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# AN INVESTIGATION OF THE PREPARATION AND USE OF LOW-CAPACITY ANION EXCHANGERS IN SINGLE-COLUMN ION CHROMATOGRAPHY

*Iowa State University* PH.D. 1983

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# An investigation of the preparation and use of low-capacity anion exchangers in single-column ion chromatography

by

Robert Eugene Barron

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"Do what you can, with what you have, where you are."

-Theodore Roosevelt

# GENERAL INTRODUCTION

Prior to the year 1975, the rapid, sensitive analysis of common inorganic anions was anything but easy and routine, especially if a variety of matrices was encountered. The analyst had a number of techniques to choose from such as spectrophotometry (1), fluorometry (2), titrimetry (3), potentiometry (4) and amperometry (5) in the case of electroactive species. However, many of these methods suffered from lack of sensitivity and were usually not completely selective, resulting in large interference problems in many applications. As a clever analyst once observed (6), the number of methods published for a given analyte is usually inversely proportional to the usefulness, simplicity and accuracy of any one of the individual methods.

With this large number of tedious, marginal procedures in use, it is no wonder that the invention of ion chromatography was greeted with such approbation. Small, Stevens, and Bauman showed that a combination of anion exchange and conductimetric detection could be used to separate and detect most common inorganic anions both rapidly and with good sensitivity (7).

Before the advent of ion chromatography, it had been common knowledge that anion exchange could separate these anions (8,9) and that conductivity was a universal detector for ions in solution (10), but certain factors prevented the successful marriage of these two techniques. Primarily, most investigators used anion-exchange resins with a high exchange capacity. The high capacity in turn required the use of highly concentrated eluents to move the analyte species down the column. Because the conductimetric detector responds to all ions, it could not sense the small amount of analyte in the presence of large quantities of the eluent ion. The co-inventors of ion chromatography solved both of these problems. First, they developed a new type of pellicular anion-exchange resin of a relatively low capacity (11-13). This allowed low concentrations (ca. 5 mM) of eluent to be used. In addition, they employed a post-column reactor (suppressor column) to eliminate the highly conductive eluent species and enhance the signal of the analyte. The eluent is typically a carbonate-bicarbonate buffer. The post-column reactor used originally was a column filled with a cation-exchange resin of high capacity in the hydrogen form. The reactor converts the eluent to carbonic acid which gives a very low background signal. In addition, it provides hydronium ions as counterions for the analyte. Because conductivity signals result from contributions of both the anion and the cation (14), greater sensitivity is achieved than would have been possible with other counterions.

Thus, a method for separating and detecting most anions (except those with small dissociation constants) at trace levels became available. An analogous system was also invented for cations, but will not be discussed further. The time-saving aspect of ion chromatography was neatly illustrated in a study of anions in phosphate rock and cement kiln dust which was carried out by Kramer and Haynes (15). These workers found that conventional analytical procedures required a different sample for each anion and that up to two days were needed to complete the analysis of one anion. When ion chromatography was used, only one sample was needed and full characterization of the anions in the sample was completed in one hour.

Despite the unquestionable value of the technique, it did have some drawbacks which have been discussed elsewhere (16). These drawbacks prodded others to examine simpler systems which could be run on conventional equipment already in use for high performance liquid chromatography (HPLC). Fritz, Gjerde and Schmuckler introduced a variation of the technique in 1979 (17,18). It is known as "non-suppressed" or single-column ion chromatography. The genesis and early development of this technique were recently reviewed by Jupille (19). This system uses eluents with very low conductivity. Such eluents allow the separator column to be linked directly to the conductivity detector. There is no need for a post-column reactor, hence the name "single-column" ion chromatography. In order to use the very low concentrations of eluent (ca. 1 mM), special anion-exchange resins had to be prepared. The resins were strong-base (Type I) anion exchangers of quite low capacity (less than 0.1 meq/gm) and were prepared from the macroreticular copolymer XAD-1, which is manufactured by Rohm and Haas. Anion exchange resins based on porous polymers are also used in the single-column ion chromatograph which has been introduced recently by the Toyo Soda Company (20). The other single-column system which is commercially available employs silica-based anion exchangers and is manufactured by Wescan Instruments (21,22).

In addition to these chemically bonded stationary phases, a number of workers have used "ion-pair" or "ion-interaction" chromatography to separate common organic and inorganic anions (23-29). The dynamic equilibrium involved takes place on stationary phases consisting of silica which is modified by the addition of alkyl chains (23-26), or on styrene-divinylbenzene copolymers (27-29).

This technique is most suited to the use of the ultraviolet-visible spectrophotometric detector because of the relatively high concentration of ions which must be maintained in the eluent to support the on-column equilibrium. However, if the separator ion is "permanently" sorbed on the column, the conductimetric detector may be used and yields good results (26,27).

A fairly complete count by this author indicates that there have been well over 200 publications in the area of ion chromatography since the inception of the technique. (See Appendix.) The majority of these have dealt with applications of the original method and its offshoots to many ions in a variety of matrices. There have been surprisingly few fundamental investigations, especially those concerned with the properties of the low-capacity resins used as stationary phases. Much speculation may be advanced to rationalize this gap in the literature, but it seems that two factors primarily share the blame. First, ion chromatography was a commercial rather than an academic development, so proprietary knowledge necessarily had to be kept from the literature. Second, there traditionally has been less interest in the development of stationary phases than in their use.

It is the aim of this dissertation to contribute some information about the preparation and relevant properties of low-capacity anion exchangers based on porous styrene-divinylbenzene copolymers. The first section deals with the reproducible preparation of low-capacity (Type I) strong-base anion exchangers. This capability is necessary so that any investigation of the properties of such resins may be carried out efficiently, without wasting time and substrate. The second section examines changes in ion-exchange behavior which can be attributed to chemical changes in the functional group and the polymer matrix. Finally, the third section is concerned with choosing optimum eluent molecules in light of the interactions of the eluent with the copolymer matrix of the anion exchanger.

# LITERATURE REVIEW

## Ion-Exchange Resins of Low Capacity

Synthetic polymeric ion exchangers are now about fifty years old; the first such synthesis has been credited to Adams and Holmes (30). These resins have found countless uses in numerous fields. Ion exchangers have proven to be exceptionally valuable in the discipline of analytical chemistry (31-33). The synthetic exchangers used in large-scale processes have been made predominantly from vinyl copolymers and phenol-formaldehyde condensation polymers. Almost all of the exchangers (both cation and anion) have one thing in common; they have a high exchange capacity. (An arbitrary minimum boundary for high capacity would be about one milliequivalent per gram.) This is a valuable property for an ion exchanger to have when one is using the material for an industrial process such as removing residual acid from a fluid stream. If the capacity is high, the size of a column or reactor used to contain the material can be made smaller, thus saving on construction costs and making processes such as heat transfer more efficient.

Analytical chemists and other individuals working on laboratory scale projects have usually used the industrial ion-exchange materials that were available rather than go through the trouble of manufacturing their own. Perhaps in most cases this was justified, but in certain instances such as chromatography, resins of less than the usual capacity would have been very useful long ago. While ion exchangers have been reduced in size to smaller than ten micrometers and they have been prepared from a number of materials, low capacity has, until recently, been looked upon as a disadvantage and resins of this type have not been heavily investigated. The literature before 1970 contains very little mention of the use of low-capacity resins.

A casual review of the literature shows that much of the work on the selectivity of ion exchangers of high capacity has been done with sulfonated cation exchangers rather than with strongly basic anion exchangers; this disparity also holds true for resins of low capacity.

The work on cation-exchange resins of low capacity has fallen into three categories; gel beads, pellicular beads and porous beads. Perhaps the earliest work on partially sulfonated cation exchange resins was done by Pepper (34). Small (35) and Parrish (36) also published early work concerned with the preparation of "surface-sulfonated" styrene-divinylbenzene gel copolymers. Horvath et al. described the preparation of pellicular beads with a sulfonated pellicle (37,38). These beads by definition have a low capacity because the core of the bead is impervious and contains no functional groups. Hansen and Gilbert (39) did some work on the optimization of the thickness of the sulfonated layer in a gel bead. This was followed by the work of Stevens and Small (11) on the same subject. Hajos and Inczedy (40,41) also did some work on the preparation and characterization of surface-sulfonated gels with the idea of using the end product for ion chromatography. Story reviewed some additional work on low-capacity cation exchangers that had been done prior to 1973 (42). The personal work of Fritz and Story added two contributions on partially sulfonated macroreticular beads (43,44). These are virtually the only known contributions concerning partially sulfonated porous copolymers for use in chromatography.

Kirkland (45) gave details for the preparation of beads with a porous surface layer which was impregnated with a sulfonated fluoropolymer to yield another type of pellicular cation exchanger. Battaerd (46) described the preparation of a pellicular bead prepared by the graft polymerization of a sulfonated olefin onto a solid polyolefin bead. Finally, Stevens and Small described the development of a surface-sulfonated bead for use in ion chromatography (12).

One other paper dealt with the use of unfunctionalized XAD-2 and XAD-4 as cation exchangers of extremely low capacity. They may act as cation exchangers because of residual carboxyl groups which are artifacts of the manufacturing process (47).

The complementary area of anion exchangers of low capacity suffers from an even greater lack of published information. This may be caused by the fact that the chloromethylation reaction is not as vigorous as the sulfonation reaction and must be performed using pre-swollen beads if a gel substrate is used. The swollen beads make control of capacity and control of spatial placement of the anion-exchange sites difficult. Sulfonation can be performed without any swelling of the gel bead. This results in the formation of a sulfonated outer shell which facilitates control of the capacity. Macroreticular beads do not require swelling, but they are also a relatively recent development and are not very popular (or at least not very well known) among experimenters who would have an interest in this work.

The solid-state synthesis of polypeptides makes use of anion exchangers of lower than usual capacity; the resins often fall in the range of 0.1-1.0 meq/g (48,49). Sparrow (50) and Merrifield and Feinberg (51) described the preparation of these types of resins using gel beads as substrates and used chloromethylmethyl ether (CMME) plus a metallic Lewis Acid or boron trifluoride as a catalyst to effect the chloromethylation. No data on selectivity coefficients were available for these resins.

Inman and Dintzis (52) described the controlled introduction of a number of functional groups including weakly basic anion exchange groups into preformed poly(acrylamide) beads. These were used for special biochemical adsorption experiments.

Horvath et al. described a method of preparing a pellicular bead with a pellicle containing a strong-base anion-exchange group based on dimethylbenzylamine (37). This was used to separate nucleotides, but the details of the resin preparation were not included in the paper.

The original paper on ion chromatography (7) described the preparation of a sort of pellicular resin of low capacity for the separation of anions. It consisted of a surface sulfonated core coated with a thin layer of latex beads which were anion exchangers of fairly high capacity. However, because there is such a thin layer of the latex, the resin has a low overall capacity. Stevens and Langhorst (13) described updated materials prepared by essentially the same process.

Gjerde and Fritz (53) described the preparation and use of macroreticular anion exchangers of low capacity for the separation of anionic complexes of transition metals and for use in single-column ion chromatography. They also showed that varying the capacity of these anion exchangers varied the distribution coefficients of common anions, but the results indicated that the relative selectivity was not greatly affected (54). The macroreticular resins were prepared by chloromethylation via the use of CMME and Lewis Acid catalysis followed by amination with trimethylamine.

Kaschuba (55) recently received a patent for a new procedure for preparing anion exchangers of low capacity for use in ion chromatography. The process involves the use of chloromethyl-2-ethylhexyl ether and $BF_3$ catalysis. The reactions are run at room temperature for 24 hours and the products are aminated with dimethylethanolamine. This chloromethylation procedure is similar to the process used by Sparrow (50).

Another paper published a short time ago by several Chinese workers reviews resins that can be used for separations in ion chromatography (56).

It is clear that there is a general lack of data concerning the chromatographic performance and characteristics of anion exchangers of low capacity, though this state of affairs will more than likely change in the next few years as a result of the great interest in ion chromatography as an analytical tool.

## The Chloromethylation Reaction

The chloromethylation reaction (here restricted to aromatic substrates) involves the replacement of a hydrogen atom with a chloromethyl group. The reaction has been known for a long time; its discovery has been credited to Grassi and Maselli (57). The reaction has been reviewed by Fuson and McKeever (58) through 1941. A later review by Olah and Tolgyesi (59) covers the work on the reaction through 1964 in a most exhaustive manner. The reader is referred to these works for specific detailed examples and information.

As one would expect, most of the work of elucidating the reaction has been done with monomeric molecules. However, the chloromethylation reaction can be carried out on aromatic (specifically styrene-divinylbenzene) copolymers as well. This yields an intermediate which can serve a number of purposes. Large volumes of both weak-base and strong-base anion exchangers are prepared from chloromethylated copolymers by treating the intermediate with the appropriate amine. The chloromethylated copolymer can be used to prepare resins containing a host of other functional groups which are especially useful in the area of polymer-aided synthesis. Some examples of functionalized polymers prepared from chloromethylated intermediates for this purpose have been compiled in recently published monographs (60-62).

The chloromethylation reaction can be carried out with a bewildering variety of solvents, chloromethylating agents and catalysts. The choice of each component is generally dependent on the reactivity of the substrate and the need to control side reactions. (The chief unwanted reaction is the coupling of two substrate molecules to one another to produce a diphenylmethane derivative.) Table 1 lists a number of solvents, catalysts and chloromethylating agents that have been used in the reaction according to the literature cited in the review by Olah and Tolgyesi (59).

Grassi and Maselli (57) used a mixture of benzene, HCl gas, paraformaldehyde($HOCH_2$-O-$(CH_2O)_n$-$CH_2OH$) and zinc chloride to prepare benzyl chloride. This is a set of conditions that work well for moderately reactive molecules and it was used with minor variations for a number of years. Zinc chloride is still one of the most popular catalysts as it tends to promote the reaction well and to minimize the unwanted coupling reaction (63).

Table 1. Solvents, catalysts and chloromethylating agents used to carry out the chloromethylation reaction

| Solvents | Catalysts | Chloromethylating Agents |
|---|---|---|
| aqueous HCl | $ZnCl_2$ | formaldehyde + HCl |
| acetic acid | $SnCl_4$ | (paraformaldehyde) |
| diethyl ether | $SnCl_2$ | (methylal) |
| dioxane | $AlCl_3$ + pyr. | (formalin) |
| methylal | $AlCl_3 + 3^o$ amine | |
| $CCl_4$ | $AsCl_3$ | bis(chloromethyl ether) |
| chloroform | $FeCl_3$ | |
| ethylene dichloride | $BF_3$ | |
| perchloroethylene | $TiCl_4$ | chloromethylmethyl ether |
| nitrobenzene | $TiF_4$ | |
| ligroin | $BiCl_3$ | |
| $CS_2$ | $SbCl_3$ | chloromethylsulfide |
| | $SbCl_5$ | |
| | HCl | |
| | $H_2SO_4$ | |
| | $H_3PO_4$ | |
| | $CH_3COOH$ | |
| | $C_6H_5SO_3H$ | |
| | $\underline{p}$-$CH_3C_6H_4SO_3H$ | |

The haloethers, bis(chloromethyl) ether and chloromethylmethyl ether, became popular after their initial uses in the late 1930s (64,65). They are especially useful for preparing chloromethylated styrene-divinylbenzene gels because of their ability to swell the polymer, thus increasing the yield of the reaction. The preparation of these intermediates has been carried out almost exclusively with the haloethers since their introduction (66-70). However, both of these haloethers are volatile and are considered to be carcinogenic making their direct handling somewhat hazardous.

There are examples of the use of paraformaldehyde and HCl gas for the chloromethylation of styrene-divinylbenzene copolymers. Trostyanskaya et al. (71) used paraformaldehyde and HCl gas in dichloroethane with a zinc chloride catalyst to effect the reaction with gel copolymers. The dichloroethane here acts to swell the copolymer so that the reaction can produce high capacities. McBurney also noted that paraformaldehyde and HCl gas can be used in the reaction (72). However, his work also dealt with the preparation of high-capacity exchangers under anhydrous conditions.

Von Braun and Nelles (73) were among the first investigators to use formalin and aqueous HCl to effect the chloromethylation of non-polymeric moieties. Fuson and McKeever (58) note that these conditions are especially suitable for multiply alkylated aromatics because the ring is more activated toward electrophilic substitution. There are many other examples of the use of these conditions for alkylated aromatics (74-77). However, there are no known reports of using these conditions on styrene-divinylbenzene copolymers. This is probably because these conditions are rather mild and would have no effect on gel copolymers which have been the mainstay of most workers in the area of ion exchange.

The mechanism of the chloromethylation reaction has been investigated by a number of workers. It seems intuitively likely that the mechanism is somewhat different in an aqueous HCl medium than it is in a medium of anhydrous chloromethylmethyl ether. Ogata and Okano (78) showed by a kinetic analysis that $^{+}CH_2OH$ is probably the reactive intermediate in hydroxylic solvents. Wadano et al. (79) also showed evidence for the presence of this cation. Once the $^{+}CH_2OH$ is substituted onto the aromatic nucleus, the -OH is replaced by -Cl with the equilibrium lying far to the right in this replacement step. Nazarov and Semenovsky (80) confirmed this hypothesis. They also showed that chloromethylation and bromomethylation gave the same isomer distribution on a number of substituted aromatics (81). This suggests a common attacking species, otherwise, the steric bulk of the bromine should have had some effect on the isomer distribution. They and others (82,83) also showed that under chloromethylation conditions, the hydroxyl group of a hydroxymethylated substrate is completely replaced by chlorine, thus strengthening this interpretation of the mechanism.

