/THE SYNTHESIS OF NITRATE SELECTIVE RESINS/

by

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A MASTER'S THESIS

submitted in partial fulfillment of the
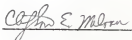requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

Kansas State University
Manhattan, Kansas
1985

Approved by:

Clifton E. Meloan

Major Professor

To my parents

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INTRODUCTION

Nitrates are present in virtually everything we eat and drink. Fortunately they are essentially non-toxic under most conditions. The toxicity of nitrates results from their conversion to nitrites under certain circumstances in the body and in food.

The first report of the harmful effects in humans of nitrates in drinking water was in 1945.[1] Nitrates are associated with a temporary, but sometimes fatal, blood disorder in infants under six months of age. This disorder is called methemoglobinemia.[1] It comes from the conversion of nitrates in the infant stomach where the pH is high enough (5-7 pH) to permit nitrate-reducing bacteria to grow in the upper portion of the gatrointestinal tract. The nitrites interact with hemoglobin to produce methemoglobin. Hemoglobin normally conveys oxygen to the tissues in the form of oxymyoglobin. However, in the presence of nitrite the iron atoms of hemoglobin are oxidized to the ferric state thereby converting hemoglobin to methemoglobin. In this oxidized state, the methemoglobin is not capable of reversibly combining with oxygen. When carried to the extreme, the end result of methemoglobinemia is acute oxygen deprivation and death.[2,3,4,5,6,7]

Methemoglobinemia is not only present in humans, it was also found in animals, especially in the ruminants. In 1895

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Mayo reported nitrate poisoning involved cattle that had eaten corn starks[8] and another case, involving oat hay was investigated by Bradley in 1939.[9] Since then, more experiments were done and indicated that the nitrate ion can be reduced to ammonia by microorganisms in the rumen. Nitrite is an intermediate in these reduction processes and participates in the methemoglobin formation in blood.[10,11,12]

Nitrites, in addition to their interaction with the red pigment in blood to form methemoglobin, can also react with secondary amines to form nitrosamines.[13,14,6,7,15] Recently, the widespread human exposure to nitrosamines has become an important public health issue. This concern has emerged because a wide range of nitrosamines have mutagenic and carcinogenic properties. [16,17,5] Numerous studies have shown specific nitrosamines are capable of inducing tumors in different organs of test animals.[18,19] Furthermore, some investigations have shown that nitrosamines readily form in vitro by reaction of various secondary amines and nitrite in human gastric juice. Currently, there is neither direct nor indirect evidence that nitrosamines are carcinogenic for humans. However, a large number of different animal species are susceptible to these compounds, and there is no reason to believe that humans are immune.[15]

There are several sources that contribute to nitrate contamination in water: natural formations in the soil, leaching of nitrates used in fertilization,[20,21] discharge of industrial and municipal wastes, septic tanks[22] and animal

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feedlots.[23]

The acceptable limit of nitrate appears to vary with the characteristics of the individual. The Public Health Service "Drinking Water Standards of 1962" set a limit of 45 mg/L of nitrate to be safe for domestic use. Then, the Federal Water Pollution Control Administration Recommended Water Quality Standards took matters a step further by suggesting permissible values at the point of use for processed water, in food processing plants, as 10 mg/L of nitrate.

There are several organic bases which selectively precipitate nitrate.[36] Among them are nitron, cinchonamine, 1,1'-dinaphthyldimethylamine, N-diphenylmethyl-diethylamine, and 1-phenyl-2-diethylaminoethyl-p-nitrobenzoate (Figure 1).

In 1973, Meloan and Gran reported the preparation of a resin in bead form to selectively remove nitrate ion from water. The initial attempt was to take reagents that are specific for nitrate and attach them to a resin bead. When a reagent is appended on a polymer backbone, the solubility of the reagent is decreased and regeneration is often possible. Two of the organic bases, 1-phenyl-2-diethylaminoethyl-4-nitrobenzoate and 1-phenyl-2-diethylamine-1-ethanol, were chosen for their investigations. The resin synthesis consisted of attaching the base to a commmercial cation exchange Bio-Rex 70 resin and Bio-Gel P-4.[46] The nitrate selectivity of these resins was apparent but the capacity was very low (approx. 0.1%). Later in 1977, nitron was chosen as an organic reagent by Chiou.[45] Nitron is known to precipitate ClO_3^-, NO_2^-, SCN^-, ReO_4^-, I^-, BO_3^-, Br^- and NO_3^-.

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Figure 1

1   Nitron

2   Cinchonamine

3   1,1-Diphenylmethyl-diethylamine

4   N-diphenylmethyl-diethylamine

5   1-Phenyl-2-diethylaminoethyl-4-nitrobenzoate

(1)

(2)

(3)

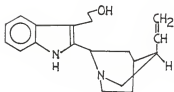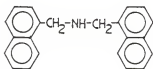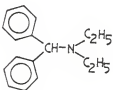(4)

(5)
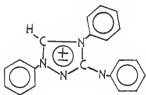
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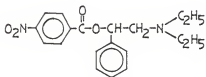
Of these, only NO_3^- and NO_2^- are normally present in water in appreciable concentrations. The others are present at concentration so low that no interference with the nitrate precipitate should be encountered (The structure of nitron-nitrate interaction was established by x-ray crystallography[37]). The data indicated the cations nitron are oriented with their mean planes approximately parallel to a face of the crystal and stacked along one direction which is perpendicular to the face. Due to the low capacities of resins made from previous methods, polymer-supported reagents had come to be recognized as an important part of this study, so Chiou modified the chain linking the nitron base to the polymer by introducing a 3-carbon leash (ethylene glycol) on the end of the base. The produced polymer was found to have better capacity than the previous polymer resin (1.04%), but it still was too low to be of commercial use. The polymer had the nitron group widely separated along the polymer backbone in order to reduce steric hindrance. It was believed that by moving the active groups closer together and placing them at the end of a long chain so that "micro crystals" could form that a crystal lattice energy could be added to force the system to have a higher capacity and improved selectivity. This was done successfully by Meloan and Chiou in 1981.[38]

Commercial polyvinylbenzyl chloride (60/40 ortho/para isomers) were employed as a polymer backbone in their synthesis. The procedures involved attaching the organic bases to the commercially available polymer. One of the resulting polymers which was a nitron derivative has individual

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capacities of 47% for NO_3^- and 42% for NO_2^-. The other one, 1-phenyl-2-diethylaminoethyl-4-nitrobenzoate polymer $\underline{6}$ (see structure shown below), yielded even better results, 76% for NO_3^- and 65% for NO_2^- but reacted much slower. Because of its high capacity and selectivity, our interest will be focused on the latter.

(6)
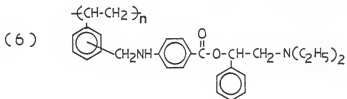
1-Phenyl-2-diethylaminoethyl-4-nitrobenzoate is also known to have a strong preference for oxidizing anions such as nitrate and nitrite. In the $\underline{6}$-nitrate precipitation, the tertiary amine group was considered to be the most important moiety. In order to understand what role the 1-phenyl ring plays in the interaction, futhermodifications of $\underline{6}$ were done: (A) A system with no 1-phenyl ring; 2-diethyl-aminoethyl-4-nitrobenzoate hydrochloride $\underline{7}$. (B) A system that possessed a good electron-withdrawing group on the para position of the 1-phenyl ring which makes the ring more positive; 1-(4'-nitrophenyl)-2-diethylaminoethyl-4-nitrobenzoate hydrochloride $\underline{8}$, and (C) A system that possessed a good electron-donating group on the para position of the 1-phenyl ring which makes the ring more negative; 1-(4'-aminophenyl)-2-diethylaminoethyl-4-

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aminobenzoate hydrochloride 9. The structures are shown below:

(7) O_2N—⟨benzene⟩—$\overset{\overset{O}{\parallel}}{C}$-O-$CH_2$·$CH_2$-N$(C_2H_5)_2$·$HCl$

(8) O_2N—⟨benzene⟩—$\overset{\overset{O}{\parallel}}{C}$-O-CH-$CH_2$-N$(C_2H_5)_2$·$HCl$
    |
    ⟨benzene⟩
    |
    NO_2

(9) O_2N—⟨benzene⟩—$\overset{\overset{O}{\parallel}}{C}$-O-CH-$CH_2$-N$(C_2H_5)_2$·$HCl$
    |
    ⟨benzene⟩
    |
    NH_2

(10)

$\left(\!CH\!-\!CH_2\!\right)_n$
⟨benzene⟩—CH_2-O-⟨benzene⟩—$\overset{\overset{O}{\parallel}}{C}$-O-CH-$CH_2$-N$(C_2H_5)_2$·$HCl$
    |
    ⟨benzene⟩
    |
    NO_2

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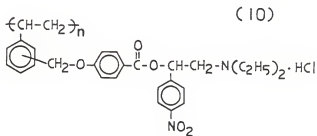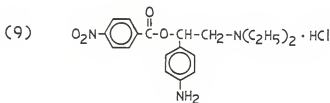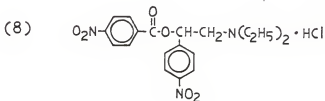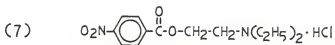
$\underline{7}, \underline{8}$ and $\underline{9}$ were tested for nitrate precipitation. A precipitate was found only in $\underline{9}$ and the rate of the reaction was increased by nearly an order of magnitude. Then, $\underline{9}$ was prepared in a polymer form $\underline{10}$ and the capacities for nitrate and nitrite increased slightly.

