, where he graduated with a Bachelor of Science degree in Industrial Chemistry in July 1989. He later enrolled in the same university as a graduate student and received a Master of Science degree in Industrial Polymer Chemistry in July 1991. In July 1993, he came to the Chemistry Department at the University of Tenneessee and began study toward the Master of Science degree in Polymer Chemistry under the guidance of Prof. Spiro D. Alexandratos. The degree was awarded in December 1996.