Other attacking species that have been proposed are the chloromethyl cation, $^{+}CH_2Cl$ (84), and protonated chloromethanol (85). Both of these options have been viewed as unlikely. Olah and Yu (86) showed NMR evidence which they claimed was an indication of the presence of protonated chloromethanol at -80°C. They prepared the moiety by adding anhydrous HCl gas to a solution of formaldehyde in a medium of $FSO_3H$-$SbF_5$-$SO_2$. They note that the protonated chloromethanol decomposed above -65°C. They showed similar evidence to indicate that protonated halomethylalkyl ethers existed under the same conditions. This led them to suggest that perhaps these protonated molecules are the actual attacking species in their respective reaction mixtures. Their conclusions seem to stretch the limits of credibility because of the fact that they observed the moieties under such extreme conditions which are far removed from the actual conditions usually employed in the reaction.

The need in this investigation is to be able to prepare anion exchangers of low capacity in a reproducible fashion using a macroreticular substrate. The above information was scrutinized to determine a suitable approach which will be outlined in a later section.

## Chemical Effects on Selectivity

### Changes in functional group structure

Many of the factors which affect the selectivity of both cation exchangers and anion exchangers have been thoroughly examined and excellent reviews exist which outline much of this research (87-89). However, one area which affects selectivity has been neglected by the majority of researchers. The question of how the chemical structure of a strong-base anion exchanger affects its selectivity for various anions would appear to be a very basic one. Yet, the only resins that have been extensively used and characterized have been the Type I resins (90) (benzyltrimethylammonium cation) and the Type II resins (91,92) in which one methyl group is replaced by a hydroxyethyl group. One can find examples of strongly basic resins prepared by treating chloromethylated styrene-divinylbenzene copolymers with such amines as dimethyldodecylamine (93), 2-mercaptopropyldimethylamine (94) and N,N,N`,N`-tetramethylethylenediamine (95), but these are generally not characterized as to selectivity coefficients and use for separations of common anions.

Some investigations of the effect of the structure of functional groups on selectivity have been initiated in the area of water treatment. Gauntlett (96) examined the behavior of Type I and Type II strong-base exchangers in the removal of nitrate from water supplies. He was not able to discern a correlation of resin type to nitrate affinity in a limited number of tests. Gregory and Dhond (97) examined the exchange equilibria of phosphate, sulfate and chloride using a sample of ten Type I and Type II commercial anion exchangers. They concluded that the Type II resins showed a higher affinity for the sulfate ion than the Type I resins. They surmised that this is probably because sulfate is a highly hydrated ion that interacts favorably with the polar Type II functional group. Boari et al. (98) examined 27 weak-base anion exchangers and five strong-base anion exchangers and evaluated their sulfate/chloride selectivities in solutions covering a wide range of salinity. Their conclusion was that the "basicity" of the resin has a strong effect on the selectivity of the resins for divalent sulfate. They found that resins with primary amine functional groups had a much greater affinity for sulfate than those containing quaternary ammonium ions. They did not indicate what cations were present in the strong-base resins that they used, though the code numbers of the manufacturers indicate that at least two of them contained Type I ions.

Clifford and Weber (99,100) produced a voluminous study of the factors affecting monovalent/divalent selectivity ($Cl^-$, $NO_3^-$, $SO_4^=$) in 30 different commercially available anion-exchange resins. A conglomeration of resins such as occurs in the work of Clifford and Weber makes it very difficult to reach any solid conclusions as to the selectivity differences caused by the variation in chemical structure of the functional groups. However, these workers used a statistical technique known as analysis of variance (101) to sort through their data and came to the conclusion that the two most important determinants of monovalent vs. divalent selectivity were resin matrix and functional group. The functional group distinction that they made was primarily between weak-base and strong-base resins. They had little comment concerning what might be expected from a number of different quaternary ammonium ions. They did indicate that the Type II resins had a higher affinity for sulfate than the Type I resins which is in agreement with the work of Gregory and Dhond which was cited above.

While these investigations shed some light on the question of selectivity vs. the chemical structure of the functional group, they are not extremely useful for the present inquiry. There are several reasons for this.

First, all of the studies employed resins of high capacity which are almost sure to behave differently than resins of low capacity in some respects. The very fact that they have a high capacity indicates that the matrix is quite polar. Many of these resins shrink and swell with electrolyte changes and are easily wet by water. Neither fact is true of macroreticular anion exchangers of low capacity. Therefore, some of their interactions with ions in solution are likely to be different than those obtained with resins of high capacity.

Second, only Type I (made with trimethylamine) and Type II (made with dimethylethanolamine) strong-base resins were represented. Thus, only a very limited indication of the effect of the structure of the strong-base ion-exchange site was given.

Third, the chemical and physical characteristics of the polymers themselves were not controlled since they were obtained from many different manufacturers. The resins were of different degrees of cross-linking and many different porosities ranging from gel to macroreticular. It is quite possible that two nominally equivalent resins from two manufacturers could exhibit two sets of behavior because of differences in the production processes. It has been shown that just the choice of inert solvent used to form macroporous resins can have an affect on selectivity (102).

Finally, because the investigations were centered around water treatment, very few ions were examined and the data are not readily translated to the area of ion chromatography because of the manner in which they were obtained.

Other studies of a more controlled nature were located. In an early attempt at characterizing resins other than those containing the Type I and Type II functional groups, Strobel and Gable (103) prepared a number of strong-base anion exchangers of high capacity from styrene-divinylbenzene gel substrates. They were interested in characterizing the basicities of the resins titrimetrically, and did not have any data concerning selectivities. Their resins were prepared from trimethylamine, triethylamine, tributylamine, dimethylethanolamine, methyldiethanolamine, dimethylisopropylamine, dimethylbenzylamine, dimethylphenylamine and pyridine.

A similar study was carried out later by Dragan, Carpov and Petrariu (104). They also prepared resins of very high capacity from gel beads and introduced a total of 14 weak-base and strong-base functional groups into the beads. Their main purpose was also to characterize the basicity of the resins via potentiometric titrations. The strong-base resins were prepared from trimethylamine, triethylamine, tributylamine, dimethylethanolamine, methyldiethanolamine, diethylethanolamine, triethanolamine, and dimethylphenylamine. They also included data for the distribution coefficients of the resins for $Cl^-$ compared to $OH^-$. They found that the trimethylamine resin had the highest distribution coefficient for chloride while the lowest distribution coefficient was evidenced by the triethanolamine resin.

Gozdz and Kolarz (105) prepared their own macroporous copolymers and then introduced both strong-base and weak-base ion exchange sites into the products. This procedure ensured that the physical characteristics of the copolymers were the same from resin to resin. They determined equilibrium selectivity coefficients for the fluoride, bromide, perchlorate and cyanide ions compared to chloride. The strong-base resins they used were prepared from trimethylamine, methyldiethanolamine, dimethylethanolamine and triethanolamine. These resins were also of high capacity.

Guter (106) examined the behavior of several strong-base gel resins toward nitrate and sulfate. The resins were prepared by a manufacturer from the same chloromethylated intermediate and were again of a high capacity. These resins were prepared from tertiary amines which included trimethylamine, triethylamine, dimethylethanolamine, methyldiethanolamine, triethanolamine, ethyldiethanolamine, diethylethanolamine, and N-methylmorpholine. He noticed that the resin which contained a triethylamine functional group had a higher affinity for $NO_3^-$ compared to $SO_4^=$ than did a Type I resin. The resins containing the polar functional groups showed, if anything, an increase in affinity for the $SO_4^=$ ion.

The original "pellicular" resin used for anion separations in dual-column ion chromatography is believed to contain a Type I quaternary ammonium ion because of the selectivity it exhibits. Clifford and Weber (100) point out that another resin with a benzyltriethylammonium group is now being used in dual-column ion chromatography because of its reduced sulfate affinity. There are few details available on how these resins are prepared.

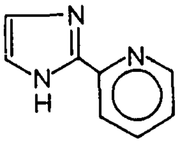
As noted in the general introduction, single-column ion chromatography makes use of three types of anion exchangers. The first is a macroreticular styrene-divinylbenzene stationary phase with chemically bonded Type I anion-exchange sites (17,18). There is also a commercially available silica based anion exchanger which is used by some workers (21,22). The chemical identity of the quaternary ammonium site in this stationary phase is unknown. The third type is polymeric in nature and is believed to be a poly(methacrylate) resin according to the promotional literature of the Toyo Soda Co. The nature of the quaternary ammonium ion in this material is also unknown.

There is currently no known published work on chemically induced selectivity differences in strong-base resins of low capacity. There is a piece of closely related work however. Iskandarani and Pietrzyk used a series of non-bonded tetraalkyl quaternary ammonium ions in dynamic equilibrium between the mobile phase and a polymeric stationary phase in order to separate organic ions (28). An analogous study of inorganic anion retention used only the tetrapentylammonium ion as the optimum hydrophobic counterion in the mobile phase (29).

### Changes in matrix

Another factor that has been largely eliminated from consideration in selectivity arguments is that of the nature of the matrix of the anion exchanger. It is only recently that there has been some sense of the influence of the matrix in ion-exchange processes expressed in the literature. Intuitively, it makes sense that the matrix should influence the interaction of the exchanger and the analyte solution by virtue of its polarity and perhaps its morphology. This should be especially true in the case of resins of low capacity because the ions spend a smaller proportion of their time interacting with ion-exchange groups in these materials. Cantwell and Puon and Afrashtehfar and Cantwell have shown that the matrix does indeed influence ionic retention when XAD-2 is used as the substrate for an anion exchanger of low capacity (107,108).

Many of the effects of matrix on selectivity deal with the physical structure of the polymer, though some examples of the influence of chemical nature can also be found. Green and Hancock (109) showed that the nature of the polymeric matrix plays a great role in practical separations. They found that the separation factor for $PtCl_6^{2-}/Cl^-$ is improved fourteen fold by substituting a 4% divinylbenzene macroporous matrix for a 4% divinylbenzene gel matrix even though the functional group (isothiouronium) was the same in both cases. Pyridinium functional groups were placed on the same two matrices and the two resins then behaved identically toward the same species. This indicates some sort of cooperative effect between the support and the functional group. They also discovered that when copper(II) and iron(III) are loaded onto pyridylimidazole resins (see below), the separation factor doubled by altering the

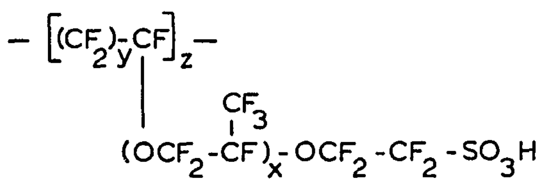


2-(2-pyridyl)imidazole

porosity of the matrix. Parrish and Stevenson (110) and Vernon and Nyo (111) both showed that polymerization methods which affect the polymer structure affect the behavior of chelating resins made from the polymer. Bayer (112) suggested quite some time ago that the polymeric backbone may exert considerable influence on the behavior of a resin.

The work of Clifford and Weber (99,100) gives a somewhat quantitative interpretation of the influence of the resin matrix in ion-exchange behavior. They found that the most critical parameter for divalent/monovalent selectivity was whether or not the active nitrogens were incorporated into or were pendant from the polymer backbone. The actual chemical nature of the polymer had some effect on selectivity with non-styrene polymers (phenol, epoxy, acrylic) showing a greater selectivity for sulfate over nitrate.

Martin et al. (113) showed that the ion-exchange polymer known as Nafion (shown below) has a higher selectivity for monovalent hydrophobic cations than for such



$$-\left[(CF_2)_y-\underset{\substack{|\\(OCF_2-\underset{\substack{|}}{\overset{CF_3}{C}}F)_x-OCF_2-CF_2-SO_3H}}{CF}\right]_z-$$

Nafion

cations as $Ca^{2+}$. This is opposite the behavior normally expected for a sulfonated styrene-divinylbenzene copolymer. He attributed this behavior to the chemical differences in the two polymeric backbones.

It seems plausible, considering the work of Cantwell and Puon and Afrashtehfar and Cantwell (107,108), that one should be able to influence the selectivity of an anion exchanger of low capacity by altering the chemical environment of the surface of the resin near the ion-exchange groups. This could be done by adding stable neutral functional groups to the polymer either before or after the ion-exchange groups are in place. However, there seems to be no readily available evidence that this approach has been used. It will be shown later that this may be a potentially useful method of altering selectivity.

# THE REPRODUCIBLE PREPARATION OF ANION EXCHANGE RESINS OF LOW CAPACITY

## Introduction

Before studying the preparation of the anion exchangers, a decision had to be made as to what type of substrate to use. The logical choice for a number of reasons is a porous styrene-divinylbenzene copolymer. While silica is usually more efficient in chromatography, it is unstable outside of the pH range of 3-8 (114,115). Moreover, silica is known to be attacked by fluoride in acid solution (115), which would not be suitable for ion chromatography. An attractive feature of the aromatic copolymer is that it can be modified easily by a wide variety of chemical reactions including acylation, alkylation, halogenation and others. Also, porous copolymers do not need to be swollen (as gel beads do) to attach functional groups. This makes control of the degree of reaction more accurate.

It is well-known that the class of porous copolymer, the conditions under which it is manufactured and even the purity of the monomers used in its preparation can influence the properties of an anion exchanger made from it.

The main classes of porous copolymer include solvent-modified copolymers, macronet copolymers and isoporous copolymers. Davankov et al. (116) describe the basic characteristics and the general method of preparing each type.

Solvent-modified copolymers can be further divided into three subclasses which are: a) copolymers prepared with a solvent which dissolves the monomers and solvates the copolymer chains resulting in a low chain density; b) copolymers prepared with a solvent which solvates the copolymer chain and acts as a chain transfer agent thus reducing the average length of the copolymer chains; and c) copolymers prepared with an inert solvent which dissolves the monomer but causes the copolymer to precipitate as microgranules which, in turn, form a rigid interconnected structure with large open pores between the granules. This last class of solvent-modified copolymer is herein called a macroreticular copolymer. Rather than using an inert solvent to precipitate the copolymer and form the pores, the copolymerization may be carried out using an inert solid agent such as finely divided $CaCO_3$ to create the voids within the bead. The solid is later extracted from the copolymer. While both of these processes create large inner pores, the morphologies of the bead interiors are almost certainly different from one another.

Macronet copolymers are prepared by using cross-linking agents which are much longer than divinylbenzene (117), thus creating a more open network. Isoporous copolymers are made by introducing secondary cross-linking into an already formed gel structure at the time the ionogenic group is added to the bead (118).

Macroreticular copolymers appeared to be good choices because of their excellent mechanical strength (for resistance to the pressures normally encountered in liquid chromatography) and high permeability, but there still remained the necessity to choose from among several contenders. The choice for most of the studies was XAD-1 which is manufactured by Rohm and Haas. It exhibited the best behavior as a stationary phase in ion chromatography. The detailed reasons for its choice will be explained in the Results and Discussion section.

The porous anion-exchange resins used by Gjerde et al. (17,18,53) were prepared by using an adaptation of the method of Goldstein and Schmuckler (63). This involves the use of chloromethylmethyl ether (CMME) and $ZnCl_2$ catalysis to effect the chloromethylation. Zinc chloride was used because it is about the weakest of the metal chloride Lewis Acid catalysts and gives the least secondary cross-linking. This method was adequate for preparing resins of moderate to high capacity, but was totally unsuitable for resins of low capacity, especially if the capacity had to be controlled carefully. The reagent was so reactive, even in small amounts, that reaction times had to be very short. This caused a lot of scatter in the capacities which were achieved with ostensibly equivalent conditions (119). A complicating factor was the behavior of the $ZnCl_2$ catalyst. It is very sensitive to water and it is also erratic in its dissolution in the solvent system which was employed. Even standardized preparation of the $ZnCl_2$ (51) did not seem to help. Also, this synthesis involves the direct handling of CMME which contains some bis-chloromethyl ether, both of which are known carcinogens.

Gjerde et al. (17,18) showed that the capacity of an anion exchanger is an important parameter in its behavior in ion chromatography. This makes it necessary to be able to control the capacity to a close tolerance. Control of the capacity would also facilitate basic studies of ion-exchange behavior with these resins. It would do so by insuring that clean, sized substrate was not wasted in futile reactions and it would allow preparation of exactly the capacity needed to demonstrate a particular point.

The main goal was to find a simple reaction system, without a catalyst if possible. Von Braun and Nelles (73) had shown that it was possible to chloromethylate non-polymeric moieties using formalin (37% formaldehyde in water) and aqueous HCl without a catalyst. Fuson and McKeever (58) note that these conditions are especially suitable for highly alkylated aromatics because the ring is more activated toward electrophilic substitution.

Macroreticular styrene-divinylbenzene copolymers are highly cross-linked with commercial grade divinylbenzene which contains about 45% ethyl styrene and other alkylated styrenes in addition to the divinylbenzene. The large amount of divinylbenzene is necessary to strengthen the copolymer beads because of their unique internal geometry. Thus the typical macroreticular copolymer contains a large proportion of multiply alkylated benzene rings, making it an ideal substrate for chloromethylation with formaldehyde and aqueous hydrochloric acid. The absence of a catalyst (besides $H^+$) also simplifies control of the reaction and should eliminate most of the secondary cross-linking commonly found in the presence of Lewis Acid catalysts.

Another advantage of this approach is that the aqueous reaction medium does not allow the copolymer to be swollen at all (120). This should confine the functional groups to the easily accessible surfaces of the resin. This means that the final ion-exchange resin should have a fast exchange rate, a property that is highly desirable for ion chromatography. Finally, the direct handling of CMME is avoided. It is known that the reaction between HCl and formaldehyde produces bis-chloromethyl ether (bis-CME) (80), but if the precautions outlined later are used, there should be minimal danger involved with the reaction.

## Experimental

### Materials and reagents

The styrene-divinylbenzene copolymer beads which were used in this investigation were obtained from Rohm and Haas, the Hamilton Co., Interaction Chemical Co., and the Benson Co. The polymerization process results in a product which is contaminated by varying amounts of many aromatic compounds (121). Because the effect of these compounds on synthetic procedures is unknown, the following clean-up procedure was used for all copolymers. Each copolymer was extracted in a Soxhlet extractor for 24 hours with each of three solvents. Methanol was used first, followed by acetonitrile and finally, diethyl ether. After extraction with ether, the copolymers were dried at 70°C overnight. The resulting products were free-flowing powders with no smell indicative of the presence of impurities. The cleaned copolymer beads were stored in sealed jars until needed.