A summary of the above experiments indicates that (1) a phenyl group must be present in the 1 position, (2) an electron withdrawing group on the phenyl group (making the ring more positive) increases reactivity, and that (3) an electron donating group (making the ring more negative) decreases activity. In addition, work by Meloan and Meloan[14] with both Nitron and compound 6 showed that precipitates would form with those anions that were either large or considered to be oxidizing anions. In both cases it is the ease of charge separation within the anion that appears to be important. Actually, nitrate is not the most reactive anion, perchlorate and dichromate for example, being more reactive.

In an effort to explain these effects a series of models were prepared. It was observed that the N on the triethyl group was directly across from the ring C closest to the 1 position and not in the middle of the ring as might be expected.
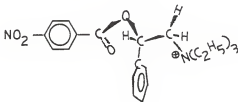
It was further observed that in polymers, the N on the triethyl group of one monomer group was directly across from the middle of the ring of an adjacent monomer group if the first monomer group was moved off center a few degrees.
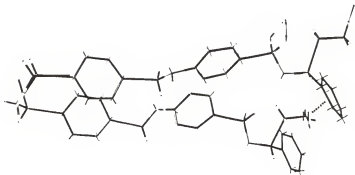
It is now easier to understand the effects of charge distribution within the ring as it relates to forming a complex with nitrate and other anions. The reaction is not due solely to a charge attraction between the protonated N of the triethyl amine and the negatively charged ion but is enhanced by the additional positive charge distribution on the ring that can either attract the negative ion or induce a small charge separation within the anion.

The models also indicated that because of free rotation about the C-N single bonds of the triethyl amine N that much steric hindrance could occur.

With all of the above observations in mind it was decided to synthesize monomers by replacing the 1-phenyl group with a pyridine ring, thus making a more positive reaction site, and to replace two ethyl groups on the triethylamine N with a piperidine ring to reduce steric effects. Three compounds were thus prepared to try to alter the selectivity, to increase the stability of the nitrate-monomer complex, thus reducing the amount of nitrate left in the water, and to reduce the possible steric effects caused by the triethyl amine. These compounds are shown below:

The associated K_a's are:[25]

Pyridine	5.62×10^{-6}
Piperidine	7.53×10^{-11}
Triethylamine	9.77×10^{-12}

This indicates that the triethylamine N is normally protonated and carries a positive charge. By changing to a piperidine ring the N retains nearly the same amount of protonation but the ethyl groups are less free to cause steric effects. Pyridine would most likely be protonated in any waters normally tested since most are acidic.

The research described discusses the preparation of these monomers, their comparative reactivity, and the polymers that can be made from them.
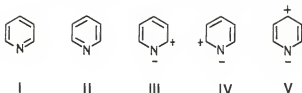
$$\text{I} \qquad \text{II} \qquad \text{III} \qquad \text{IV} \qquad \text{V}$$

There are several resonance forms of pyridine. The I and II forms can be considered as the major contributing states and III, IV and V as activated states whose contributions are significant in the reactions of pyridine by virtue of the electron attraction of the nitrogen atom.[33,34] Therefore, if the phenyl ring is replaced by pyridine, it would be expected that the positive charge distribution would to be greater, causing more interaction with nitrate.
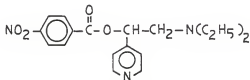
Let us consider the amine groups. From a charge distribution point of view, an alkyl group is an electron-donating group and should make the non-bonding electrons on the N more negative or hold an hydrogen ion more strongly. However, due to free rotation about a single bond (C-N), models show that the diethyl groups can sterically block an interaction with the N. The aliphatic cyclic group should help the quarternary amine to possess more positive charge when

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compared to the dialkyl group. The structures of the amine-substituted compounds, with or without phenyl substitution, are shown below:

$$O_2N-\langle\bigcirc\rangle-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH-CH_2-N\bigcirc$$

$$O_2N-\langle\bigcirc\rangle-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH-CH_2-N\bigcirc$$
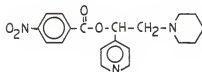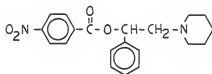
The above three monomer compounds were tested for nitrate precipitation. Then, a polymer of each was prepared and tested for their capacities for nitrate. In addition, their reactions with 47 anions were determined and solubilities obtained on those that formed precipitates. All of these results will be reported and discussed in the next section.

EXPERIMENTAL

(A) SYNTHESIS

CHEMICALS

Methylene chloride- Fisher Scientific Company
                    Fair Lawn, NJ 07410

Phosphorous pentoxide- MCB Manufacturing Chemists, Inc.
                       2909 Highland Ave., Cincinnati, Ohio

Benzene- MCB Manufacturing Chemists, Inc.

Anhydrous calcium chloride- J T Baker Chemical Co.,
                            Phillipsburg, NJ 08865

N,N-Dimethylformamide- Aldrich Chemical Company
                       Miwaukee, WIS 53233

Barium oxide- Fisher Scientific Company

4-Vinyl pyridine- Aldrich Chemical Company

Styrene Oxide (or 1,2-Epoxyethylbenzene)
              - Eastman Kodak Company, Rochester, NY 14650

4-Nitrobenzoylchloride- Aldrich Chemical Company

Sodium hydride- Alfa Products, 152 Andover St.,
                Danvers, MA 01923

Piperidine- Aldrich Chemical Company

Diethylamine- Fisher Scientific Company

Hexanes- Fisher Scientific Company

Chloroform- Fisher Scientific Company

Ethyl ether- MCB Manufacturing Chemists, Inc.

Acetone- Fisher Scientific Company

Chloroform-d- Aldrich Chemical Company

Polyvinylbenzyl chloride- Aldrich Chemical Company

5% Palladium on activated carbon- Aldrich Chemical Company

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Methylene chloride was washed with 5% sodium hydrogencarbonate followed by water, dried over anhydrous calcium chloride, then distilled and collected at 40.0-40.1°C.[31] Benzene was treated with anhydrous calcium chloride before being redistilled over sodium wires.[31]

N,N-Dimethylformamide was distilled from barium oxide.[31]

4-Vinyl pyridine, styrene oxide, and 4-nitrobenzoylchloride were freshly distilled before use. Sodium hydride (50% in oil) was washed with petroleum ether several times to remove the oil.[31]

The following chemicals were all reagent grade and used without further purification or preparation: piperidine, diethylamine, absolute ethanol, hexanes (contains a mixtures of isomers), chloroform, diethyl ether, chloroform-d and isopropyl alcohol.

APPARATUS

All melting points were obtained without correction using a Fisher-Johns melting point apparatus.

C.H.N. analyses were done at Galbraith Laboratories, Knoxville Tennessee.

The following instruments were used in their normal modes of operation:

Bruker WM-400 NMR Spectrometer

Varian T-60 NMR Spectrometer

Perkin-Elmer Model-1330 IR Spectrophotometer

Finnigan Model-4021 Mass Spectrometer

SYNTHETIC PROCEDURES

1-Phenyl-2-piperidine ethanol   A-1

The following procedure was a modification of that of Shapiro.[41]

To a 30 mL (31.62 g, 0.26 mole) of distilled styrene oxide in a 200 mL single-neck (24/40) R.B. flask fitted with a Friedrichs condenser and stirrer, a 39 mL (33.59 g, 0.39 mole) of piperidine were added.

After 4-6 hours of reflux, a brown oily mixture had formed and a light-brown solid precipitated when the mixture was cooled. The solid was collected by water aspirator filtration, and removed from the starting materials by washing with a small quantity of hexanes.