All microspherical copolymers were used without grinding. The XAD series was received as 250-850 micrometer beads and had to be ground and sized before use. The clean copolymers were ground in a ball mill or a shear mill and the fractured beads were sized using U.S. Standard Sieves. The fines were removed by slurrying a given size fraction in methanol and decanting the material which remained in suspension after the large particles settled completely.

The copolymers which were used for chromatography were prepared either by elutriation (122,123) or sedimentation. Elutriation was discovered to be far too tedious to perform on the XAD copolymers and was not used extensively. The sedimentation was used on material which passed through a sieve of 38 micrometer nominal size. This material was slurried in methanol and the larger particles were allowed to settle for ten minutes before the remaining slurry of fine particles was decanted. This procedure was repeated until the supernatant liquid was only slightly cloudy. This produced a crop of particles of fairly uniform size although they were of irregular shape. The particles were examined microscopically in a qualitative fashion, but a quantitative size distribution was not determined. The particles are of numerous shapes with many long, thin shards as well as angular blocks. Sedimentation can only differentiate these particles on the basis of their apparent spherical diameter; therefore, many shapes and dimensions appear in a fraction which is supposedly composed of particles of equal diameter.

All solvents used for resin preparation were at least of practical grade. The gases were obtained from Matheson and were 99% pure. The p-nitrophenol was purified by a double recrystallization from water. All other reagents were the best commercially available grade and were normally used as received.

All eluents and fluids for packing columns were prepared from distilled, deionized water and were filtered through a 0.45 micrometer filter membrane before use. All eluent feed lines were equipped with a ten micrometer inlet filter.

### Apparatus

The liquid chromatograph was assembled from components manufactured by a number of companies. The equipment included a Milton Roy Mini-Pump, a Rheodyne Model 7010 injection valve with interchangeable sample loops, a Li Chroma Damp II pulse dampener and an Alltech two micrometer in-line filter placed before the injection valve. The detector was a Wescan Model 213A conductimetric detector equipped with a three microliter cell. A Curken two-pen recorder was used to obtain permanent records of the chromatographic separations. The configuration of the system is shown in Figure 1.

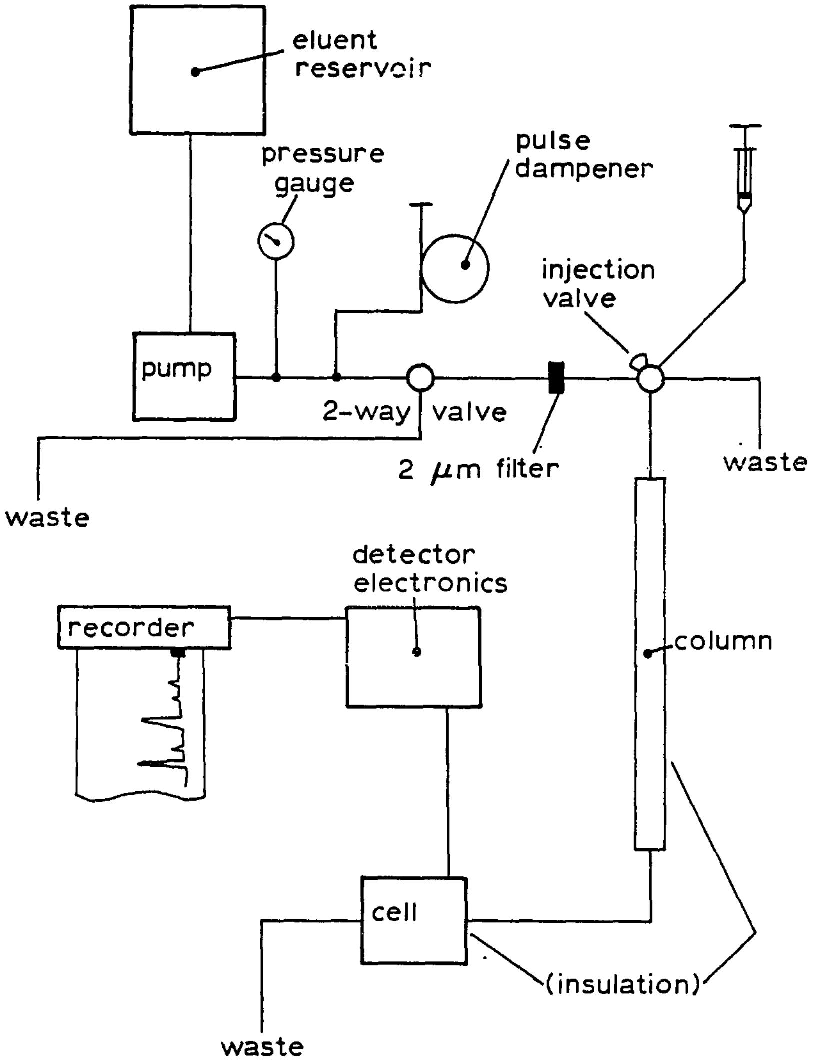


Figure 1. Configuration of the liquid chromatograph used in this work.

## Copolymer surface area determination

The specific surface areas of the porous copolymers were determined by adsorbing p-nitrophenol onto the copolymer from solution as suggested by Giles et al. (124). An accurately weighed sample of copolymer (about 0.1 g) was placed in a twelve milliliter screw-cap vial with a teflon seal. Then, 0.2 mL of methanol was added to wet the material. Next, 10.00 mL of a 0.0500 M solution of p-nitrophenol was added to the vial. The solution also had a concentration of 0.0025 M $NaH_2PO_4$ and 0.0025 M $Na_2HPO_4$ as well as 2% methanol v/v.

A plot of mmole/g of dye adsorbed vs. concentration of dye solution shows that a concentration of 0.0500 M p-nitrophenol is necessary to be on the plateau of the curve (indicating complete surface coverage) for copolymers with a surface area less than or equal to about 550 $m^2/g$. If the first result with a copolymer indicated that the surface area was this large or larger, the experiment was repeated with a sample of 0.05 g to get a more accurate figure.

After the solution was added, the vials were shaken gently overnight on a Burrell shaker. The resin was then filtered off using a small funnel with a glass wool plug in the neck or a Gelman Acro-Disc filter. The solutions were then diluted and the amount of dye left in the solution was quantified via spectrophotometry. This allowed the surface area to be calculated by using equation 1.

$$S=Y_m N_{AV} a \qquad (1)$$

Here, S is the specific surface area, $Y_m$ is the amount of dye adsorbed per gram, $N_{AV}$ is Avogadro's number and a is the area of an individual dye molecule. The area of p-nitrophenol was calculated to be 52.5 square angstroms by Giles and Nakhwa (125).

The accuracy of this procedure was assessed by using a sample of Lot 322 of Hamilton PRP-1. Published figures (126) indicate that this lot has a specific surface area of 415 $m^2/g$ and the dye adsorption gave a result of 401 $m^2/g$. Obviously, this method is only useful for copolymers with relatively high surface areas (>50 $m^2/g$) if accurate results are needed.

Mercury porosimetry was used to determine the relative pore size distributions for the XAD copolymers. These data were collected by the members of the Materials Analysis Laboratory using a Quantachrome Scanning Mercury Porosimeter.

## Chloromethylation procedure

The chloromethylation reactions were carried out in a two-neck 250-mL round-bottom flask. One neck was fitted with a rubber stopper which held a gas delivery tube which reached to the bottom of the flask. This tube was used for bubbling HCl gas through the reaction mixture. The other neck was fitted with a vent consisting of a 24/40 standard taper inner joint, the top of which was drawn out to form a ribbed hose fitting. A length of Tygon tubing was attached to the hose fitting and the other end was submerged in a vessel containing sodium hydroxide solution to absorb the vapors being emitted from the flask. All chloromethylations were carried out in a good hood. CAUTION: The reaction between HCl and paraformaldehyde can produce bis-chloromethylether (bis-CME) (80) which is a carcinogen now under government scrutiny (127). Therefore, the above precautions should be observed. If small quantities of paraformaldehyde are used and the reactions are carried out for short periods of time at room temperature, the formation of bis-CME should be minimized. Also, the base trap should hydrolyze the bis-CME to formaldehyde. This reaction should not be carried out outside of a hood, even with the use of a trap.

The reaction was carried out using two basic procedures depending on what HCl concentration was to be used. If a concentration less than 12 M was needed, the following practice was employed: A suitable quantity of concentrated hydrochloric acid was added to the reaction flask and the appropriate amount of paraformaldehyde was added and dissolved by stirring and bubbling HCl gas through the mixture. The copolymer was wetted with the diluent (usually glacial acetic acid) and was agitated in an ultrasonic bath to break up any clumps of beads. When the paraformaldehyde was dissolved completely, the slurry of copolymer plus diluent was added to the reaction vessel. Any residual copolymer was rinsed out of its container with the remaining diluent and was added to the reaction mixture. The addition of the copolymer usually required less than a minute to complete and the reaction was timed as soon as the copolymer was completely added to the mixture.

If the use of 12 M HCl was necessary, the method of introducing the copolymer into the reaction vessel had to be modified. The copolymer was wetted with the solvent normally used as a diluent (glacial acetic acid), but then the diluent was filtered off and the copolymer was rinsed once or twice with 12 M HCl to displace any remaining diluent. The damp copolymer was then added to the reaction vessel. In this way, the copolymer was wetted and the HCl in the reaction mixture suffered no dilution.

Agitation of the suspension was accomplished only by the bubbling HCl gas. Macroreticular copolymers tend to be somewhat friable under mechanical agitation, especially at higher temperatures, so the above method of agitation was used as a precaution. While only a small amount of HCl should be consumed by the reaction, it was found that capacities would vary unacceptably unless HCl gas was bubbled through the mixture throughout the course of the reaction. Mechanical agitation which appeared to yield mixing equivalent to that achieved with the bubbling gas was wholly inadequate as far as reproducing capacities and reaching high capacities were concerned.

After the desired reaction time had elapsed, the chloromethylation process was quenched by adding water until the flask was full. The flask was allowed to stand for about fifteen minutes to allow any bis-CME to be hydrolyzed. The product was then filtered (in the hood) and washed with water, isopropyl alcohol, water and methanol.

### Amination procedure

Immediately after the chloromethylated product received its methanol rinse, it was suspended in an excess of 25% trimethylamine in methanol. Similar results were obtained using 25% trimethylamine in water as shown in Table 2.

Table 2. Equivalence of TMA in water and methanol[a]

| | TMA in water | | TMA in methanol | |
|---|---|---|---|---|
| resin | AN196A | AN196B | AN196C | AN196D |
| capacity (meq/g) | 0.032 | 0.033 | 0.034 | 0.034 |

[a] One batch of resin was chloromethylated and divided into four parts. Two portions were aminated with 25% TMA in methanol and two portions were aminated with 25% TMA in water.

Liquefied trimethylamine gas was also used with success, but is much less convenient to work with than the solutions. The methanol solution was used in most of this work. This reaction was allowed to continue for 24 hours in the unstirred solution. NOTE: Trimethylamine is highly volatile (b.p. 4°C) and has a disagreeable fishy odor. It should be used only in a hood.

Because it was decided to use the chloromethylation reaction to control the capacity of the resins, it was necessary to discover how long the amination reaction took to go to completion. At the time that this study was carried out, a quantity of chloromethylated XAD-4 was available. It has the smallest average pore diameter of the styrene-divinylbenzene XAD copolymers (50 angstroms), and so it was assumed that it would probably be the slowest to react. Small portions of the chloromethylated copolymer (0.5 g) were weighed and each was aminated with trimethylamine in methanol. The reactions were quenched at various times up to fifteen hours and the results are shown in Figure 2. The curve had not quite leveled out at fifteen hours and since the time period was already so long, the decision was made to run all aminations for 24 hours to insure both completeness and uniformity.

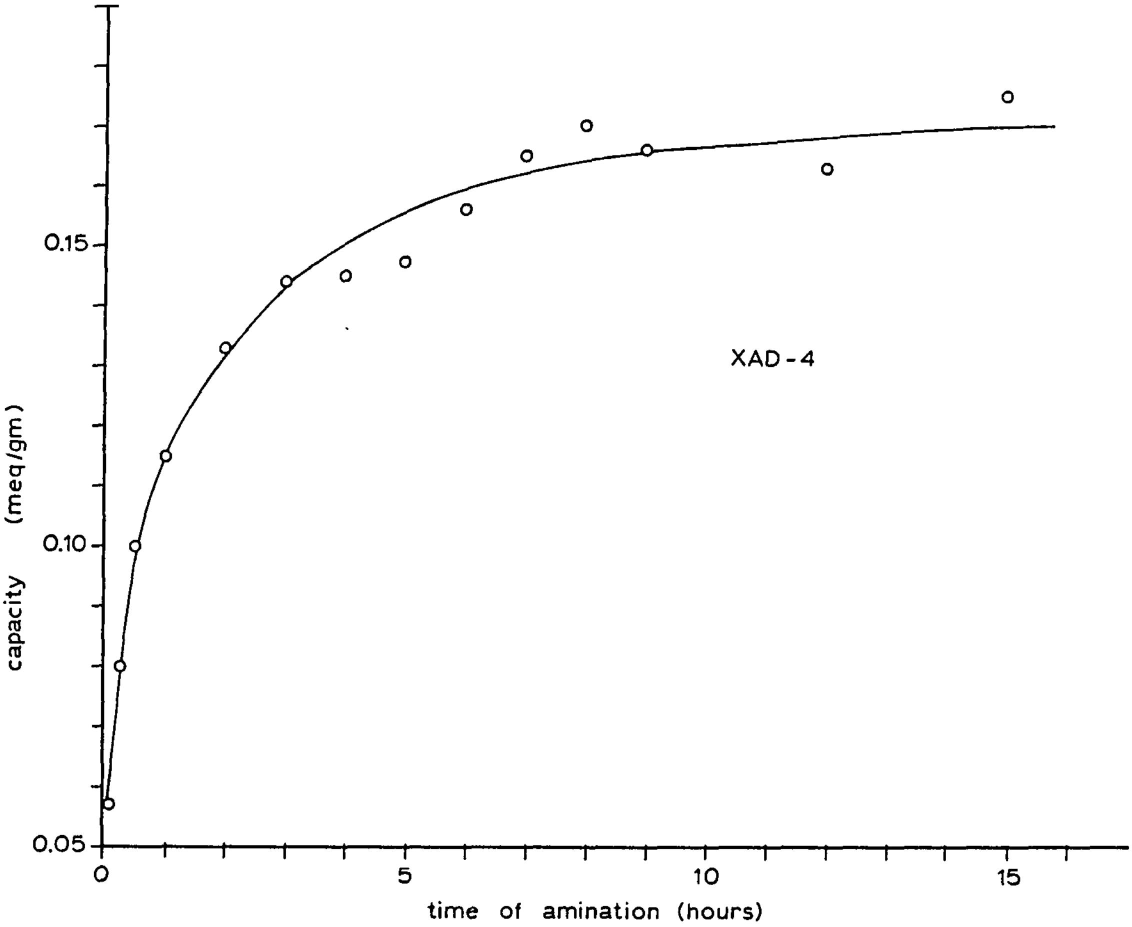


Figure 2. Capacity vs. reaction time for the amination of XAD-4 with trimethylamine in methanol.

## Characterization

The parameter which is of the most concern in this study is the strong-base anion-exchange capacity of the resin. Normally, the capacity of an ion-exchange resin is determined titrimetrically (128), but the capacities of these resins are too low to allow accurate titrations. The method that is used is a column ion-exchange technique. A sample of the resin (0.15-0.25g) is packed into a 10 cm. column fitted at the top with a 24/40 standard taper outer joint. It is then converted to the nitrate form using 15 mL of 0.5 M nitric acid. The resin bed is then rinsed with five column volumes of water (ca. 75 mL) This volume is necessary to make sure that removal of non-bound $NO_3^-$ is complete. See Table 3. The table represents a "worst case" in which 30 mL of 1 M nitric acid is used to perform the original resin conversion. The combination of the use of less nitrate and five rinses for actual determinations should insure that all interstitial $NO_3^-$ is removed. After rinsing, the bound $NO_3^-$ is eluted from the resin using 15 mL of 0.005 M $K_2SO_4$. The sulfate has such an affinity for the resin that it easily drives off the nitrate. The sulfate eluent containing the nitrate plus one column volume of rinse water is collected in a volumetric flask and then the nitrate is determined spectrophotometrically at 225 nm.

Table 3. Effectiveness of column rinsing for $NO_3^-$ removal

| column volume | Absorbance @ 225 nm[a] |
|---|---|
| 1 | 1.073 |
| 2 | 0.016 |
| 3 | 0.005 |
| 4 | 0.004 |
| 5 | 0.002 |

[a] Each successive column volume of rinse water was collected in a 50-mL volumetric flask and diluted to the mark.

This method excludes any weak base functional groups from being counted because the pH of the wash water is high enough to cause any such groups to become deprotonated.

The determination is quite repeatable as demonstrated by the data in Table 4. Four samples were obtained from one batch of anion-exchange resin. The resin was initially in the chloride form. Each sample was packed in a column and run through the $NO_3^-/SO_4^=$ cycle four times. The absorbance data for each sample show that the determination is reproducible on a given sample and the calculated capacities show that the determination is repeatable among different samples of the same batch.

Elemental analyses were carried out by members of the Ames Laboratory Analytical Services Group. The nitrogen analyses were carried out on a Perkin-Elmer Model 240 Elemental Analyzer and the chlorine analyses were carried out using an oxygen flask combustion technique with the appropriate finish.

### Column packing

Almost all of the chromatographic work was carried out using glass columns with dimensions of 500 mm x 2.0 mm i.d. These columns were packed using a balanced density slurry. The columns were packed in the upward direction using a

Table 4. Reproducibility of capacity determination for anion exchangers of low capacity (XAD-1)

| | S1[a] | S2 | S3 | S4 |
|---|---|---|---|---|
| weight | 0.2090g | 0.2238g | 0.1791g | 0.2769g |
| | | Absorbance Data | | |
| trial | S1 | S2 | S3 | S4 |
| 1 | 0.313 | 0.336 | 0.268 | 0.421 |
| 2 | 0.315 | 0.329 | 0.270 | 0.423 |
| 3 | 0.310 | 0.337 | 0.269 | 0.422 |
| 4 | 0.311 | 0.339 | 0.270 | 0.420 |
| avg. | 0.312 | 0.335 | 0.269 | 0.422 |
| std. dev. | ±0.0022 | ±0.0043 | ±0.00096 | ±0.0013 |
| rel. | ±(0.71%) | ±(1.3%) | ±(0.36%) | ±(0.31%) |
| | S1 | S2 | S3 | S4 |
| capacity (meq/g) | $0.043_5$ | $0.043_7$ | $0.043_9$ | $0.044_4$ |

[a] S1="Sample" 1.

reservoir of the type shown in Figure 3. The densities of the copolymers were determined using a pycnometer according to a known procedure (129). The density was then matched to a solution of water and ethylene glycol of the correct proportions. The density of XAD-1 was found to be $1.05_7$ g/mL. This corresponds to a solution of 40% ethylene glycol in water. The columns were normally packed at a pressure of 10,350 kPa (1500 psi) and were operated under pressures of about 2100 kPa (300 psi).

## Results and Discussion

### Choice of macroreticular substrate

Although XAD-1 had been used with some success by Gjerde et al. (17,18), it was thought that other macroreticular copolymers might be more useful, especially if they were available in the form of small spherical beads rather than large irregular shards. Accordingly, a number of styrene-divinylbenzene copolymers were obtained from the companies listed in the Experimental section. However, it soon became clear that most of these copolymers would be unsuitable. Some of them proved to be almost uncontrollably reactive compared to XAD-1 which reacted in a slow, smooth

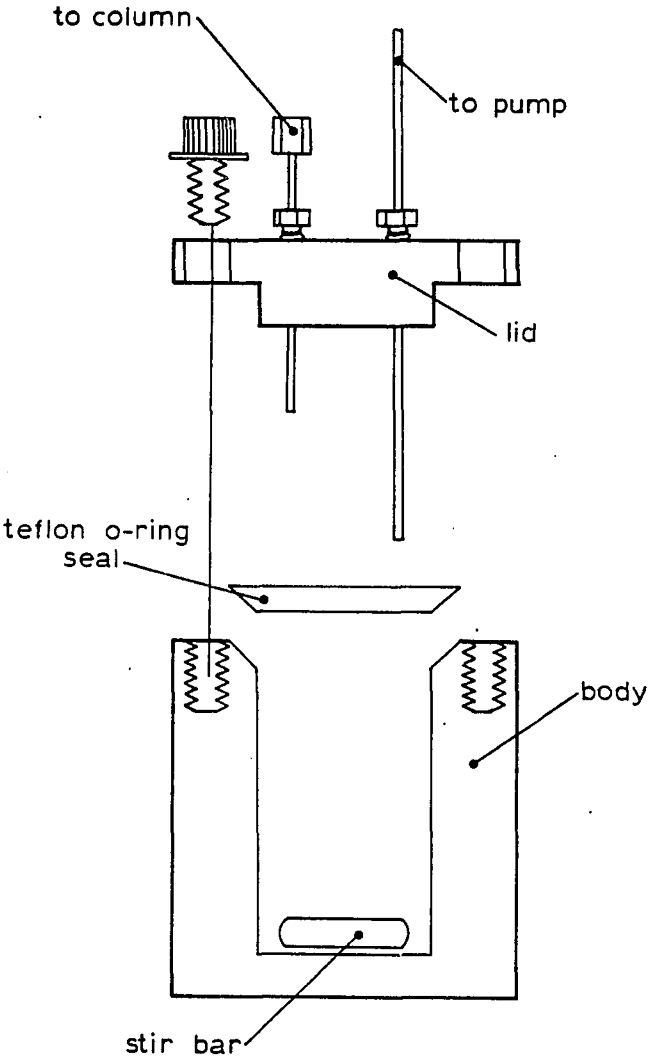


Figure 3. Cross-section of the slurry-packing chamber used to pack the chromatographic columns.

manner. A number of anion exchangers prepared from various copolymers were packed into columns and their behavior in chromatography was examined. Here, too, a spectrum of behavior was observed. Some resins took over a day of pumping to achieve equilibrium with the eluent and even then did not show signs of being extremely efficient despite their small size or their spherical nature. The only resin that equilibrated in a reasonably short time and seemed to yield good chromatograms was XAD-1. The reasons for this behavior were unknown. It was reasoned that since these copolymers are all nominally the same in chemical composition, (though with different proportions of monomers), physical characteristics must be the causes of their behavioral traits. The three most pertinent physical traits were judged to be surface area, pore size distribution and pore shape. The determination of a large number of pore size distributions would be prohibitively expensive, but the determination of a rough figure for surface area can be easily accomplished by using the adsorption of dye molecules of known area from a solution onto the copolymer.

The surface areas of all of the porous copolymers were determined by the adsorption of p-nitrophenol from solution as outlined in the Experimental section. Pore size distributions were also run on the copolymers XAD-1, XAD-2 and XAD-4 in the hope of seeing something different in XAD-1 compared to the other two materials. At the same time, each copolymer was chloromethylated and aminated under a set of "standard conditions" with the thought that perhaps reactivity might correlate with surface area. The standard chloromethylation conditions included 8 M HCl, 2.2 M formaldehyde, and a one hour reaction time at room temperature. Amination was carried out as usual.

The composition of the copolymers procured from the Benson Co. is shown in Table 5 along with the ion-exchange capacity which was generated with each under these standard reaction conditions. The table contains information for a number of gel resins which were also subjected to these conditions. No evidence of anion-exchange activity was exhibited by these gels. Also, a 2% cross-linked gel obtained from Dow Chemical Co. was chloromethylated for three hours at 55°C using 12 M HCl and 2.2 M formaldehyde and showed absolutely no measurable capacity after amination with trimethylamine according to standard practice. Table 5 indicates that a significant amount of pore-forming agent needs to be present in order for the copolymer to be reactive. Those that did not react under standard conditions failed to do so under more strenuous conditions.

Table 5. The relationship of polymer composition to capacity under standard reaction conditions

| resin | styrene | (52%) divinylbenzene | solid diluent[a] | capacity (meq/g) |
|---|---|---|---|---|
| A-104 | 95% | 5% | --- | ---- |
| 1-65 | 94 | 6 | --- | ---- |
| A-38 | 92 | 8 | --- | ---- |
| A-165 | 85 | 15 | --- | ---- |
| A-170 | 65 | 35 | --- | ---- |
| A-197 | 64.5 | 35 | 0.5% | ---- |
| A-210 | 91.5 | 6 | 2.5 | ---- |
| A-198 | 62.5 | 35 | 2.5 | ---- |
| A-177 | ---- | 95 | 5 | ---- |
| A-176 | ---- | 85 | 15 | 0.0027 |
| A-179 | ---- | 75 | 25 | 0.20 |
| A-128 | ---- | 67 | 33 | 0.15 |
| A-134 | ---- | 67 | 33 | 0.26 |
| A-142 | ---- | 40 | 60 | 0.31 |
| A-138 | ---- | 33 | 67 | 0.35 |

[a] Pore forming agent.

The A-176 copolymer could be functionalized to usable levels if fairly vigorous reaction conditions were employed. Fifteen percent appears to be the threshold of the concentration of pore-forming agent needed to prepare a reactive bead. However, because no control over manufacturing processes was possible, it is not known how the preparative method influenced the physical properties of the copolymer. A display of the surface area of the reactive copolymers along with the capacity that was achieved with each under standard conditions is even more revealing. This is shown in Figure 4. These data show that XAD-1 is virtually alone with its particularly low surface area and reactivity. The other porous copolymers are significantly more reactive. The capacity of each copolymer was found to be roughly proportional to its surface area. This can be seen especially in a series which is carefully manufactured such as XAD-1, XAD-2 and XAD-4.

The high surface area of most of the copolymers probably accounts for their slow equilibration with the eluent as well. It is speculated that one reason for the broad peaks observed with most of these other copolymers is that the pore size distributions are more heavily skewed toward small sizes. The literature of the manufacturer indicates that

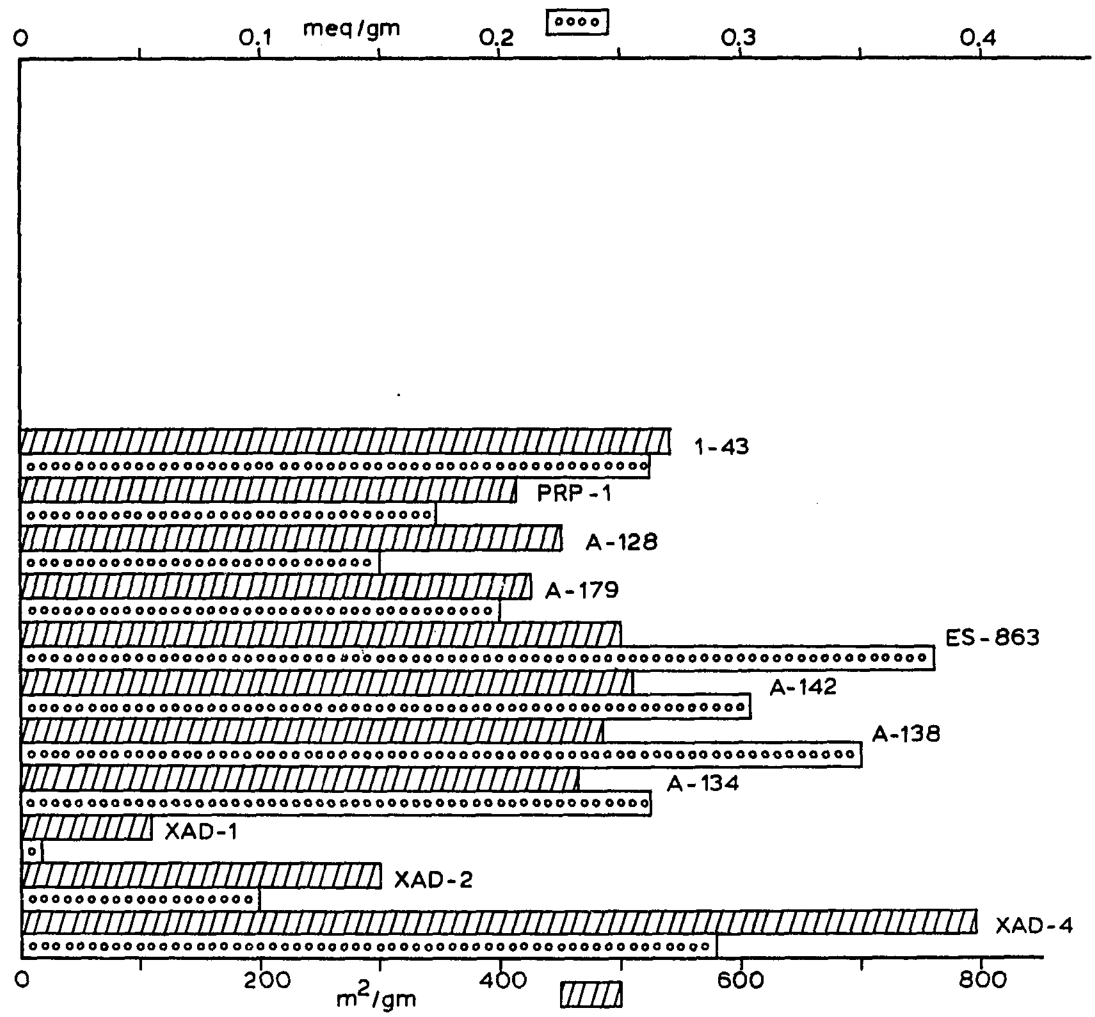


Figure 4. Comparison of surface areas and relative reactivities for several porous styrene-divinylbenzene copolymers.

the average pore diameter of XAD-1 is larger than 200 angstroms, whereas that of XAD-2 is about 90 angstroms and that of XAD-4 is about 50 angstroms. If there were larger proportions of small pores in the beads with high surface areas, the movement of a hydrated ion through such a bead would necessarily be slower and more tortuous than through a bead with a lot of large pores. This roundabout path would contribute to spreading out the band of a particular ion on the column.

The relative pore size distributions of these three copolymers (as obtained by mercury porosimetry) are shown in Table 6. (A good general discussion of the principles of mercury porosimetry can be found in the dissertation of O.Z. Cebeci (130).) The raw data produced by the porosimeter are converted into percent volume over a given pore size range according to a simple procedure (131). The percentage of total pore volume above 500 Angstroms was negligible in each case. It can be seen that XAD-1 does indeed have a larger percentage of its pores concentrated in the range of 100-500 Angstroms. Because of the layout of the raw graphical data supplied by the porosimeter, it is difficult to obtain more detailed information about the larger pore size ranges.

A potentially more significant difference can be found in another parameter. The porosimeter shows how much

Table 6. Relative pore-size distributions of XAD-1, XAD-2, and XAD-4

| pore size range | % of total pore volume<br>XAD-1 | XAD-2 | XAD-4 |
|---|---|---|---|
| 18-20 Angstroms | 0.83 | 1.06 | 1.01 |
| 20-30 | 4.03 | 5.46 | 5.25 |
| 30-40 | 3.78 | 4.82 | 4.65 |
| 40-50 | 3.44 | 4.33 | 4.26 |
| 50-100 | 15.22 | 16.50 | 16.50 |
| 100-500 | 72.73 | 67.83 | 68.32 |

(percentage) of the total pore volume of the sample empties when the mercury pressure is released. Only 17% of the pores in XAD-1 empty, whereas the analogous figures for XAD-2 and XAD-4 are 45 and 55% respectively. The degree to which the pores empty reflects the shape of the pores (132). The high degree of emptying exhibited by XAD-2 and XAD-4 probably indicates a high proportion of tubular capillary pores. The low degree of emptying exhibited by XAD-1 is probably indicative of pores which are shaped like long strings of interconnected spherical cavities. Because mercury and water are both non-wetting fluids for polyolefins, it is anticipated that aqueous solutions would show the same emptying behavior in these copolymers. It is not known what impact this parameter has on chromatographic performance or if it is a significant parameter at all, but it is about the only glaring difference between the three copolymers as indicated by mercury porosimetry. This is an area that deserves further study, but is outside of the scope of this work and was not pursued further.

The combination of easily controlled reactivity, rapid equilibration with eluents and fairly good chromatographic efficiency led to the choice of XAD-1 as the major copolymer to be used in this study. It is anticipated that if a spherical bead of ten-micrometer diameter should become available which possesses the physical characteristics of XAD-1, the chromatographic efficiency could be increased dramatically.

## Concentration of HCl and formaldehyde

The. concentrations of HCl and formaldehyde were studied concurrently in various combinations. The paraformaldehyde concentration was varied from 0.22 M (as formaldehyde) to 2.8 M, which was approaching the amount that would easily go into solution. (Formalin could not be used as a source of formaldehyde as it seemed to be inactive. This is probably because of the methanol which it contains as a polymerization inhibitor. Methanol is known to be detrimental to the reaction when present in the system (133).)

Hydrochloric acid concentrations ranged from 6-12 M. Below 6 M HCl, the resin capacities were very low and were not generally in a useful range. The concentrations of hydrochloric acid reported are the initial concentrations, no corrections being made for volume changes on mixing or for any additional HCl that might have been absorbed while the gas was bubbled through the reaction mixture. Although it seems unlikely that these effects could be ignored, literally hundreds of batches of resin have been prepared and the final capacity could always be related to the initial concentration of HCl.

Because the copolymer matrix is so hydrophobic, a wetting agent must be used to facilitate the suspension of the particles in the aqueous medium. Glacial acetic acid was used in this phase of the investigation. A total volume of 30 mL of liquid was used and one gram of copolymer was chloromethylated in each reaction. The reaction was repeated at least twice at each set of conditions and the capacity of each batch of resin was determined using duplicate samples. The reactions were carried out at room temperature (23°C) for one hour to minimize the effects of small timing errors. The results are summarized in Table 7.

The first fact of note is that above 1.7 M, the formaldehyde concentration seems to have no influence on the final capacity of the resin. This is not clear at 6 M HCl but is easy to see above this concentration of acid. This fortuitous occurrence eliminates one variable from consideration and thereby makes control of the capacity easier if one can keep the formaldehyde concentration in this plateau region. It is not clear exactly why the anion-exchange capacity is so insensitive to the formaldehyde concentration. The generally accepted mechanism for this form of the reaction (78-83) is one in which the electrophile ($^+CH_2OH$) attacks the aromatic ring to form a

Table 7. Effect of reagent concentrations on anion-exchange capacity

| Formaldehyde concentration | Resin capacity, meq/g, at the given HCl concentration. | | | |
|---|---|---|---|---|
| | 6 M | 8 M | 10 M | 12 M |
| 0.22 M | ---- | ---- | 0.010 | 0.046 |
| 0.56 M | ---- | ---- | 0.019 | 0.067 |
| 1.1 M | 0.0056 | 0.0082 | 0.028 | 0.086 |
| 1.7 M | 0.0069 | 0.013 | 0.033 | 0.088 |
| 2.2 M | 0.0052 | 0.014 | 0.030 | 0.080 |
| 2.8 M | 0.0080 | 0.014 | 0.032 | 0.084 |

hydroxymethylated moiety. Then, the hydroxymethyl group is converted to a chloromethyl group by the HCl which is present. If one accepts this mechanism, then a conceivable explanation is that above 1.7 M formaldehyde, the diffusion of the electrophile from the bulk solution into the bead and to the copolymer surface controls the rate of reaction. The amount of hydrogen ion needed to effect the reaction should be theoretically only a catalytic amount, so it is likely that the large amounts of acid present can form the electrophile faster than it can be used up. Therefore, one would expect more electrophile to be present at 12 M HCl than at 6 M HCl. Fick's First Law of Diffusion states that the mass flux of a species is proportional to the concentration gradient (134), so if more electrophile is present at 12 M HCl, one would expect that the rate of diffusion would be greater and so the degree of functionalization would be higher in a given time period than it would be at 6 M HCl. This appears to be the case according to Table 7.