Pure white crystals were obtained after the recrystallization from hexanes.   mp 68-70°C.   Yield 89%. NMR (Fig. 8),   IR (Fig. 16)

1-Phenyl-2-piperidino ethyl-4-nitrobenzoate   A-2b [40]

The alcohol compound A-1 (22.0 g, 107 mmole) and the freshly distilled 4-nitrobenzoyl chloride (28.0 g, 148 mmole) were dissolved into two separate 200 mL portions of benzene. Both were added to a single neck (24/40), 500 mL flask fitted with a Friedrichs condenser and magnetic stirring was applied. Heat was given off and a milky yellow precipitate started to form. After 3-4 hours of stirring at 55°C, the precipitate was

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collected upon a water aspirator filter and washed with diethyl ether.

Next, the amine $\underline{A-2b}$ HCl salt obtained from above was dissolved in chloroform (or methylene chloride), an excess amount (1:5 by equivalents) of sodium hydrogencarbonate was added to the HCl salt and the mixture was stirred for 8-12 hours.

The resulting solid materials were filtered, the filtrate was then concentrated in a rotary evaporator and approximately 10-15 mL of hexanes was added. Yellow crystals precipitated after shaking one minute. mp 75-77°C. Yield 70%. NMR (Fig. 9). IR (Fig. 17)

1-Phenyl-2-piperidinoethyl-4-aminobenzoate $\underline{A-3}$

A solution of 15 g of the nitro ester $\underline{A-2b}$ in 200 mL of absolute ethanol was hydrogenated at room temperature using 50 psi (344 KPa) H_2 over 1.0 g of 5% palladium on activated carbon. After the H_2 uptake was complete (24 hours), the catalyst was removed by water aspirator filtration and the solvent was evaporated in a rotary evaporator. mp 107-111°C. Yield 90%. NMR (Fig. 10). IR (Fig. 18)

Reaction of 1-phenyl-2-piperidinoethyl-4-aminobenzoate with polyvinylbenzylchloride (60/40 mixture of 1,3- and 1,4-isomers) $\underline{A-4}$

To a stirred solution of 10 g (30.9 mmole) of 1-phenyl-2-piperidinoethyl-4-aminobenzoate and 3.14 g (20.6 mmole) of polyvinylbenzylchloride in 150 mL of dry N,N-dimethylformamide,

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a 0.84 g (3.5 mmole) of sodium hydride was added under nitrogen at 0-5°C. After three hours of stirring, the mixture was poured into 800 mL of water and water aspirator filtered. The gummy solid was washed with an extra amount of water, then dried at 80°C under a vacuum of 10 mm Hg (1,333 Pa).

$C_{29}H_{32}N_2O_2$ Anal. Calculated: (100% reaction)

                                    76.69 C% 8.31 H% 3.82 N%
                         Found: (50% reaction)
                                    79.09 C% 7.27 H% 6.36 N%

4-Epoxyethylenepyridine 1-oxide B-Q [32]

To a suspension of 3-chloroperbenzoic acid (35.53 g, 175 mmole) in 250 mL of dry methylene chloride at 0°C, 4-vinylpyridine (5.55 mL, 50.0 mmole) was added solwly with stirring. The reaction mixture was allowed to warm to room temperature (0.5 hour), then refluxed for 40 hours (the acid initially went into solution when heated, but solwly formed a precipitate after 3 hours).

Once the reaction was completed, the mixture was placed in a freezer for 1.5-2.0 hours, then filtered and washed with a further 50 mL portion of cold methylene chloride. The solvent was removed by a rotary evaporator (40°C bath). The resulting yellow oil was extracted first with 150 mL of diethyl ether and then with 150 mL of water. The ether layer was washed with a further 100 mL portion of water, and both water phases were individually extracted with an additional 100 mL of diethyl ether.

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The combined water phases were then concentrated in rotary evaporator under vacuum (1-3 mm Hg / 40°C) to approximately 10 mL. The resulting yellow oil was diluted with 200 mL of methylene chloride, treated with anhydrous magnesium sulfate, filtered, and the solvent removed in vacuo. A light orange solid was obtained which was recrystallized from THF. (the epoxide product was used immediately for the next step due to its instability) mp $114-117^{\circ}$C. Yield 60%. NMR (Fig. 12). IR (Fig. 19)

1-(1-Oxido-2-pyridyl)-2-piperidino ethanol B-1 [32]

To 5.0 g (36.5 mmole) of epoxide B-0 in 400 mL of ice-cooled absolute ethanol was added 18.0 mL (182.5 mmole) of piperidine. The reaction, after gradual warming to room temperature, was allowed to proceed for 12 hours.

The solvent was removed in vacuo, the residue was extracted with 500 mL of chloroform. The solvent was removed under vacuum. The resulting yellowish-brown solid was recrystallized from benzene. mp $109-111^{\circ}$C. Yield 65%. NMR (Fig. 13). IR (Fig. 20)

1-(1-Oxido-4-pyridyl)-2-diethylamino ethanol C-1

To an ice-cooled solution of the epoxide B-0 (5.0 g, 36.5 mmole) in 300 mL of absolute ethanol was added diethylamine (15.2 mL, 146.0 mmole) and the reaction was completed using the same procedure as that for B-1. The semisolid product was used for the next reaction without recrystallization.

Yield 60%. NMR (Fig. 15)

* Compound C-1 was relatively light sensitive and decomposed slowly even when stored under nitrogen at 0°C in a container wrapped with aluminum foil.

1-(1-Oxido-4-pyridyl)-2-piperidinoethyl-4-nitrobenzoate B-2b

To 7.0 g (31.53 mmole) of the amino alcohol B-1 in 300 mL of dry benzene under nitrogen, the freshly distilled 4-nitrobenzoyl chloride (9.0 g, 47.3 mmole) in 100 mL of dry benzene was added solwly. The mixture turned brownish-orange (excessive heat will be given off if 4-nitrobenzoyl chloride is added in a large amount at a time).

After half an hour, the solution was heated and stirred for 3 hours while the temperature was kept at 50-55°C. The ester hydrochloride B-2b was collected upon a filter and washed with diethyl ether. The solvent was removed under vacuum, the product obtained was brownish-yellow. Yield 70%

To 5.0 g of the HCl salt B-2b in 300 mL of absolute ethanol, an excess amount of sodium hydrogencarbonate (1:5 by equivalents) was added. After several hours of stirring, the excess sodium hydrogencarbonate and sodium chloride were removed by filtration and the solvent was removed under vacuum. This resulted in brownish-red oily product. Yield 72%.

NMR (Fig. 14).   IR (Fig. 21)

1-(1-Oxido-4-pyridyl)-2-diethylaminoethyl-4-nitrobenzoate HCl C-2

Amino alcohol C-1 (3.0 g, 14.3 mmole), freshly distilled

4-nitrobenzyl chloride (3.98 g, 21.4 mmole) and dry benzene (250 mL) were used in this reaction. The procedure followed that of B-2b. A dark-brown solid was obtained. The compound decomposed at approximately 70°C.   Yield 50%

1-(1-Oxido-4-pyridyl)-2-piperidinoethyl-4-aminobenzoate
B-0 (32,43,44)

A solution of 6.0 g of the nitroester B-2b in 200 mL of absolute ethanol was hydrogenated under 50 psi (344 KPa) at room temperature in the presence of 0.8 g of 10% palladium on activated carbon. Hydrogen uptake was complete in 24 hours (the pressure drop kept almost constant after 10 hours). After removal of the catalyst and solvent, a yellowish-brown solid was obtained. mp 123-130°C.   Yield 93%.   IR (Fig. 22)

Reaction of 1-(1-oxido-4-pyridyl)-2-piperidinoethyl-4-aminobenzoate with polyvinylbenzyl chloride B-4

Compound B-3, polyvinylbenzyl chloride and sodium hydride were used in this reaction in the ratio 1.5: 1.0: 1.5. The reaction was completed as described under the procedure for A-4. The resulting product was light brown.

$C_{29}H_{31}N_3O_2$ Anal. calculated: (100% reaction)

72.77 C%	7.20 H%	3.93 N%

Found: (30% reaction)

76.19 C%	7.03 H%	9.52 N%

(B) ANALYTICAL TESTS

CHEMICALS AND REAGENTS

Chromosorb-W (acid washed)- Alltech Associates
                            2051 Waukegan Rd., Deerfield, ILL 60015

The reagents used were sodium nitrite, potassium nitrate, dry N,N-dimethylformamide, Chromosorb-W (acid washed)

The reagents for the solubility test were prepared by dissolving the synthesized HCl salts (A-2b), (B-2b) and (C-2) in deionized water. All of the 0.1 M anion solutions were prepared from reagent grade chemicals which were used without further treatment and these chemicals are: strontium titanate, sodium vanadate, potassium chromate, potassium dichromate, sodium molybdate, sodium tungstate, potassium permagnate, sodium borate, sodium (tetra)fluroborate, sodium aluminate, potassium carbonate, sodium bicarbonate, sodium silicate, potassium nitrate, sodium nitrite, potassium phosphate monobasic, potassium phosphate dibasic, potassium phosphate, sodium arsenate, sodium antimonate, sodium arsenite, sodium bismuthate, sodium sulfate, sodium bisulfate, sodium sulfite, sodium bisulfite, potassium sulfide, sodium thiosulfate, sodium hydrosulfite, potassium persulfate, sodium selenate, sodium selenite, potassium cyanide, potassium thiocyanate, potassium ferrocyanide, sodium nitroferricyanide, potassium fluoride, potassium chloride, potassium bromide, potassium iodide,, potassium chlorate, sodium bromate, potassium iodate, potassium perchlorate, potassium periodate, sodium hydroxide.

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APPARATUS

A glass column (2.0 cm in diameter and 60 cm in length) with a medium porous glass fritted disc sealed at the bottom was used to test the synthesized polymers.

A nitrate selective electrode (Orion, model 92-07) with a LAZAR model DPH digital pH/mv meter was used to detect the nitrate concentration as described by Shalts.[42]

PROCEDURES

Anion solubility tests [39]

5 g of each HCl free ester compound was dissolved into 55 mL of deionized water, (the calculated concentration per test tube of the A-, B- and C- solutions were 0.238, 0.231 and 0.225 mmole respectively). 1 mL of the sample solution was added into each of the 47 test tubes and acidified by adding 1-3 drops of concentrated HCl, then 5 mL (5 x 10^{-4} mmole) of each 0.1 N anion solution was added into the reagents and the reaction was immediately noted. The precipitate was allowed to digest at room temperature for two days. The precipitate was separated by a glass microfibre filter (water aspirator was applied), wshed, and transferred to beakers with 25 mL of distilled water. The beakers were shaken daily and kept at room temperature for two weeks to attain solubility equilibrium.

20 mL of sample solutions were transferred into aluminum weighing dishes and dried at $70^{\circ}C$. The weight of the residue was determined by using a Mettler balance (type H, to 0.0001 g sensitivity). A blank was determined on the distilled water used and the results corrected accordingly. The test results were discussed on page 41.

Determination of nitrate capacity of polymers A-5 and B-5

In general, 0.3 g of polymer was dissolved in 150 mL of N,N-Dimethylformamide and 14 g (1:45 w/w) of acid-washed Chromosorb-W (30-60 mesh) was added. The solvent was then evaporated on a rotary evaporator which resulted in a good coating of the polymer on the supporting material. The mixture was powdered and dried under vacuum (0.5 mm Hg, 67 Pa) at $100^{\circ}C$. The mixture was then packed into a column (2 cm in diameter and 60 cm in length) and rinsed with deionized water. A solution of 0.1 M potassium nitrate was passed through the column, the effluents were collected and the nitrate concentrations determined. [42] An Orion nitrate-selective electrode was standardized by successive dilutions of a stock 0.1 M KNO_3 solution and the electrode response was linear from 10^{-1} M to 10^{-4} M nitrate as shown in Figure 2.

The test fraction was placed in a 50 mL beaker and stirring of the solution was accomplished by using a magnetic stirrer. The capacity of each nitrate-selective polymer to remove nitrate was determined as defined in Equation 1.

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$$\% \text{ Capacity} = \frac{(M_1-M_2) \times L}{N} \qquad (1)$$

M_1 (mole/L): Initial concentration of anion.

M_2 (mole/L): Concentration of anion in collected effluent.

L (L)   : Volume of collected effluent.

N (mole) : Moles of nitrate-selective polymer being
            employed.

In this section, we will summarize the results of the syntheses and tests of the nitrate selective compounds. The problems encountered in this study will also be dealt with in this section.

1-Phenyl-2-piperidino-ethyl-4-nitrobenzoate
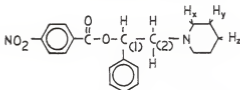
The sequence of reactions for the preparation of this compound is shown on scheme A and the assignments of the NMR and IR spectra are listed in the Tables 1-a and 1-b.

The synthesis of 1-hydroxy-1-phenyl-2-piperidine <u>A-1</u> was accomplished in a yield of 89%. The NMR gave the expected patterns and location of peaks, and the multiplet at   4.7 is attributed to the methine proton   split by non-equivalent methylene protons.

The ester salt was synthesized and treated with sodium hydrogencarbonate to remove HCl and gave the HCl free ester compound.   The completion of the reaction can be tested by litmus paper which was observed turning from red to a light blue color.   The protons of di-substituted benzene located at

8.23-8.31 which is at a lower field than that by mono-substituted benzene.   The IR spectrum showed strong carbonyl

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Scheme A

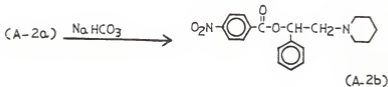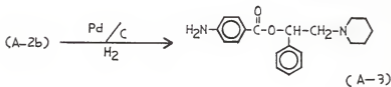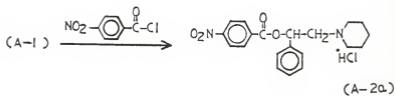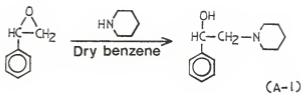The sequence of reactions for the preparation of

A- compounds

$(A-1)$

$(A-1) \xrightarrow{\text{NO}_2\text{—} \overset{O}{\underset{}{C}}\text{—Cl}}$

$(A-2a)$

$(A-2b) \xrightarrow[\text{H}_2]{\text{Pd}/\text{C}}$

$(A-3)$

$(A-2a) \xrightarrow{\text{Na HCO}_3}$

$(A-2b)$

Table 1-a

NMR assignments of A- compounds

A-1	$-C_{(1)}-H$,	1H	δ 4.70	dd	J=1.4, 0.4 Hz
	$-C_{(1)}-OH$,	1H	δ 4.25		
	$-C_{(2)}H_2$,	2H	δ 2.65		
	$-N(C_5H_{10})$,	$4H_x$	δ 2.34-2.47		
		$4H_y$	δ 1.55-1.63		
		$2H_z$	δ 1.45		
A-2	$-C_6H_4-$,	4H	δ 8.23-8.31		
	$-C_6H_5-$,	5H	δ 7.26-7.44		
	$-C_{(1)}H-$,	1H	δ 6.22	dd	J=0.9, 0.4 Hz
	$-C_{(2)}H2-$,	1H	δ 2.98	dd	J=1.3, 0.9 Hz
		1H	δ 2.70	dd	J=1.4, 0.4 Hz
	$-N(C_5H_{10})-$,	$4H_x$	δ 2.43-2.61		
		$4H_y$	δ 1.45-1.54		
		$2H_z$	δ 1.35-1.41		
A-3	$-C_6H_4-$,	2H	δ 7.92		
		2H	δ 6.36		
	$-(C_6H_5)-$,	5H	δ 7.14-7.41		
	$-NH_2$,	2H	δ 6.00		
	$-C_{(1)}H-$	1H	δ 5.02		
	$-C_{(2)}H_2$,	2H	δ 2.90-2.98		
	$-N(C_5H_{10})$,	$4H_x$	δ 2.65-2.86		
		$4H_y$	δ 1.75-1.81		
		$2H_z$	δ 1.52		

Table 1-b

IR assignments of A- compounds

A-1	$\underline{-OH}$		
	3120 cm^{-1}		
A-2b	$\underline{-C(=O)-}$	$\underline{-C(=O)O-}$	$\underline{-NO_2}$
	1718 cm^{-1}	$\int$asy. 1260 cm^{-1}	$\int$ sy. 1345cm^{-1}
		$\int$ sy. 1100cm^{-1}	$\int$asy. 1515cm^{-1}
A-3	$\underline{-C(=O)-}$	$\underline{-C(=O)O-}$	$\underline{-NH_2}$
	1690 cm^{-1}	$\int$asy. 1220 cm^{-1}	3200 cm^{-1}, 3300 cm^{-1}
		$\int$ sy. 1080 cm^{-1}	bending 1620 cm^{-1}

peak at 1718 cm^{-1} and the aromatic ester bands at 1260 and 1100 cm^{-1}. The two strong bands at 1515 and 1345 cm^{-1} were attributed to the stretching of the aromatic nitro group. Both IR and NMR spectra show the absence of the hydroxide group.