An alternative explanation is that because of this excess of hydrogen ion, the degree of hydroxymethylation is the same for all acid concentrations if the formaldehyde concentration is above 1.7 M. Then, the assumption is that the degree of conversion of the hydroxymethyl groups to chloromethyl groups depends on the concentration of HCl. This would then make it necessary for there to be a large number of unreacted hydroxymethyl groups on the copolymers prepared with 6 M HCl. The results shown in Table 8 seem to favor the first explanation. The batch designated as AH2 was prepared with 3 M HCl and 2.2 M formaldehyde and the batch designated as AH3 was prepared with 12 M HCl and 2.2 M formaldehyde. Both batches were dried and half of each was treated with chloroacetyl chloride to react with any leftover hydroxymethyl groups. The other half of each batch was reacted with trimethylamine. The results show only a small difference in chlorine analysis between the plain chloromethylated copolymer and the chloromethylated copolymer after treatment with chloroacetyl chloride for both the 3 M and 12 M reactions. This indicates that there are very few residual groups left on the chloromethylated copolymers which are capable of reacting with the acid chloride.

The chlorine analyses in Table 8 indicate that the resins are not that far away from each other in chlorine content, but yet their ion-exchange capacities are separated by a wide gulf. It was not known whether this was a chance happening or not, so more batches of chloromethylated

Table 8. Comparison of plain and treated chloromethylated copolymer by chlorine analysis (Treatment with chloroacetyl chloride)

| batch | molarity[a] HCl | % chlorine (before) | % chlorine (after) | % nitrogen[b] | strong base capacity[c] |
|---|---|---|---|---|---|
| AH2 | 3 M | 0.42 | 0.46 | 0.39 | 0.0022 |
| AH3 | 12 M | 0.55 | 0.62 | 0.61 | 0.065 |

[a] Used in chloromethylation reaction.

[b] In aminated resin (chloride form).

[c] In meq/g.

copolymer were prepared. Table 9 shows the chlorine analysis values for four batches of chloromethylated copolymer. The chloromethylations were carried out using 2.2 M formaldehyde in all four reactions but the HCl concentration was varied from 3 M to 12 M and the reactions were carried out at room temperature for one hour each. The table shows that the chlorine analyses are again rather close together compared to the expected anion-exchange capacities. One would expect the anion-exchange capacities to be closer together if all of the chlorine was present in chloromethyl groups. Therefore, chlorine must be introduced into the copolymer in some other way besides chloromethyl groups. It is doubtful that there are residual vinyl groups which can add HCl so it is not known what form this extra chlorine is in.

One other unexpected aspect of the resins can be seen in Table 10. This table shows a comparison of the nitrogen analyses for a few batches of resin compared to the actual strong-base anion-exchange capacities obtained with these resins. The identity of the nitrogen in excess of the strong-base capacity is unknown. It is possible that the nitrogen is present as weak-base functional groups. A sample of XAD-1 with a capacity of 0.15 meq/g was converted

Table 9. Chlorine analyses of four batches of chloromethylated copolymer compared to the expected ion-exchange capacity for each resin

| batch | molarity[a] HCl | % chlorine | expected[b] capacity | found[c] capacity |
|---|---|---|---|---|
| AN415 | 3 M | 0.43 | <0.005 | 0.0027 |
| AN416 | 6 M | 0.42 | 0.007 | 0.0063 |
| AN417 | 9 M | 0.48 | 0.025 | 0.021 |
| AN418 | 12 M | 0.59 | 0.085 | 0.080 |
| blank | -- | <0.01 | ----- | ----- |

[a] In chloromethylation reaction.

[b] If aminated with trimethylamine; (meq/g).

[c] In meq/g.

Table 10. Comparison of strong-base anion-exchange capacity calculated from nitrogen analysis to actual strong-base ion-exchange capacity

| Resin | % nitrogen | calc. capacity[a] | found capacity[a] | $\frac{\text{found}}{\text{calc.}} \times 100$ |
|---|---|---|---|---|
| AN237[b] | 0.54 | 0.38 | $0.28_4$ | 75 |
| AN241[b] | 0.56 | 0.40 | $0.29_4$ | 74 |
| AN244[b] | 0.59 | 0.42 | $0.30_6$ | 73 |
| AN328[c] | 0.28 | 0.20 | $0.15_1$ | 76 |

[a] In meq/g.

[b] Made from ES-863 copolymer.

[c] Made from XAD-1 copolymer.

to the hydroxide form and directly titrated with standard acid. The titration curve was difficult to obtain because of the low capacity of the resin, but there were two inflection points. This is indicative of some weak base functionality but the reason for its presence is unknown. It is remotely possible that the excess nitrogen is present as trimethylamine that is trapped in the pores of the resin. This is suggested by the fact that if a resin (which has been washed and dried) is stored in a sealed bottle for a while, a slight odor of trimethylamine will be evident when the bottle is reopened.

The odor of trimethylamine does not appear to arise from the degradation of functional groups. Because the vials which had an odor of trimethylamine present had been stored for a few weeks on the laboratory benchtop, it was decided to test the stability of the resins toward exposure to the ultraviolet component of fluorescent room lights. To accomplish this end, a batch of resin was prepared and, when dry, was split in half. This batch of resin had a capacity of 0.030 meq/g. Half of the material was stored in the dark and half was spread in a thin layer in the bottom of a Petri dish. This half of the resin was then exposed to long-wave ultraviolet radiation (from a thin layer chromatography visualization lamp) for eight hours each day at a distance of one centimeter from the resin. This radiation was continued until 96 hours of exposure had been accumulated. A sample was taken after every 32 hours of exposure and no loss of capacity was noted even after 96 hours of exposure to the UV light. Also, the capacity was never different from samples taken from the resin which was stored in the dark during the period of irradiation.

The capacities of two batches of resin were determined when the resins were fresh and after about 15 months of dry storage in sealed vials. The resin batches AN312 and AN317 had initial capacities of 0.040 and 0.046 meq/g respectively. After the storage period, the capacities were exactly the same as those determined when the resins were fresh, thus indicating that dry storage has essentially no effect on the resins.

The wet storage of the resins was not investigated systematically, because resins were not normally stored for long periods of time while wet. However, occasional spot-checks of resins which had been stored wet while packed in columns showed some loss of capacity after two months of such storage. Therefore, it is recommended that all resins be stored dry when not in use.

Particle size

The effect of the copolymer particle size on final resin capacity was examined using the following size fractions of pulverized XAD-1: 38-45 micrometer, 45-53 micrometer, 53-75 micrometer, 75-104 micrometer, 104-150 micrometer, and 150-180 micrometer. The HCl concentration for all batches was 10 M and the formaldehyde concentration was 2.2 M. The reactions were carried out at room temperature for one hour. Each particle size range was represented by three batches of resin and the capacity of each of these batches was determined in duplicate. The results are shown in Table 11.

There is no significant change of capacity with a change in particle size. This is a reasonable result because the inner surface area of a macroreticular copolymer is much greater than the increase that would be expected from grinding the beads into smaller particles.

Once these results were known, particles in the size range of 75-150 micrometers were used for most experimentation because they are considerably easier to prepare than those of the size used in chromatography.

The capacity of some unground beads (250-850 micrometer) treated under the same conditions was slightly higher than the pulverized beads by about three microequivalents/g. It is not known why this occurred. However, it is not

Table 11. Particle size vs. anion-exchange capacity under one set of reaction conditions

| | Particle size (micrometers) | | | | | |
|---|---|---|---|---|---|---|
| | 150-180 | 104-150 | 75-104 | 53-75 | 45-53 | 38-45 |
| batch 1 | 0.028[a] | 0.029 | 0.029 | 0.028 | 0.028 | 0.031 |
| batch 2 | 0.028 | 0.029 | 0.028 | 0.028 | 0.030 | 0.028 |
| batch 3 | 0.029 | 0.029 | 0.028 | 0.030 | 0.028 | 0.029 |
| average | $0.028_3$ | 0.029 | $0.028_3$ | $0.028_7$ | $0.028_7$ | $0.029_3$ |

[a] All capacity values have units of meq/g.

significant because the unground beads are not used in any facet of the investigation.

### Time of chloromethylation

The time of chloromethylation was studied while holding all other parameters constant. Hydrochloric acid concentrations of 8 M, 10 M, and 12 M were used. The formaldehyde concentration was 2.2 M for all reactions. One gram of XAD-1 was used for each batch and two batches were made for most reaction times. The reactions were all run at room temperature. The results are shown in Figure 5. Typically, the shorter the reaction time chosen for chloromethylation, the more difficult it is to predict the final anion-exchange capacity. However, chloromethylation times of five minutes have been used successfully to produce batches of resin whose capacities agree quite closely.

### Reaction temperature

The effect of reaction temperature on the extent of chloromethylation was also studied. It is sometimes desirable to have a resin with an exchange capacity greater than 0.086 meq/g. This is about the maximum attainable at room temperature using an XAD-1 substrate without going to an extremely long chloromethylation time. Accordingly,

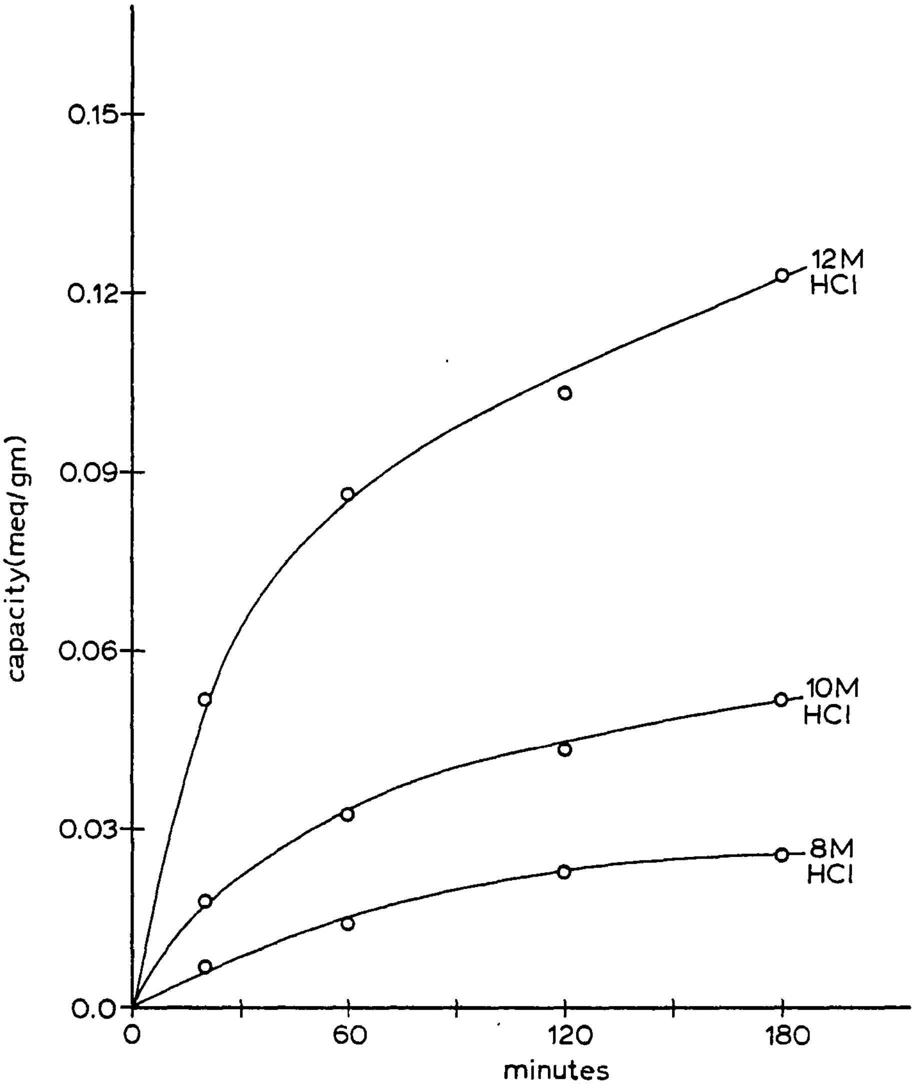


Figure 5. Relationship of capacity to time of chloromethylation and to HCl concentration.

reactions were run at temperatures of 10°C, 30°C, 50°C and 70°C in a constant temperature bath with one gram of XAD-1 copolymer for one hour. The reactions were run using a 2.2 M formaldehyde concentration and 10 M and 12 M HCl concentrations. The results of this study are summarized in Table 12. The results obtained at higher temperatures were slightly less reproducible than those at room temperature, but were still quite good. Also, the results at 30°C appear to match those reported earlier for room temperature. This is because the reactions run at 30°C were run in a thermostatted bath, whereas the reactions run at room temperature were run in a non-thermostatted flask. This allowed the temperature to increase somewhat during the room temperature reaction causing results to be equivalent to those obtained at 30°C in the constant temperature bath.

### Wetting agent

Several solvents were compared as the wetting agent for the chloromethylation reaction. The reaction mixture contained 25 mL of concentrated HCl, 5 mL of the wetting agent being tested (resulting in a 10 M initial HCl concentration), 2.2 M formaldehyde and one gram of XAD-1. The reaction time was again one hour. The results are shown in Table 13. Clearly, glacial acetic acid and dimethyl sulfoxide interfere the least with the chloromethylation

Table 12. Dependence of capacity on chloromethylation temperature

| | Capacity (meq/g)[a] | |
|---|---|---|
| Temp, °C | 10 M HCl | 12 M HCl |
| 10 | 0.019 | ----- |
| 30 | 0.031 | 0.086 |
| 50 | 0.050 | 0.116 |
| 70 | 0.076 | 0.159 |

[a] Average of two batches.

Table 13. Effect of wetting agent identity[a]

| Wetting Agent | Resin Capacity |
|---|---|
| glacial acetic acid | 0.032 meq/g |
| dimethyl sulfoxide | 0.030 |
| ethylene glycol | 0.014 |
| propionic acid | 0.013 |
| propylene glycol | 0.011 |
| ethanol (95%) | 0.0068 |
| isopropyl alcohol | 0.0067 |
| tetrahydrofuran | 0.0062 |

[a] All reaction conditions were identical except for the identity of the wetting agent.

reaction. Glacial acetic acid was selected as being more agreeable to use than dimethyl sulfoxide. The choice of a wetting agent is, of course, most critical when less than 12 M HCl is being used in the reaction.

### Miscellaneous considerations

The ion-exchange capacities of these resins seem to be independent of the amount of copolymer present in a given volume of reaction mixture as long as the concentrations of soluble components remain constant. Most of the reactions done for this section of the dissertation were done using one gram of copolymer in a total of 30 mL of reagent solution. To ascertain the effect of having more or less volume in relation to the weight of copolymer, several batches of resin were prepared using one gram of copolymer and volumes of 12 mL to 90 mL. The concentrations of all soluble components were kept equal in all batches. The capacities of the resins obtained through these reactions were about the same as those obtained using 30 mL of reagents. The results are shown in Table 14. This is the behavior that would be expected if the activity of a solid is taken to be equal to one.

The preparation of these resins was normally done in small batches of about one gram in order to conserve

Table 14. Effect of changes in the ratio of reagent volume to weight of copolymer being chloromethylated

| batch | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| weight of copolymer (grams) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| ml glacial acetic acid | 4 | 7 | 10 | 15 | 20 | 25 | 30 |
| ml HCl (conc.) | 8 | 14 | 20 | 30 | 40 | 50 | 60 |
| total vol. (ml) | 12 | 21 | 30 | 45 | 60 | 75 | 90 |
| grams of paraformaldehyde | 0.8 | 1.4 | 2.0 | 3.0 | 4.0 | 5.0 | 6.0 |
| capacity (meq/g) | 0.015 | 0.017 | 0.013 | 0.013 | 0.010 | 0.016 | 0.016 |
| ratio[a] | 12:1 | 21:1 | 30:1 | 45:1 | 60:1 | 75:1 | 90:1 |

[a] Ratio = (reagent volume/weight of copolymer).

carefully sized copolymer, but batches of up to five grams have been made without any difficulty. The only precaution necessary is to make sure that the method of gas dispersion used for the HCl is efficient enough to saturate the increased volumes associated with the larger batches.

When the resins are dried prior to capacity determination, it is imperative that they be air-dried rather than oven-dried. The resins in this study were originally oven-dried and this practice resulted in erratic, occasionally large losses of capacity. Some batches were not affected, whereas some lost up to 50% of their expected capacity. Resins with a quaternary ammonium group are known to deteriorate at high temperatures when they are in the hydroxide form (135); however, all of these resins were in the chloride form. The mechanism responsible for the loss of capacity in these resins is unknown. An air-drying period of 48 hours was used thereafter and no unexplained losses of capacity were noted in subsequent batches of resin.

### Comparison of copolymer substrates

Although a large majority of the work was performed on XAD-1 copolymer, several anion exchangers were made starting with other copolymer substrates. The experiments with the other copolymers show that this chloromethylation reaction works in the same general way as with XAD-1. This method of resin preparation can be easily adapted to any porous copolymer. The other copolymers that were examined for the purpose of this report were Rohm and Haas XAD-2, Benson A-128 and Diamond Shamrock ES-863. All three are porous styrene-divinylbenzene copolymers, although the porosity of each is generated in a different manner. The ES-863 is particularly different from the others as it will increase in volume by about 80% when soaked in methanol, whereas the other copolymers are not noticeably affected by methanol. Table 15 summarizes the behavior of all resins examined under four sets of conditions which bracket the concentrations found to be useful with XAD-1. The capacities of all four copolymers show relatively little sensitivity to the amount of formaldehyde present in the range which was examined. Most of the time, the ion-exchange capacity of a resin was easily varied by changing the concentration of HCl used during the chloromethylation. The capacities of repetitive batches agree fairly well, though this is less true as the surface area of the copolymer increases.

It is believed that in all of the copolymers, the functional groups are introduced onto the fixed inner

Table 15. Comparative behavior of four copolymers under certain chloromethylation conditions

| | | Capacity at conditions listed[a] (meq/g) | | | |
|---|---|---|---|---|---|
| copolymer | Approx. surface area | 1[b] | 2[c] | 3[d] | 4[e] |
| XAD-1 | 110 $m^2/g$ | 0.0056 | 0.0080 | 0.086 | 0.084 |
| XAD-2 | 300 | 0.057 | 0.065 | 0.197 | 0.194 |
| A-128 | 450 | 0.169 | 0.186 | 0.237 | 0.232 |
| ES-863 | 500 | 0.281 | 0.302 | 0.596 | 0.538 |

[a] Reactions were run for one hour at room temperature.

[b] 6 M HCl, 1.1 M formaldehyde.

[c] 6 M HCl, 2.8 M formaldehyde.

[d] 12 M HCl, 1.1 M formaldehyde.

[e] 12 M HCl, 2.8 M formaldehyde.

surface of the porous beads without any significant penetration of the copolymer matrix. This is suggested by three observations: 1) Gel copolymers (which have no easily accessible inner surfaces) show no evidence of ion-exchange capacity under conditions which would produce fairly high capacities in XAD-1. Recall that XAD-1 has the lowest surface area of all of the porous copolymers examined; 2) the higher the surface area of the copolymer, the more ion-exchange groups are introduced in a given reaction time; and 3) each copolymer reaches a limit of ion-exchange capacity when reacted according to the procedures already described. This limit is proportional to surface area. The limiting capacities for XAD-1, XAD-2 and XAD-4 are about 0.16, 0.46 and 0.57 meq/g respectively. These capacities are not exceeded even at high concentrations of HCl, high temperatures and long chloromethylation times. (However, amination times longer than 24 hours would increase the capacity of these resins somewhat.) These capacities are lower than one would expect if every aromatic nucleus was to contain a functional group. They are also lower than the capacity that can be achieved when a polymer-swelling reagent such as chloromethylmethyl ether is used to effect the chloromethylation.

### Preparing resins of a desired capacity

The reaction conditions needed to attain a given ion-exchange capacity are easily estimated by plotting ion-exchange capacity against the concentration of HCl used in the chloromethylation reaction. It is best to keep the formaldehyde concentration high enough so that it no longer affects the reaction. At high HCl concentrations where the capacity increases rapidly with a small change in concentration, it is easier to adjust the time of chloromethylation rather than try to control the acid concentration. The recommended procedure is to use 12 M HCl and 2.2 M formaldehyde and then time the chloromethylation reaction to control the capacity. If too short a time is needed, then the concentration of formaldehyde can be lessened. This allows the HCl concentration to be kept at 12 M thus keeping the chloromethylation times as short as possible.

The capacities obtained by this reaction are easy to reproduce. The reproducibility was demonstrated by preparing eighteen different batches of resin under varying conditions, which, according to Table 7, should give the same capacity. The HCl concentration was 8 M in all reactions while five batches were made with 1.7 M formaldehyde, eight batches were made with 2.2 M formaldehyde, and five batches were made with 2.8 M formaldehyde. These reactions were spaced over the period of about a year in order to involve different lots of reagents. The average capacity of these eighteen batches of resin was 0.013 meq/g with a standard deviation of 0.002 meq/g. This small variation does not significantly affect the chromatographic behavior of the resin. The precision is not quite this good at higher concentrations of HCl, but is still adequate.

The reaction also seems to be reproducible from lot to lot of the copolymer. Table 16 shows the results of preparing anion exchangers from three separate lots of XAD-1 under the same conditions.

### Chromatographic separations

The resins made via the procedure just described exhibit good chromatographic performance within their limitations. It appears that the limiting conditions which now exist are the large size and irregular shape of the particles. A typical performance of the XAD-1 which is prepared for chromatography is usually about 2800 plates per meter based on the chloride peak while using a 1 mM benzoic acid eluent. Reproducible performance is not hard to achieve. As long as the capacities of different resins are the same, the performances seem to be equivalent if the columns are packed

Table 16.[a] Variation of anion-exchange capacity from one lot of XAD-1 copolymer to another

| | Lot 7800 | Lot 5079 | Lot 6-9511 |
|---|---|---|---|
| batch 1 | 0.052 meq/g | 0.046 | 0.044 |
| batch 2 | 0.044 | 0.041 | 0.046 |
| batch 3 | 0.048 | 0.050 | 0.051 |
| average | 0.048 | 0.046 | 0.047 |

[a] Chloromethylation conditions were constant at 12 M HCl, 2.2 M formaldehyde and a 20-min reaction at room temperature.

in the same fashion.

Figures 6, 7 and 8 show chromatograms which are routinely obtained with these resins. Chromatographic conditions are noted in the Figure captions. The separation of methanesulfonate and ethanesulfonate in Figure 7 is one which was recently reported as beyond the capability of dual-column ion chromatography (136).

Table 17 and Figures 9 and 10 compare resins made by the current procedure and conventional chloromethylation. The "conventional" chloromethylation was carried out by generating chloromethylmethyl ether in situ by the reaction between methylal and acetyl chloride in ethylene dichloride solvent. The catalyst used was $BiCl_3$ because it is less moisture sensitive than $ZnCl_2$ and is only slightly greater in catalyst strength. The same column was used for each resin and equivalent elution conditions were used. The behavior of the two resins is similar but not identical. The figures show that the conventional resin cannot resolve glycolate and azide whereas the HCl:formaldehyde resin can do so. Table 17 indicates that the polarizable late-eluting ions such as $I^-$ and $BF_4^-$ have longer retention times on the conventional resin. This last observation suggests that perhaps the conventional chloromethylation allows some

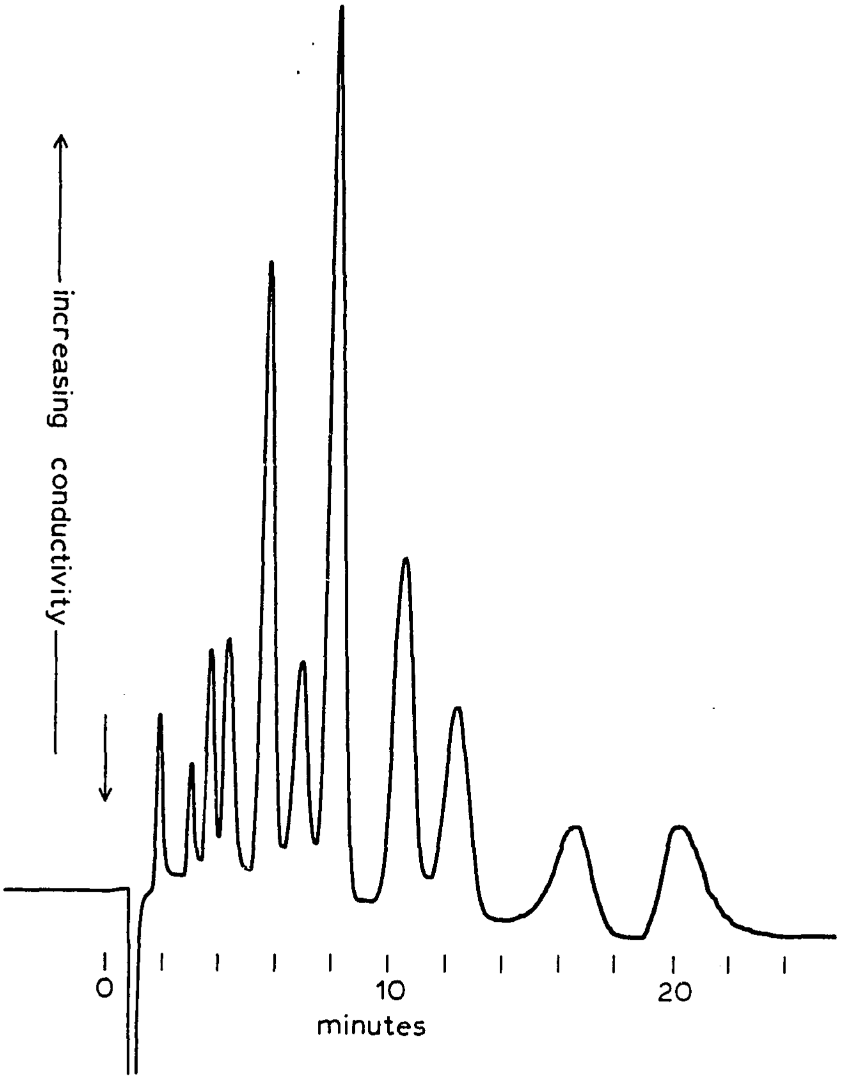


Figure 6. Separation of eleven monovalent anions in twenty minutes. Trimethylamine resin, 0.027 meq/g in a 500 x 2.0 mm i.d. column. Eluent: 0.001 M benzoic acid at a flow rate of 0.93 mL/min. Peak identities and concentrations are as follows in order of elution; acetate (20 ppm), azide (10 ppm), glycolate (14 ppm), formate (6.2 ppm), fluoride (4.0 ppm), dihydrogen phosphate (8.1 ppm), chloride (8.3 ppm), nitrate (8.3 ppm), chlorate (10.2 ppm), 1-propanesulfonate (16.7 ppm) and iodide (15.3 ppm). A 20 microliter sample was injected. (ppm = micrograms/mL)

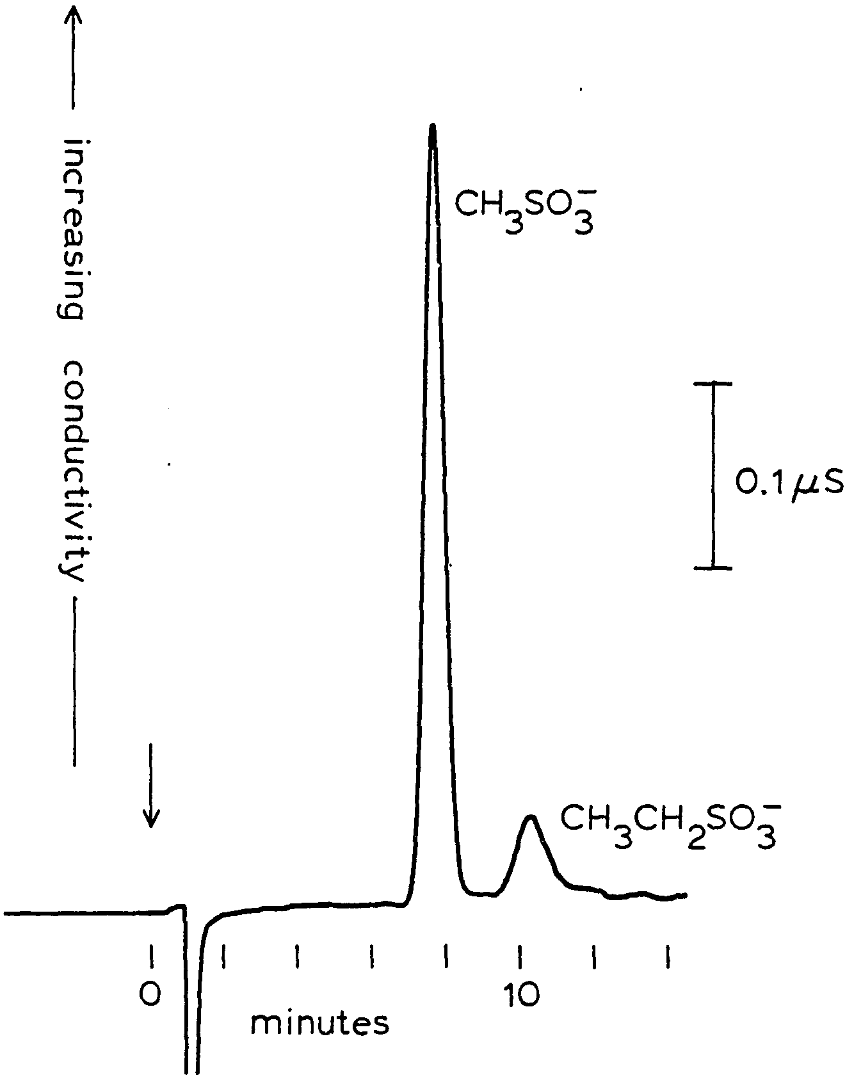


Figure 7. Separation of methanesulfonate and ethanesulfonate on a column packed with trimethylamine resin. Capacity: 0.040 meq/g, 500 x 2.0 mm i.d. column. Eluent: 0.015 M nicotinic acid at a flow rate of 1.25 mL/min. A 20 microliter sample was injected.

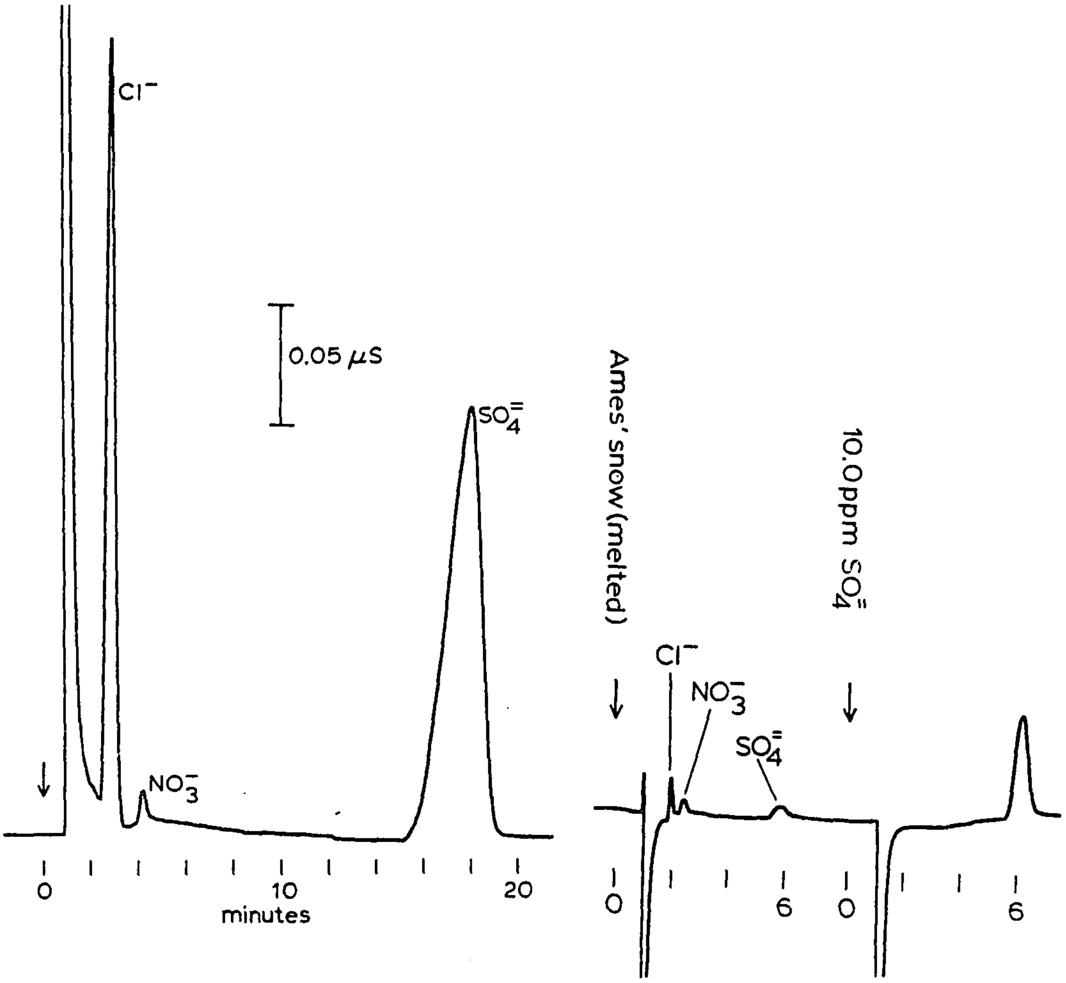


Figure 8. Separations of chloride, nitrate and sulfate in natural water samples. Left half: trimethylamine resin, 0.046 meq/g in a 500 x 2.0 mm i.d. column. Eluent: 0.2 mM KHP at a pH of 6.0; flow rate 1.0 mL/min, 20 microliter sample of tap water. Right half: trimethylamine resin, 0.027 meq/g in a 500 x 2.0 mm i.d. column. Eluent: 0.4 mM KHP at a pH of 5.6; flow rate 1.0 mL/min, 20 microliter sample of melted snow.

Table 17. Comparison of relative retention times for various ions on resins prepared by two chloromethylation routes

| Ion | #1[a] HCl:formaldehyde chloromethylation $t_r$ ion/$t_r$ chloride | #2[b] CMME:Bismuth trichloride chloromethylation $t_r$ ion/$t_r$ chloride |
|---|---|---|
| $Cl^-$ | 1.00 ($t_r$=8.9 min) | 1.00 ($t_r$=7.6 min) |
| $F^-$ | 0.66 | 0.67 |
| $Br^-$ | 1.19 | 1.23 |
| $I^-$ | 2.37 | 2.72 |
| formate | 0.51 | 0.56 |
| acetate | 0.22 | 0.26 |
| nicotinate | 0.30 | 0.34 |
| glycolate | 0.44 | 0.46 |
| lactate | 0.46 | 0.47 |
| $ClO_3^-$ | 1.51 | 1.53 |
| $BrO_3^-$ | 1.04 | 1.04 |
| $IO_3^-$ | 0.82 | 0.83 |
| $MeSO_3^-$ | 1.00 | 1.00 |
| $EtSO_3^-$ | 1.15 | 1.17 |
| $PropSO_3^-$ | 2.00 | 2.01 |
| $NO_2^-$ | 0.90 | 0.82 |
| $NO_3^-$ | 1.26 | 1.32 |
| $H_2PO_4^-$ | 0.83 | 0.83 |
| $N_3^-$ | 0.34 | 0.46 |
| $BF_4^-$ | 2.57 | 3.39 |

[a] Capacity of #1 = 0.027 meq/g.