During the hydrogenation of 1-phenyl-2-piperidino-ethyl-4-nitrobenzoate, the drop of the hydrogen pressure was close to the calculated value. The nitro bands in the IR spectrum disappeared while the NH$_2$ bands at 3200, 3300 and 1620 cm^{-1} were observed. The yield of this reduction was approximately 90%. (regard to NMR fig. 10, the triplet at $\oint$ 1.2 is the solvent ethanol peak, the peaks at $\oint$ 1.35 and $\oint$ 4.3 are possibly resulted from , ethyl 4-aminobenzoate, the product of side reaction)

1-pyridyl-2-piperidino-ethyl-4-aminobenzoate
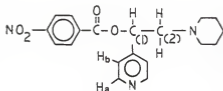
Scheme B shows the steps of the preparation. The IR and NMR major assignments are listed in Tables 2-a and 2-b.

The epoxide was obtained in a yield of 60% and the NMR spectrum gave the expected patterns and location of peaks. The NMR spectrum of the ethylene protons are located at a higher field $\oint$ 2.77-3.87 compared to the spectrum of 4-vinylpyridine (Fig. 11). This shift is attributed to the proton shielding by

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Scheme B

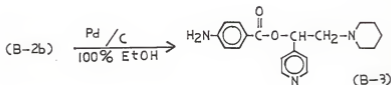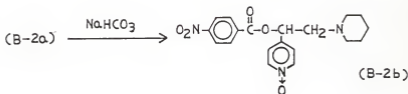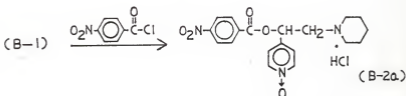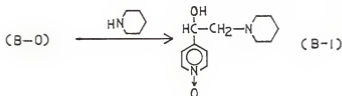The sequence of reactions for the preparation of

B- compounds
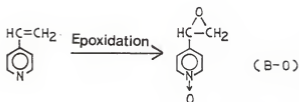
Table 2-a

NMR assignments of B- compounds

B-0	Ha,	2H	⌠ 8.19
	Hb,	2H	⌠ 7.23
	$-C_{(1)}H-$,	1H	⌠ 3.87
	$-C_{(2)}H_2-$,	1H	⌠ 3.22
		1H	⌠ 2.77

B-1	Ha,	2H	⌠ 8.17		
	Hb,	2H	⌠ 7.32		
	$-C_{(1)}H$,	1H	⌠ 4.70	dd	J=1.0, 0.4 Hz
	$-OH$		⌠ 5.05		
	$-C_{(2)}H_2-$,	2H	⌠ 2.64		
	$-N(C_5H_{10})$,	4H	⌠ 2.30-2.40		
		4H	⌠ 1.57-1.64		
		2H	⌠ 1.48		

B-2b	$-(C_6H_4)-$,	4H	⌠ 8.15-8.33		
	Ha,	2H	⌠ 8.15-8.33		
	Hb	2H	⌠ 7.39	dd	J=0.7 Hz
	$-C_{(1)}H-$,	1H	⌠ 5.02		
	$-C_{(2)}H_2-$,	2H	⌠ 2.50-3.17		
	$-N(C_5H_{10})$,	4H	⌠ 2.50-3.17		
		6H	⌠ 1.39-1.85		

Table 2-b

IR assignments of B- compounds

B-0	$-C(O)C-$	$N \quad O$		
	1240 cm^{-1}	1220 cm^{-1}		
	1600 cm^{-1}	1480 cm^{-1}		

B-1	$-OH$	$-C-N(C_5H_{10})$		
	3100 cm^{-1}	1100 cm^{-1}		
		1080 cm^{-1}		

B-2b	$-C(=O)-$	$-C(=O)O-$	$-NO_2$	
	1720 cm^{-1}	1255 cm^{-1}	$\mathcal{S}$ sy.	1340 cm^{-1}
	1100 cm^{-1}		$\mathcal{S}$ asy.	1520 cm^{-1}

B-3	$-NH_2$			
	3250 cm^{-1}, 1615 cm^{-1}			

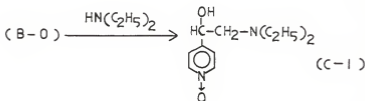the epoxide oxygen. The bands in the IR spectrum at 1240 and 1600 cm^{-1} also indicated the presence of the epoxide group.

The epoxide was reacted immediately in the next reaction. The IR and NMR spectra of the hydroxide group were located at 3100 cm^{-1}, and at δ 5.05 individually. The two epoxide bands in the IR spectrum disappeared.
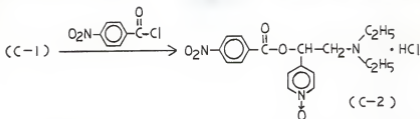
The synthesized ester compound <u>B-2b</u> is a yellow crystaline substance. Two bands of carbonyl were at 1720 and 1100 cm^{-1} and the ester at 1255 cm^{-1}. The hydroxide bands disappeared and two nitro bands were located at 1340 and 1520 cm^{-1}. (the NMR spectrum shows the impurities contained in the ester product)

The reduced amine group of the hydrogenation product can be identified by the presence of the bands at 3250 and 1615 cm^{-1} in the IR spectrum and the absence of nitro bands at 1340 and 1520 cm^{-1}.

1-Pyridyl-2-diethylamino ethyl-4-nitrobenzoate

The steps of preparation are shown in the following scheme.

$$(B-0) \xrightarrow{HN(C_2H_5)_2} \overset{OH}{HC}-CH_2-N(C_2H_5)_2 \qquad (C-1)$$

$$(C-1) \xrightarrow{\hspace{2cm}} O_2N-\underset{}{\bigcirc}-\overset{O}{\overset{\|}{C}}-O-CH-CH_2-N\overset{C_2H_5}{\underset{C_2H_5}{\diagup}} \cdot HCl$$

(C-2)

. The resulting IR spectra of products <u>C-1</u> and <u>C-2</u> were very close to those of <u>B-1</u> and <u>B-2</u>. In NMR spectrum of <u>C-1</u>, the methyl protons in diethylamine located at $\oint$ 1.0, the rest protons in diethylamine and two protons from ethanol were at $\oint$ 2.30-2.75.

Solubilities of the less soluble anion salts of compounds A-1, B-3 and C-3

The purpose of this work was to test the <u>A-3</u>, <u>B-3</u> and <u>C-3</u> monomers with several anions to determine reactivity for those compounds found to react and to measure the anion-compound solubilities in water. A total of 47 anions were tested and the results were listed in Table 3.

Among the three compounds, <u>A-3</u> has the most precipitates formed. <u>C-3</u> showed the least reactivity. When we look further at these data, an interesting observation was that most of those anions that reacted with <u>B-3</u> and <u>C-3</u> are doubly-charged. This might indicate that the positive character between the quaternary amine moiety and the pyridine group in the <u>B-3</u> and <u>C-3</u> compounds is much stronger than that in <u>A-3</u>. Although the singly-charged anions interact with <u>B-3</u> and <u>C-3</u> compounds, the positive character can not be completely neutralized. In addition, the steric hindrance likely prohibits two singly-

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Table 3

Solubilities of A-3, B-3 and C-3 compounds
with 47 anions in water

Table 3   (--- means no precipitate formed)

Anions	Solubility (g/L)		
	A-3	B-3	C-3
Vanadate	0.61	0.29	0.36
Chromate	0.90	0.57	0.03
Dichromate	0.90	0.47	0.71
Molybdate	0.12	0.25	0.28
Tungstate	0.29	0.55	0.96
Permagnate	0.94	0.27	0.09
Tetrafluroborate	1.07	---	---
Silicate	0.35	0.21	0.02
Nitrate	1.92	---	---
Nitrite	1.64	---	---
Bisulfite	0.67	---	---
Thiosulfate	1.15	0.01	---
Hydrosulfite	1.03	0.02	---
Persulfate	1.63	0.13	---
Cyanide	0.52	---	---
Thiocyanate	0.77	---	---
Ferrocyanide	0.76	---	0.01
Nitroferricyanide	0.70	0.03	0.02
Bromide	2.41	---	---
Iodide	1.82	---	---
Chlorate	2.01	---	---
Bromate	0.26	0.52	0.07
Iodate	---	0.11	---
Perchlorate	0.61	---	---

(continued)

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Table 3 (continued)

The anions which do not precipitate with any of the monomers are: titanate, borate, aluminate carbonate, bicarbonate, phosphate, phosphate monobasic, phosphate dibasic, phosphite, arsenate, anitmonate, arsenite, bismuthate, sulfate, bisulfate, sulfite, sulfide, selinate, selinite, fluroride, chloride, periodate, hydroxide.

* The MnO_4^- probably converted to MnO_2 as its color changed continuously and was obviously an impure material.

charged anions form associating with the compounds. Thus, only the doubly-charged anions can fully accommodate the charge.