[b] Capacity of #2 = 0.022 meq/g.

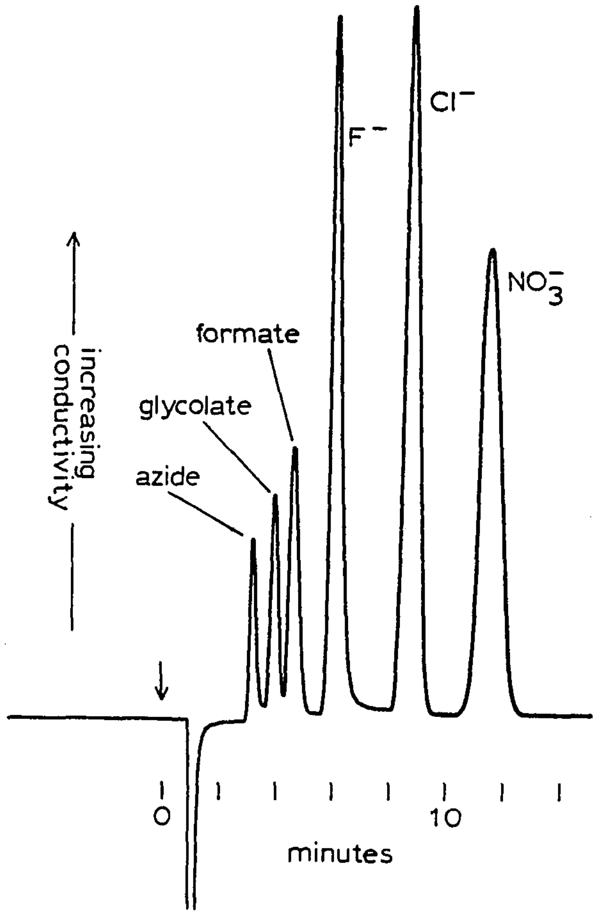


Figure 9. Separation of six anions on a trimethylamine resin prepared via HCl:formaldehyde chloromethylation. The column is 500 x 2.0 mm i.d. Eluent: 0.001 M benzoic acid at a flow rate of 0.93 mL/min.

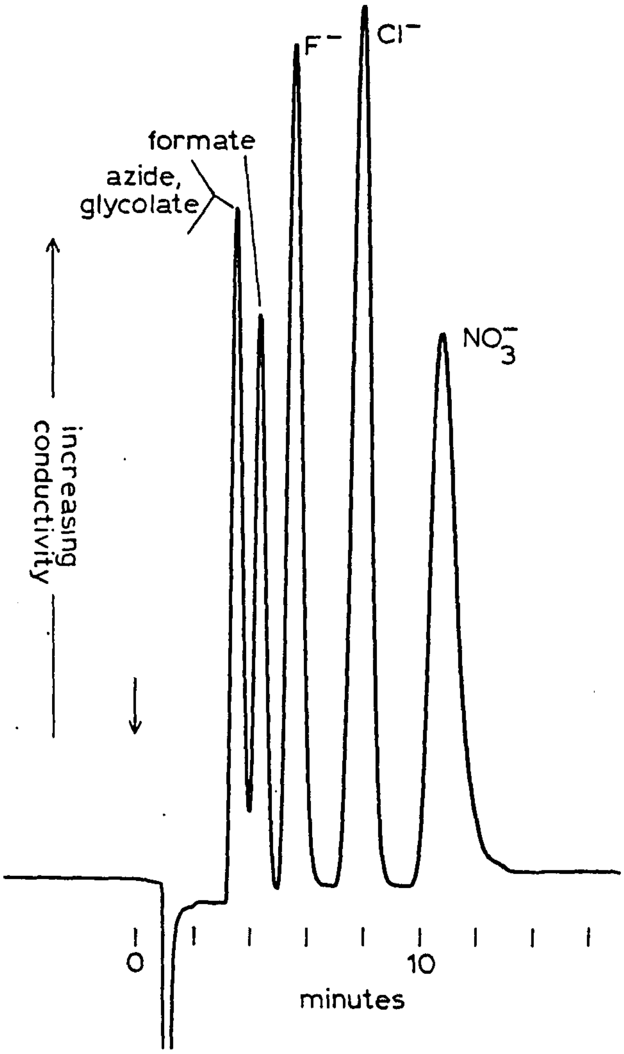


Figure 10. Separation of a mixture of six anions on a trimethylamine resin prepared via in situ generation of CMME with bismuth trichloride catalysis. The column is again 500 x 2.0 mm i.d. The eluent is 0.001 M benzoic acid at a flow fate of 0.93 mL/min.

ion-exchange groups to be located deeper in the copolymer matrix than does the HCl:formaldehyde chloromethylation. This could conceivably occur because of the swelling ability of the solvents used in the conventional reaction. Alternatively, some surface modification may have occurred in the conventional chloromethylation in addition to the introduction of chloromethyl groups. The most likely cause would be acylation by some acetyl chloride which had not formed chloromethylmethyl ether.

The next section will examine the changes in anion-exchange selectivity that can be obtained by altering the chemical structure of the quaternary ammonium ion and by deliberately adding a neutral functional group to the resin surface.

# THE EFFECTS OF FUNCTIONAL GROUP STRUCTURE AND MATRIX POLARITY ON THE SELECTIVITY OF ANION EXCHANGERS OF LOW CAPACITY

## Introduction

The preceding section establishes a solid foundation for further examinations of porous anion exchangers of low capacity. The ability to prepare these materials in a wide range of capacities allows one to undertake a systematic approach to the study of their behavior in single-column ion chromatography.

The Type I strong-base anion exchangers prepared according to the procedures of the last section are capable of performing many separations, but they have some shortcomings. The separation of bromide and nitrate cannot be performed conveniently using a Type I resin within the practical constraints of single-column ion chromatography. Variation of eluent conditions is not effective because these are anions of strong acids, so their selectivities are not changed significantly by varying the pH. It would be impossible to predict all of the combinations of two or three anions that might be present in the same sample which would pose intractable problems for a Type I exchanger.

A general scenario in which Type I resins are somewhat deficient is in the separation of mixtures of monovalent ions and divalent ions. The monovalent ions elute early in a group followed later by the divalent ions which are spread well apart. It would be advantageous to be able to spread the monovalent ions out and allow the divalent ions to elute closer to the monovalent ions or to be interspersed with them if possible. The particular instance where this would be most useful is in the analysis of natural waters where sulfate is almost always present along with chloride and nitrate, among other ions.

Because of these deficiencies, it is necessary to find other factors which will affect selectivity besides adjustments to the eluent. One parameter which can be varied at will is the structure of the quaternary ammonium ion in the anion exchanger. This structural variation is easily accomplished by using a number of tertiary amines after the chloromethylation step instead of trimethylamine. Many such resins were prepared and a systematic evaluation was undertaken to uncover any effects on selectivity caused by the changes in the structure of the quaternary ammonium ion.

A second factor that should be important is the nature of the surface to which the anion-exchange groups are attached. It seems reasonable that the surface of the copolymer should have something to do with the retention of ions, especially since there are so few functional groups present compared to a resin of high capacity. This expectation is borne out by the work of Cantwell and Puon and Afrashtehfar and Cantwell (107,108).

The surface of a styrene-divinylbenzene copolymer is basically non-polar except for the ion-exchange sites themselves and whatever residual groups are left over from the functionalization reactions. The obvious experiment is to change the chemical nature of the polymer that anchors the anion-exchange groups. This would thus change the polarity of the surface and its interactions with a liquid phase and, most likely, the selectivity it exhibits toward anions. However, this approach is not readily taken because of the difficulty of preparing polymer beads with the correct physical properties for chromatography. When using a copolymer such as XAD-1, one has the advantage of having a material with a stable, well-characterized physical structure which behaves well in chromatography. This advantage would be lost if other polymeric materials were substituted for XAD-1. The evidence from the last section seems to indicate that the anion-exchange groups are introduced at the surfaces of the macroreticular channels within the beads. Because of this assumed location of functional groups, one can argue that the selectivity may be affected just by adding neutral functional groups to the surface of the resin either before or after the anion-exchange groups are introduced. This would allow one to retain the well-established polymer as well as to vary the chemical nature of the surface environment near the ion-exchange sites. Some experiments of this sort have been carried out also showing that the potential exists to make more use of the general concept.

## Experimental

### Materials and apparatus

The XAD-1 was prepared in the same manner as in the last section. The preliminary reactions were carried out on material in the size range of 75-150 micrometers because it was demonstrated earlier that the particle size did not make any difference in the capacity that was achieved. All tertiary amines were better than 95% pure and were used as received. All other reagents were the same as those used earlier.

The liquid chromatograph was the same as that used in the last section. See Figure 1.

### Preparation of anion exchangers

The chloromethylations were carried out according to the procedures outlined in the last section. When trimethylamine was used to aminate resins, the procedure was the same as used previously. When other amines were used, the aminations were carried out at 65-70°C in a round-bottom flask fitted with a reflux condenser. The amines were used as 20-25% solutions in methanol. The aminations involving trioctylamine had to be carried out using isopropyl alcohol as a solvent rather than methanol because of solubility limitations.

### Addition of carbonyl groups to the copolymer matrix

The carbonyl groups were added to the copolymer after the anion-exchange groups were in place. The reaction was carried out via Friedel-Crafts acylation with acetyl chloride. Earlier experiments had determined that if the carbonyl groups were added first, no anion-exchange groups could be introduced. The reactions were carried out in carbon disulfide using either titanium tetrachloride or aluminum trichloride as the catalyst. The resins prepared using a titanium catalyst were dark brown in color, whereas those prepared with an aluminum catalyst were just slightly off-white. Analysis of the resins by x-ray fluorescence showed that the titanium-catalyzed resin contained 0.7%

residual titanium. The aluminum-catalyzed resin contained only 0.17% aluminum. A batch of aluminum-catalyzed resin was then Soxhlet extracted in a glass thimble for 24 hours with a constant-boiling (20%) mixture of HCl. This procedure did not seem to harm the functional groups. The resin was found to contain only 0.05% aluminum after this treatment. Therefore, aluminum trichloride was used as the catalyst thereafter with the acid extraction used as a means of cleaning the material.

A typical batch of resin to be used for chromatography was prepared by chloromethylating the copolymer for six minutes using 12 M HCl and 2.2 M formaldehyde at room temperature. This was then aminated for 24 hours at room temperature with trimethylamine in methanol. After cleaning, about two grams of the anion exchanger was added to a cold mixture of 15 mL of $CS_2$ and 2 g of $AlCl_3$. Then, 3 mL of acetyl chloride were added to the slurry. After this addition had taken place, the flask was warmed to about 45°C for 1.5 hours. The reaction mixture was poured onto a mixture of ice and HCl to quench the reaction. The material was then cleaned and air dried before use.

The presence of carbonyl groups was confirmed by treating a portion of the resin with an acidified methanolic solution of 2,4-dinitrophenylhydrazine. The excess was then rinsed off with methanol. Plain XAD-1 was not affected by this treatment, but the acylated resin turned a characteristic deep orange color indicating the presence of a substantial number of carbonyl groups.

## Results and Discussion

### Preparation of resins

To ascertain the effect of functional group structure on selectivity, the various resins have to be of a similar capacity so that identical elution conditions can be used for each resin. Only one substrate was used to prepare the anion exchangers for the same reason. The use of a single copolymer substrate allows the physical properties of the resin to remain constant so that changing physical properties will not confuse the results of the chemical changes.

The first step in preparing a number of resins with similar capacities is to gauge the relative reactivities of the various tertiary amines toward the chloromethylated substrate. This objective was accomplished by chloromethylating each of the required number of batches of XAD-1 under a set of identical conditions. These conditions included 12 M HCl, 2.2 M formaldehyde, one gram of XAD-1 and a 20-min reaction time at room temperature. Each batch of the chloromethylated copolymer (all batches contained equal amounts of active chlorine) was then aminated for 24 hours with one of the chosen tertiary amines. The strong-base anion-exchange capacity of each batch of resin was then determined. The results are shown in Figure 11.

Once these relative reactivities were known, it was a simple matter to predict the chloromethylation time needed for each resin so that all batches would have almost the same capacity. A capacity range of about 0.025-0.030 meq/g was chosen as a target for the resins to be made for chromatographic evaluation. A batch of resin was prepared with each tertiary amine by adjusting the chloromethylation time appropriately and aminating the resin for 24 hours as usual. Most of the calculated chloromethylation times fell in the 8-20 min range, except for the resin prepared with triethanolamine. A reaction time of about 3 1/2 hours was necessary to produce a resin of 0.031 meq/g capacity. This long reaction time was a result of the low reactivity of triethanolamine toward the chloromethylated substrate. The consequences of this extended chloromethylation time will be pointed out later.

The capacities of all resins produced for the study of selectivity toward monovalent ions are listed in Table 18.

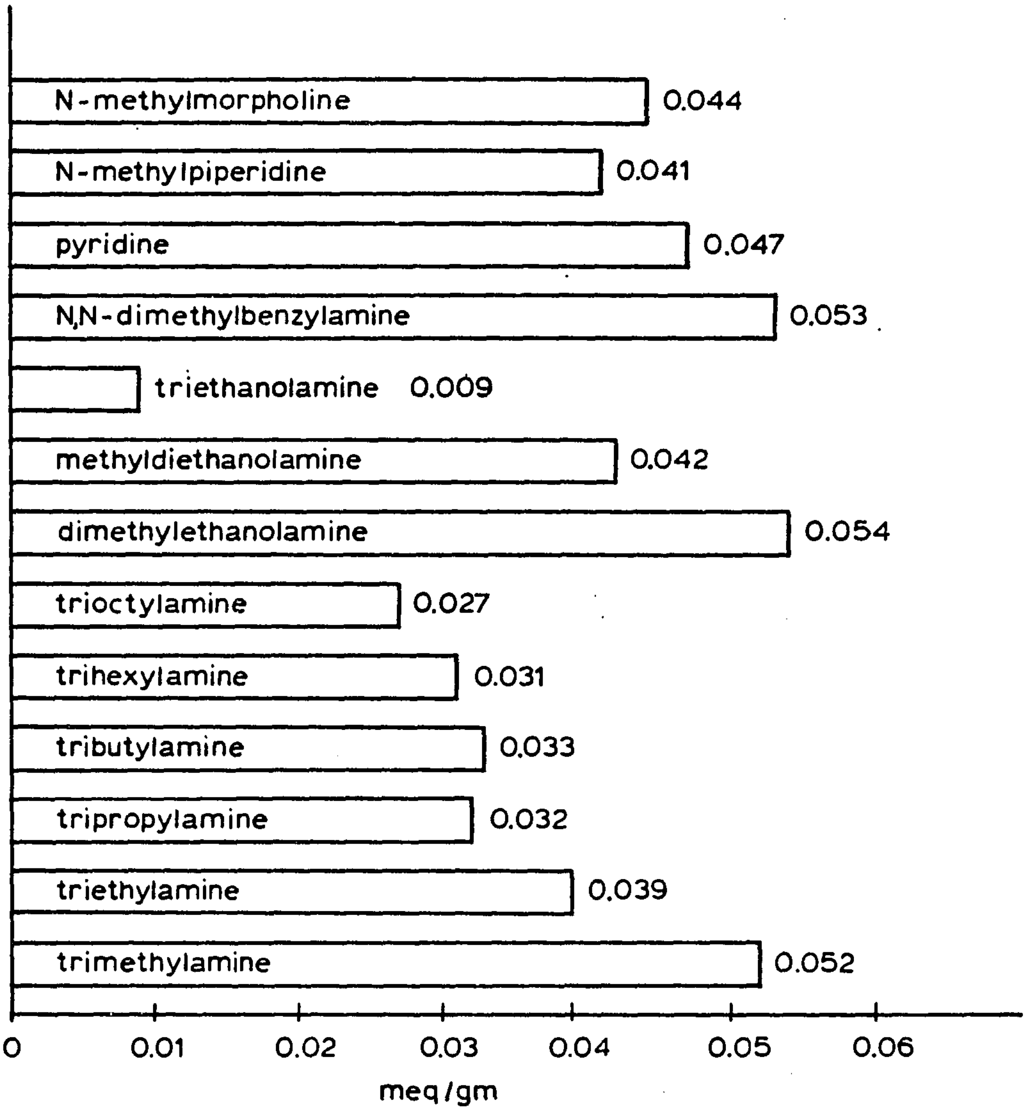


Figure 11. Relative reactivities of the tertiary amines toward chloromethylated XAD-1. The chloromethylation time for all resins was 20 min and the amination time was 24 hours.

Table 18. Capacities of the resins used to study the selectivities toward monovalent ions

| tertiary amine | capacity (meq/g) |
|---|---|
| trimethylamine (TMA) | 0.027 |
| triethylamine (TEtA) | 0.026 |
| tripropylamine (TPA) | 0.026 |
| tributylamine (TBA) | 0.027 |
| trihexylamine (THA) | 0.028 |
| trioctylamine (TOA) | 0.028 |
| dimethylethanolamine (DMEA) | 0.025 |
| methyldiethanolamine (MDEA) | 0.026 |
| triethanolamine (TEA) | 0.031 |
| pyridine (PYR) | 0.025 |
| N-methylmorpholine (NMM) | 0.029 |
| N-methylpiperidine (NMP) | 0.029 |
| N,N-dimethylbenzylamine (DMBA) | 0.024 |

The average capacity of these resins is 0.027 meq/g with a standard deviation of 0.002 meq/g. The capacities are on a dry-weight basis with all resins in the chloride form. It should be pointed out that the chloromethylation process is reliable enough that the correct capacity was achieved on the first try for nearly every amine.