In order to find out the results of the polymer form of these compoumds with the various anions, A-3 and B-3 were selected to be synthesized as polymers and subsequently were tested with nitrate, nitrite etc. The sequence of preparation was shown in the following scheme.

45
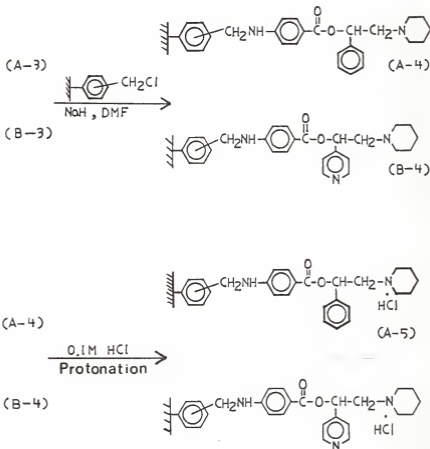
Both $\underline{A-3}$ and $\underline{B-3}$ were reacted with polyvinylbenzyl
chloride to obtain polymer form compounds. The CHN analysis of
$\underline{A-4}$ showed: 76.69 %C, 8.31 %H, 3.82 %N (theoretically
calculated value is: 79.09 %C, 7.27 %H, 6.36 %N), and $\underline{B-4}$
showed: 72.77 %C, 7.20 %H, 3.93 %N (theoretically calculated
value is: 76.19 %C, 7.03 %H, 9.52 %N). These data indicated
that the chloride group in polyvinylbenzyl chloride had not
reacted completely. About 50% of the polyvinylbenzyl chloride
reacted to form $\underline{A-4}$ and about 30% to form $\underline{B-4}$. The proposed
formulas for $\underline{A-4}$ and $\underline{B-4}$ are shown below:
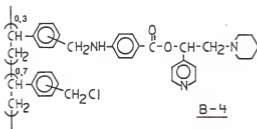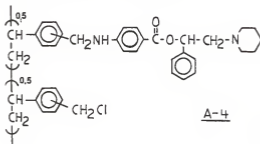
The $\underline{A-4}$ and $\underline{B-4}$ polymers were protonated by stirring each
with 0.1 N HCl. The nitrate and nitrite capacity of these
protonated polymers, $\underline{A-5}$ and $\underline{B-5}$, were then tested by the

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procedures described in the experimental section. The concentration of nitrate in the effluents were determined with the results dipicted in Figures 3 and 4.

As we can see from Figure 3 the concentration of nitrate in the first 5 mL of effluent was 9.37×10^{-3} M. Therefore, the moles of nitrate being absorbed by the synthesized polymer was calculated from Eq. 1 as follows:

$$(10^{-1} \text{ M} - 9.37 \times 10^{-3}) \frac{5 \text{ mL}}{1000 \text{ mL}}$$
$$\frac{}{\frac{2.875 \text{ g}}{440 \text{ g/mole}}}$$

$$= \frac{4.53 \times 10^{-4} \text{ mole}}{6.53 \times 10^{-3} \text{ mole}} = 0.0693$$

This corresponds to a capacity of 7.70%.

The concentration of nitrates in each fraction of the collected effluent was calculated using the same method and the overall capacity of the nitrate-selective polymer to remove nitrate from water was calculated. The results for <u>A-5</u> is 45% and <u>B-5</u> is 11%. (Both calculated capacities were based on 100% conversion in the reaction of <u>B-3</u>, <u>A-3</u> and polyvinylbenzyl chloride by the procedure described earlier, the corrected % for actual monomer on the polymer, <u>A-4</u> is 90 and <u>B-4</u> is 37)

Capacity of regenerated polymer

For economical reasons, the synthesized polymer must be capable of regeneration. Thus the polymers were tested to see if the resin can be successfully regenerated.

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Figure 2

Nitrate Standard Curve

(An Orion nitrate-selective electrode was
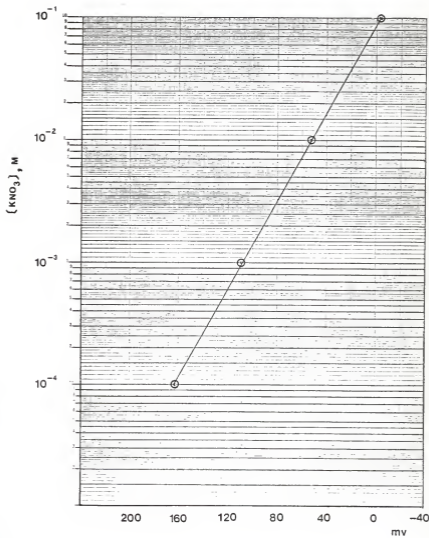standardized by successive dilutions of a
stock 0.1 M KNO_3 solution)

Figure 3

Nitrate capacity of the synthesized polymer _A-4_
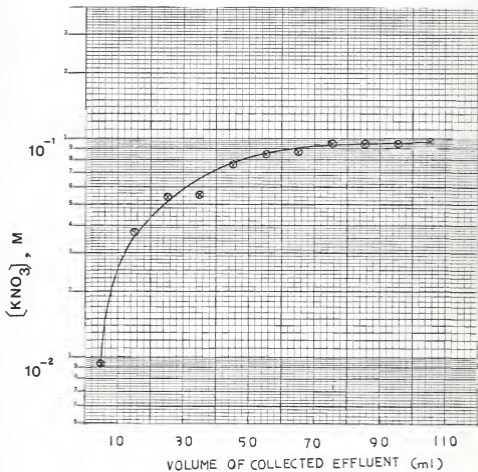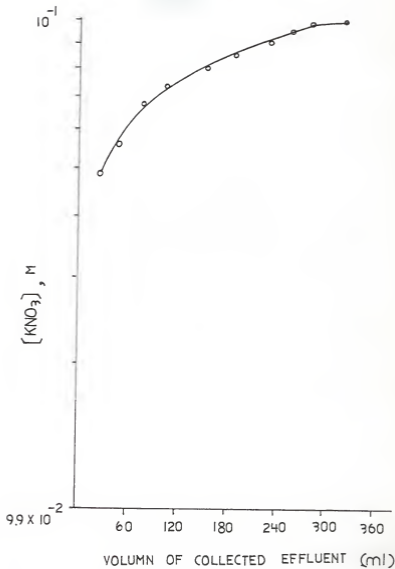(2.875 g of polymer A-4 was coated on 100 g of
acid-washed Chromosorb W)

Y-axis: $[KNO_3]$, M

X-axis: VOLUME OF COLLECTED EFFLUENT (ml)

Figure 4

Nitrate capacity of the synthesized polymer B-4
(3.098 g of polymer B-4 was coated on 120 g of
acid-washed Chromosorb W)

$[KNO_3]$, M

VOLUM OF COLLECTED EFFLUENT (ml)

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To determine the capacity of the regenerated polymer, the column was treated with 0.1 N NH_4Cl as described above. It was then washed with deionized water until the effluent contained no chloride ion as evidenced by the lack of a detectable precipitate upon adding an aqueous silver chloride solution. Potassium nitrate (0.1 M) was then passed through the column and collected effluents were analyzed as described earlier. The regeneration and testing procedure was then repeated for twenty times with the results shown below:

Times of regeneration	Capacities (%)	
	A-5	B-5
5	40	11
10	35	9
15	40	6

These analyses were complicated somewhat by the fact that the nitrate-selective electrode responds to certain other anions as well as nitrate ion. In a solution containing nitrate ion and an interfering ion, the electrode behavior is given by Equation 2.

$$E = E_v - 0.059 \log (A_{NO_3^-} + K_x A_x^{1/n}) \quad (2)$$

E   : Electrode potential.

E_v : Standard electrode potential.

$A_{NO_3^-}$: Activity of nitrate ion.

A_x : Activity of the interfering ion.

K_x : Selectivity constant for the interfering ion.

  n : The charge on the interfering ion.

For chloride ion, $K_x = 4 \times 10^{-3}$, n = 1. Therefore,

$$E = E_v - 0.059 \log ([NO_3^-] + 4 \times 10^{-3} [Cl^-])$$

A solution of 0.1 M of NH_4Cl should respond as:

$$E = E_v - 0.059 \log (4 \times 10^{-3} \times 10^{-1})$$
$$= E_v - 0.059 \log (4 \times 10^4)$$

E was set at 119 mv for 0.1 M NH_4Cl in this study. Therefore,

$$119 \text{ mv} = E_v - 0.059 \log (4 \times 10^{-4})$$
$$E_v = 119 \text{ mv} + 0.059 \log (4 \times 10^{-4})(1000 \text{ mv})$$
$$= 119 \text{ mv} - 200.5 \text{ mv}$$
$$= -81.5 \text{ mv}.$$

If the electrode potential, E, of 10 mL of collected effluent was 112 mv. The concentration of nitrate ion in the effluent can be calculated as follows:

$$E = E_v - 0.059 \log ([NO_3^-] + 4 \times 10^{-3} [Cl^-])$$
$$(E_v - E) / 0.059 = \log ([NO_3^-] + 4 \times 10^{-3} [Cl^-])$$
$$[NO_3^-] = 10^{(E_v - E)/0.059} - 4 \times 10^{-3} [Cl^-]$$
$$= 5.25 \times 10^{-4} - 4 \times 10^{-3} [Cl^-] \qquad (3)$$

Because one nitrate ion was replaced by one chloride ion , and the initial concentration of chloride ion was 0.1 M. Thus, equation 4 should hold for all the collected effluents.

$$[NO_3^-] = 0.1 - [Cl^-] \qquad (4)$$

Equation 4 was substituted into equation 3 and had the following equations:

$$[NO_3^-] = 1.25 \times 10^{-4} / (1 - 4 \times 10^{-3})$$

$$= 1.26 \times 10^{-4} \text{ M}$$

Therefore, the amount of nitrate being replaced with the 10 mL of ammonium chloride solution was found to be 1.26×10^{-6} mole.

The results of the regeneration of the polymers indicated that the capacity remained constant within experimental error for B-4 but dropped after several times with B-5. Thus, only A-4 has the capability of the regeneration.

Nitrite capacities of A-5 and B-5

As we mentioned earlier, the nitrate-selective electrode responds to certain other anions as well as nitrate ion. In a solution containing nitrate ion and an interfering anion, electrode behavior is given by equation 2. For nitrite ion, $K_x = 4 \times 10^{-2}$, n = 1. Therefore,

$$E = E_y - 0.059 \log ([NO_3^-] + 4 \times 10^{-2} [NO_2^-])$$

Pure nitrite solution should respond as:

$$E = E_y - 0.059 \log (4 \times 10^{-2} [NO_2^-]).$$

Thus, the electrode was standardized by diluting a stock solution of 0.1 M sodium nitrite and measuring each diluted solution. The electrode response was linear from 10^{-1}M to 10 $^{-3}$M nitrite as demonstrated by Figure 5.

A 10^{-1}M sodium nitrite solution was passed through a column which was packed with the protonated polymer, the effluents were collected, and the concentration of nitrite in the effluents determined from Figure 5, the results are

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Figure 5

Nitrite Standard Curve
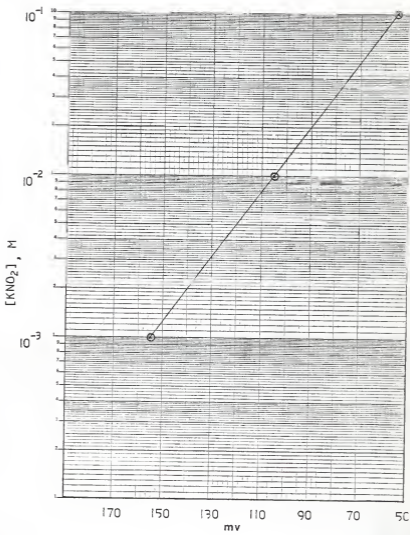
Figure 6

Nitrite capacity of the synthesized polymer A-4
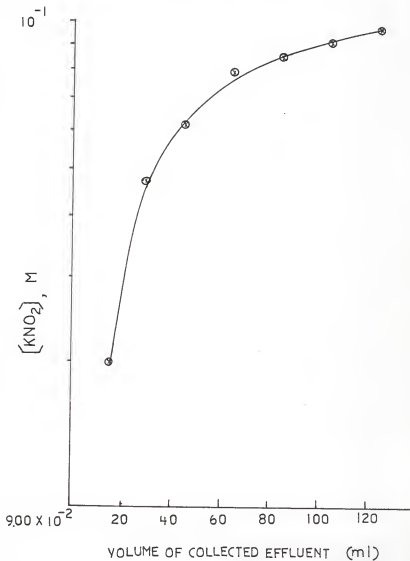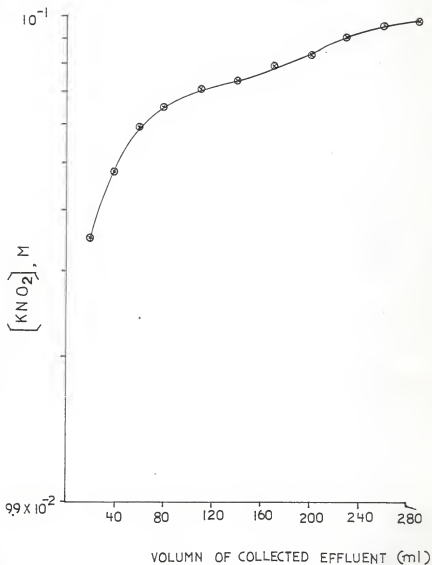(0.3 g of polymer A-4 was coated on 12.7 g of
acid-washed Chromosorb W)

VOLUME OF COLLECTED EFFLUENT (ml)

60

Figure 7

Nitrite capacity of the synthesized polymer <u>B-4</u>
(0.3 g of polymer <u>B-4</u> was coated on 12 g of
acid-washed Chromosorb W)

VOLUMN OF COLLECTED EFFLUENT (ml)

62

depicted in Figure 6 and 7. The nitrite capacity thus obtained was calculated to be 30.6% for $\underline{A-5}$ and 9% for $\underline{B-5}$ based on 100% conversion in the reaction of $\underline{A-3}$, $\underline{B-3}$ and polyvinylbenzyl chloride and 62% with 30% corrected for actual monomer present.

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SUMMARY

The nitrate capacity of polyvinylbenzyl-1-phenyl-2-piperidinoethyl-4-aminobenzoate A-4, which is 90% based on 50% conversion indicated that the replacement of diethylamine by piperidine did decrease the steric factor and help the quarternary amine to posses more positive charge during the interaction with the nitrate.

The solubility test of 1-(1-oxido-4-pyridyl)-2-diethylaminoethyl-4-nitrobenzoate HCl C-3 did not show the precipitation with nitrate. Furthermore, due to C-3 instability and the difficulty of seperation from impurity during the preparation, it is not recommended to use C-3 compound be used for anion selectivity test.

The polyvinylbenzyl-1-pyridyl-2-piperidinoethyl-4-aminobenzoate had low nitrate capacity (37% based on 100% conversion) and was unable to be regenerated. However, the solubility test showed the very interesting results that B-3 was more selective to several doubly-charged or huge, easily oxidized singly-charged anions. This indicated an increased positive character between pyridine and piperidine groups compared to that between phenyl and diethylamine groups.

64

Figure 8

NMR Spectrum of

1-Phenyl-2-piperidine ethanol (A-1)
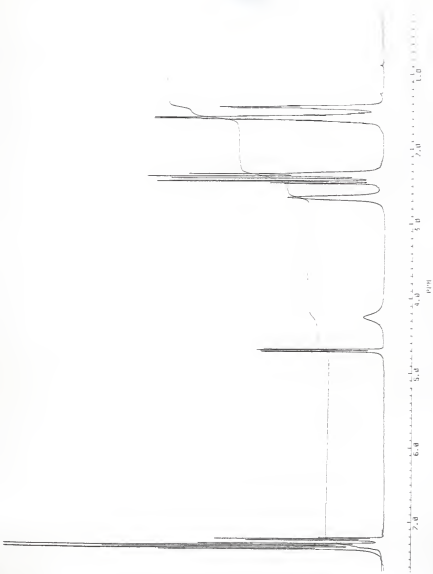
Figure 9

NMR Spectrum of

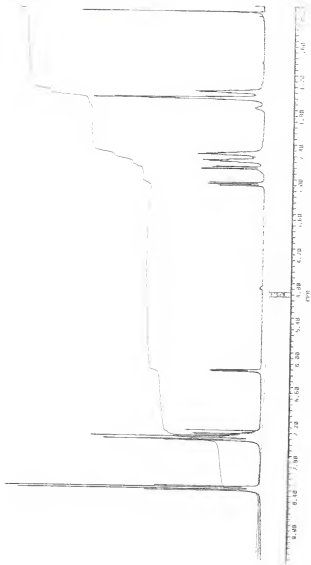1-Phenyl-2-piperidinoethyl-4-nitrobenzoate (A-2b)

68

Figure 10

NMR Spectrum of

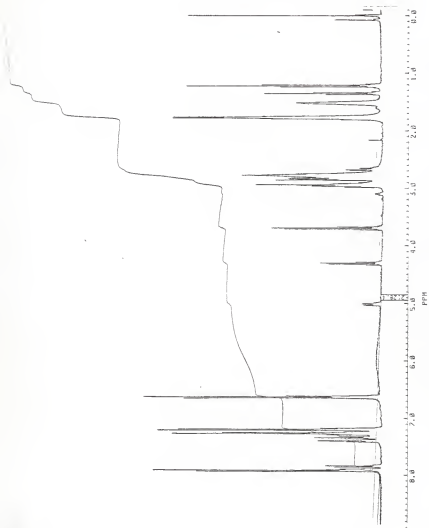1-Phenyl-2-piperidinoethyl-1-aminobenzoate (A-3)
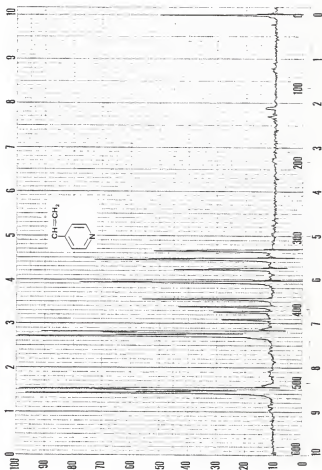
Figure 11

NMR Spectrum of
4-Vinylpyridine
(Aldrich library of NMR spcetra)

V526-4
4-Vinylpyridine, 98%
M.W. 105.14 b.p. 62-65°/15mm. n_D^{20} 1.5500
d 0.975 Beil. 20(2),170 IR 1,957/G 2,1141E

72

Figure 12

NMR Spectrum of

4-Epoxyethylenepyridine 1-oxide (B-0)
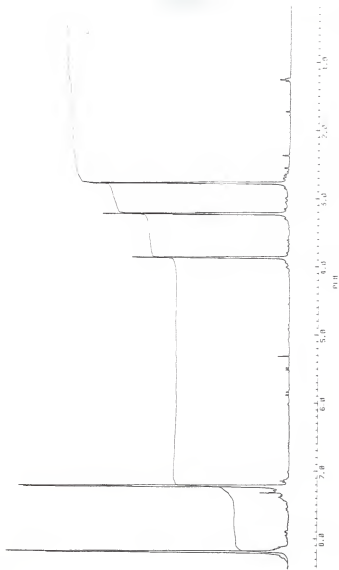
Figure 13

NMR Spectrum of

1-(1-oxido-4-pyridyl)-2-piperidino ethanol   (B-1)
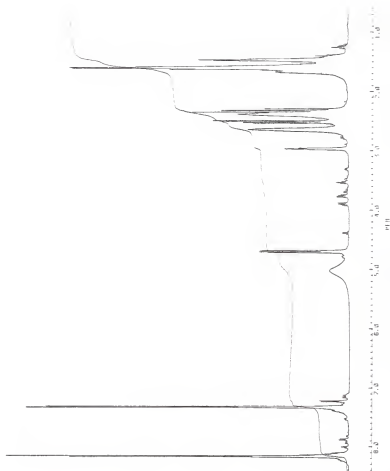
Figure 14

NMR Spectrum of

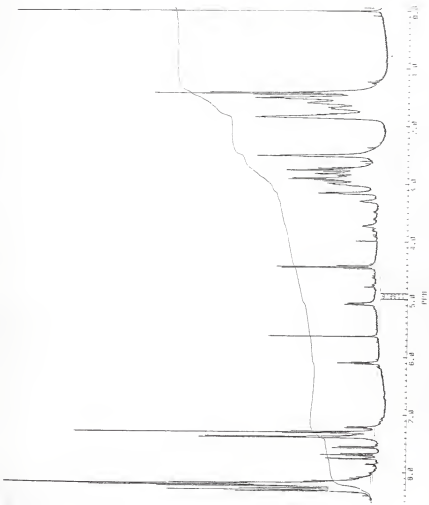1-(1-oxido-4-pyridyl)-2-piperidinoethyl-4-nitrobenzoate

(B-2b)

Figure 15

NMR Spectrum of

1-(1-oxido-4-pyridyl)-2-diethylamino ethanol (C-1)

Figure 16

IR Spectrum of

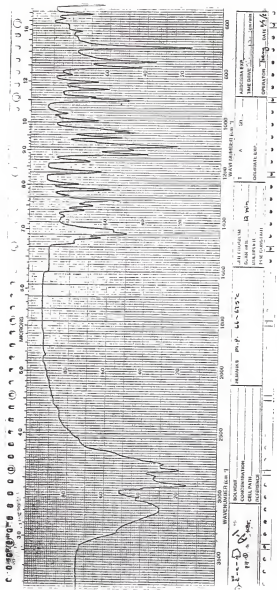1-Phenyl-2-piperidino ethanol (A-1)

Figure 17

IR Spectrum of

1-Phenyl-2-piperidinoethyl-4-nitrobenzoate   (A-2b)
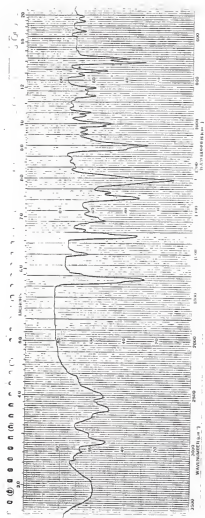
Figure 18

IR Spectrum of

1-Phenyl-2-piperidinoethyl-4-aminobenzoate (A-3)

Figure 19

IR Spectrum of

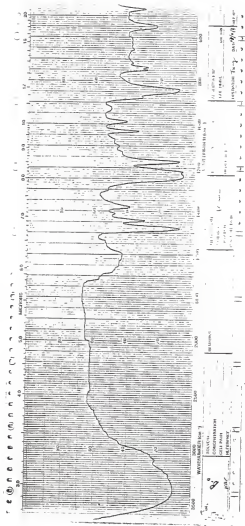4-Epoxyethylenepyridine 1-oxide (B-0)

Figure 20

IR Spectrum of

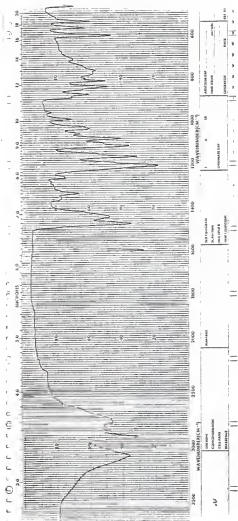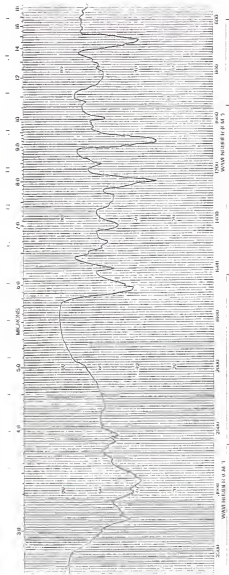1-(1-oxido-4-pyridyl)-2-piperidino ethanol (B-1)

Figure 21

IR Spectrum of

1-(1-oxido-4-pyridyl)-2-piperidinoethyl-4-nitrobenzoate

(B-2)

Figure 22

IR Spectrum of

1-(1-oxido-4-pyridyl)-2-piperidinoethyl-4-aminobenzoate

(B-3)

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THE SYNTHESIS OF NITRATE SELECTIVE RESINS

by

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AN ABSTRACT OF A MASTER'S THESIS

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1985

ABSTRACT

Since first reported in 1945, human nitrate poisoning has
been implicated in numerous illness and death of infants,
especially those under three months of age. The disorder
produced by excess nitrate is called methemoglobinemia.

In 1980, the polymer form of 1-phenyl-2-diethylaminoethyl-
4-nitrobenzoate was reported to have high capacities of
removing nitrate and nitrite. In an attempt to improve the
selectivity, three resins were synthesized as the analogues of
1-phenyl-2-diethylaminoethyl-4-nitrobenzoate in this study.
The synthesis of the three derivatives involved the replacement
of the 1-phenyl ring by pyridine and 2-diethylamine by
piperidine. The three compounds prepared and studied are 1-
phenyl-2-piperidinoethyl-4-nitrobenzoate, 1-(1-oxido-4-
pyridyl)-2-piperidinoethyl-4-nitrobenzoate and 1-(1-oxido-4-
pyridyl)-2-diethylaminoethyl-4-nitrobenzoate.

The capacity for removing nitrate and nitrite, the
reactions with 47 other anions, regeneration capability and the
solubility of the 24 anions that reacted were determined. The
low capacities for removing nitrate showed that the steric
factor, the replacement of 1-phenyl by pyridine, did not affect
the interaction between the resin and nitrate. In addition,
the results of the solubility tests indicated an increased
positive character between pyridyl and the amino groups
compared to that between phenyl ring and amine, resulting in
these compounds being more selective for doubly-charged anions.