### Evaluation of resin selectivity for monovalent ions

A true selectivity coefficient for an anion exchanger is normally obtained by shaking a weighed portion of a resin in a given ionic form (usually $Cl^-$) with a solution of the ion of interest until the resin and the solution have attained equilibrium. Then, the amount of each ion in solution is determined and the amount of each in the resin is inferred from these results. The equilibrium selectivity coefficient is then calculated (137).

This method is tedious to perform and takes a lot of time, especially if one is interested in a large number of ions. Therefore, the decision was made to acquire selectivity-related information via the use of a dynamic method rather than using the traditional method. Besides saving time, the results are directly applicable to single-column ion chromatography. The dynamic method consists of packing each resin into a 500 x 2.0 mm i.d. column and determining the retention time of the analyte ions under identical elution conditions for each resin. The first portion of the study is concerned only with monovalent ions and makes use of a monovalent eluent, the benzoate ion. The retention times of seventeen different anions were determined on each column. (Several other ions were also run on selected columns.) The data were then tabulated as relative retentions compared to the chloride ion. (That is, the retention time of a given anion was divided by the retention time of chloride.) This method of presenting the data is easier to follow than raw retention times. It also reduces the influence of such factors as slight variations in volume from column to column, minor fluctuations in flow rate and recorder speed, and the small differences in capacity which exist between the resins (either because of preparation or degradation.)

Tables 19, 20 and 21 contain the relative retention data. Each table contains the data for the TMA resin (Type I) as a point of reference. The ions are listed in order of increasing relative retention on a Type I resin compared to chloride. Table 19 contains the resins which have trialkylammonium functional groups; Table 20 contains the resins which have hydroxyalkylammonium functional groups; and Table 21 contains the resins which have rings associated

Table 19. Relative retention of anions on trialkylammonium resins ($t_{r\ anion}/t_{r\ chloride}$)

| anion | TMA | TEtA | TPA | TBA | THA | TOA |
|---|---|---|---|---|---|---|
| acetate | 0.25 | 0.28 | 0.23 | 0.25 | 0.22 | 0.22 |
| nicotinate | 0.31 | 0.32 | 0.31 | 0.31 | 0.31 | 0.33 |
| $N_3^-$ | 0.36 | 0.39 | 0.34 | 0.37 | 0.35 | 0.37 |
| lactate | 0.44 | 0.49 | 0.46 | 0.47 | 0.45 | 0.49 |
| glycolate | 0.45 | 0.48 | 0.44 | 0.45 | 0.43 | 0.45 |
| formate | 0.52 | 0.54 | 0.51 | 0.52 | 0.51 | 0.53 |
| $F^-$ | 0.66 | 0.70 | 0.69 | 0.71 | 0.68 | 0.69 |
| $NO_2^-$ | 0.82 | 0.82 | 0.86 | 0.90 | 0.89 | 0.98 |
| $H_2PO_4^-$ | 0.84 | 0.85 | 0.84 | 0.85 | 0.83 | 0.83 |
| $Cl^-$ | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| $CH_3SO_3^-$ | 1.00 | 1.06 | 1.01 | 1.06 | 1.01 | 1.07 |
| $BrO_3^-$ | 1.05 | 1.06 | 1.03 | 1.08 | 1.08 | 1.14 |
| $Br^-$ | 1.20 | 1.19 | 1.25 | 1.34 | 1.32 | 1.41 |
| $NO_3^-$ | 1.30 | 1.32 | 1.38 | 1.54 | 1.63 | 1.72 |
| $ClO_3^-$ | 1.53 | 1.55 | 1.56 | 1.73 | 1.92 | 2.15 |
| $I^-$ | 2.51 | 2.48 | 3.05 | 3.82 | 5.00 | >5.0 |
| $BF_4^-$ | 2.70 | 2.58 | 3.41 | 4.34 | >7.5 | ---- |
| $t_{r\ Cl^-}$ (min) | 8.3 | 8.0 | 9.5 | 8.9 | 10.6 | 9.4 |

Table 20. Relative retention of anions on hydroxyalkylammonium resins ($t_{r\ anion}/t_{r\ chloride}$)

| anion | TMA | DMEA | MDEA | TEA |
|---|---|---|---|---|
| acetate | 0.25 | 0.22 | 0.24 | 0.14 |
| nicotinate | 0.31 | 0.30 | 0.33 | 0.22 |
| $N_3^-$ | 0.36 | 0.35 | 0.36 | 0.22 |
| lactate | 0.44 | 0.46 | 0.49 | 0.38 |
| glycolate | 0.45 | 0.42 | 0.45 | 0.38 |
| formate | 0.52 | 0.52 | 0.55 | 0.44 |
| $F^-$ | 0.66 | 0.67 | 0.74 | 0.64 |
| $NO_2^-$ | 0.82 | 0.91 | 0.82 | 0.79 |
| $H_2PO_4^-$ | 0.84 | 0.83 | 0.88 | 0.88 |
| $Cl^-$ | 1.0 | 1.0 | 1.0 | 1.0 |
| $CH_3SO_3^-$ | 1.00 | 1.05 | 1.07 | 0.95 |
| $BrO_3^-$ | 1.05 | 1.05 | 1.10 | 1.05 |
| $Br^-$ | 1.20 | 1.22 | 1.19 | 1.30 |
| $NO_3^-$ | 1.30 | 1.28 | 1.22 | 1.38 |
| $ClO_3^-$ | 1.53 | 1.53 | 1.43 | 1.58 |
| $I^-$ | 2.51 | 2.60 | 2.11 | 2.95 |
| $BF_4^-$ | 2.70 | 2.44 | 1.93 | 2.29 |
| $t_{r\ Cl^-}$ (min) | 8.3 | 9.4 | 8.4 | 18.6 |

Table 21. Relative retention of anions on miscellaneous ring-containing strong-base resins ($t_{r\ anion}/t_{r\ chloride}$)

| anion | TMA | PYR | NMP | NMM | DMBA |
|---|---|---|---|---|---|
| acetate | 0.25 | 0.25 | 0.24 | 0.24 | 0.26 |
| nicotinate | 0.31 | 0.32 | 0.31 | 0.30 | 0.35 |
| $N_3^-$ | 0.36 | 0.36 | 0.35 | 0.34 | 0.42 |
| lactate | 0.44 | 0.47 | 0.46 | 0.44 | 0.48 |
| glycolate | 0.45 | 0.45 | 0.44 | 0.42 | 0.46 |
| formate | 0.52 | 0.50 | 0.49 | 0.49 | 0.56 |
| $F^-$ | 0.66 | 0.69 | 0.68 | 0.69 | 0.72 |
| $NO_2^-$ | 0.82 | 0.85 | 0.88 | 0.82 | 0.86 |
| $H_2PO_4^-$ | 0.84 | 0.83 | 0.82 | 0.85 | 0.89 |
| $Cl^-$ | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| $CH_3SO_3^-$ | 1.00 | 1.05 | 1.02 | 1.03 | 1.06 |
| $BrO_3^-$ | 1.05 | 1.04 | 1.05 | 1.06 | 1.10 |
| $Br^-$ | 1.20 | 1.18 | 1.24 | 1.26 | 1.22 |
| $NO_3^-$ | 1.30 | 1.25 | 1.33 | 1.34 | 1.30 |
| $ClO_3^-$ | 1.53 | 1.49 | 1.58 | 1.60 | 1.52 |
| $I^-$ | 2.51 | 2.39 | 2.99 | 2.90 | 2.62 |
| $BF_4^-$ | 2.70 | 2.31 | 3.02 | 3.00 | 2.58 |
| $t_{r\ Cl^-}$ (min) | 8.3 | 8.4 | 9.2 | 9.6 | 7.2 |

with their quaternary ammonium ions.

It is evident that the changes in the chemical structure of the quaternary ammonium ion have a pronounced effect on the relative retention of many of the anions. Small changes from resin to resin are to be expected because of experimental conditions and should be ignored. An idea of the repeatability can be obtained from Table 22. It shows the relative retention of glycolate and chlorate for four separate injections of each ion plus chloride on a column containing TEtA resin. This shows that for an ion such as glycolate, a relative retention range of 0.49 to 0.53 might be expected; for chlorate, a range of 1.35 to 1.41 is probably normal. Table 23 shows the "buffering" effect of presenting the data as relative retentions. The first part of the table indicates some deviation among the retention times of the ions even though the same resin and elution conditions are used. This is probably because of variations in volume among the glass columns. However, when the data are reduced to relative retentions, the effect of the volume differences is masked quite well.

Table 22. Experimental variation of relative retention time for two representative anions

| run | $^{t}r$ glycolate/$^{t}r$ $Cl^-$ | $^{t}r$ chlorate/$^{t}r$ $Cl^-$ |
|---|---|---|
| 1 | 0.48 | 1.35 |
| 2 | 0.50 | 1.42 |
| 3 | 0.52 | 1.37 |
| 4 | 0.52 | 1.40 |
| avg. | 0.051 ± 0.02 | 1.38 ± 0.03 |

Table 23. Buffering effect of using relative retention instead of raw retention times

Average Retention Times[a]
(minutes)
(3 injections for each ion)

| Ion | column 1 | column 2 | column 3 |
|---|---|---|---|
| glycolate | 3.82 | 3.48 | 3.82 |
| $F^-$ | 5.64 | 5.31 | 5.67 |
| $Cl^-$ | 7.97 | 7.33 | 7.90 |
| $NO_3^-$ | 10.26 | 9.43 | 10.10 |
| $ClO_3^-$ | 11.94 | 10.80 | 11.70 |
| $I^-$ | 18.83 | 17.20 | 18.10 |

Relative Retentions ($t_r/t_{r\ Cl^-}$)

| Ion | column 1 | column 2 | column 3 |
|---|---|---|---|
| glycolate | 0.48 | 0.47 | 0.48 |
| $F^-$ | 0.71 | 0.72 | 0.72 |
| $Cl^-$ | 1.0 | 1.0 | 1.0 |
| $NO_3^-$ | 1.29 | 1.29 | 1.28 |
| $ClO_3^-$ | 1.50 | 1.47 | 1.48 |
| $I^-$ | 2.36 | 2.35 | 2.29 |

---

[a] Each of three different columns (nominally 500 x 2.0 mm) were packed with TEtA resin with a capacity of 0.026 meq/g and eluted with 1 mM benzoic acid at 1.0 mL/min.

## Selectivity of resins with alkyl substituents

The data in Table 19 show that the relative retentions of the weak-acid anions (which elute largely before chloride) are virtually independent of the size of the R groups at the anion-exchange sites. However, as the size of the R groups increases, large changes begin to occur among the more polarizable anions which elute after chloride in the order $Br^- < NO_3^- < ClO_3^- < I^- < BF_4^-$. The term "polarizable" is used here to indicate a large ion with a single negative charge spread over a considerable volume. The order of increasing selectivity is roughly in line with the decreasing charge-to-volume ratios of the anions. The volumes of the anions were estimated roughly by using Pauling Univalent Radii for the spherical anions (halides) and Yatsimirskii Thermochemical Radii for the non-spherical anions (138).

The fixed cations of the low-capacity anion-exchange resins (benzyltrialkylammonium) have an effect similar to the polarizable anions; the retention of a given anion increases as the ratio of charge-to-volume of the quaternary ammonium ion decreases. Also, the differences between relative retention values for a given anion at successively larger anion-exchange sites become greater as the retention of the anion increases on a Type I resin. This is illustrated in Figure 12.

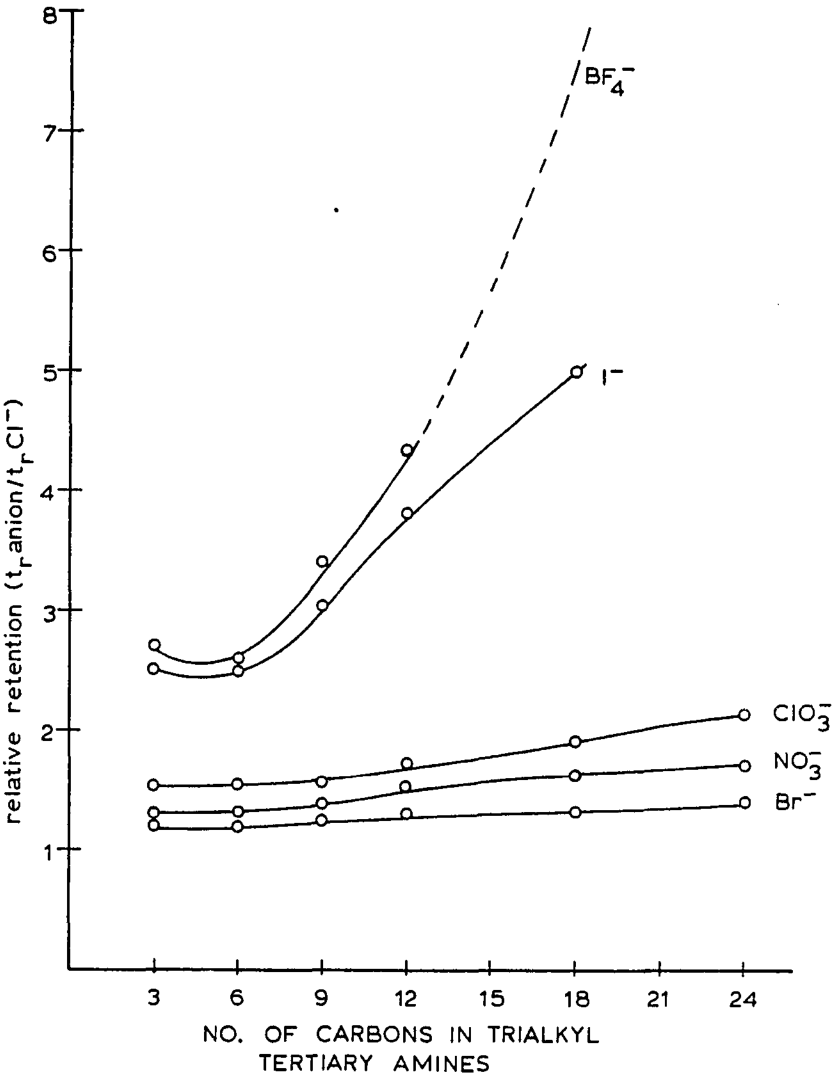


Figure 12. Dependence of relative retention on the molecular weight of the amine in the benzyltrialkylammonium functional group.

Such an increase in relative retention as the hydrophobicity of the anion-exchange site increases is paralleled by the recent work of Iskandarani and Pietrzyk (28). They showed that at a given solvent composition, retention of a series of tetraalkylammonium bromides on a column packed with a styrene-divinylbenzene copolymer (Hamilton PRP-1) is dependent on the number of carbons in the quaternary ammonium ion. Their data seem to imply a liquid-liquid partition phenomenon with the copolymer acting as the hydrophobic phase. Apparently as the quaternary ammonium ion becomes more hydrophobic, it spends more time as an ion pair with the bromide and this ion pair is then more easily sorbed (extracted) from solution by the stationary phase.

The primary purpose of this report is not to produce a rigorous, thermodynamically correct description of all of the phenomena exhibited by the low-capacity anion exchangers. It is of practical interest, however, to find a logical way to categorize their behavior so that the resins may be more intelligently applied to specific analytical situations. The main approach to describing the behavior of the resins will encompass evidence which indicates that the selectivity of the resins can be understood in terms of the combined effect of both the anions and cations on the structure of water in solution.

The helpful concept of "water-structure enforced ion pairing" was first suggested by Diamond (139) to try to rationalize the order of retention of anions on a Type I anion-exchange resin. When considering large polarizable ions, one must keep in mind that electrostatic ion pairing is minimized because, as Diamond points out, electrostatic ion pairing requires small, highly-charged ions and solvents of low dielectric constant. However, water-structure enforced ion pairing should occur most readily with large monovalent ions in aqueous solutions. According to this concept, the pairing of ions results because the large anions with diffuse charge have a disturbing influence on the equilibrium structure of water. Diamond suggested that the anions have trouble orienting a primary adjacent layer of water molecules. This causes the water molecules nearest the anion to become associated with other water molecules nearby in an anomalous manner. Thus, the larger and more poorly hydrated the anion, the more the local water structure is disrupted (or rearranged). Because the water attempts to correct this imbalance and maintain its equilibrium structure, a large, poorly hydrated anion would be more easily forced into an association with the benzyltrimethylammonium cation of the Type I anion-exchanger. Small, well-hydrated ions would disturb the structure of water less and would tend not to form water-structure enforced ion pairs as easily.

Although this explanation is intuitively satisfying, it is somewhat ambiguous in that the specific effect of an anion on the structure of water is only speculative. Consider also the effect of increasing the size of the fixed cation on the resin. It is tempting to conclude that the cations must also disrupt the structure of water because an increase in the size of the cation also results in greater retention for a given anion. The physical evidence accumulated in the literature does suggest that it might be wise to think in terms of separate contributions from the anion and the cation. However, the effect on the structure of water is quite different for a quaternary ammonium cation compared to an inorganic anion as will be demonstrated in the following pages.

Previous work seems to show that simple, nominally spherical anions such as bromide, iodide, and chlorate may indeed disrupt water structure making the solution less ordered than pure water as envisioned by Diamond. Table 24 shows data taken from the work of Halliwell and Nyburg (140) and Krestov and Egorova (141) on the enthalpy of hydration

Table 24. Enthalpies of hydration of some anions

| Anion | Enthalpy of Hydration[a] |
|---|---|
| chloride | -87.6 |
| bromide | -79.8 |
| nitrate | -74.5 |
| iodide | -69.7 |
| tetrafluoroborate | -71.2 |
| perchlorate | -57.1 |

[a] At 25°C, kcal/mole.

of some anions. The retention time of an anion increases (See Table 19) as its enthalpy of hydration becomes less exothermic. The decrease in exothermicity indicates a progressively less favorable interaction of the anions with water as the anions become larger. This suggests, then, that the degree of organization inherent in the water is diminished by the presence of the anion which must occupy some sort of self-created discontinuity in the prevailing water structure. (More data showing the disruptive effect of inorganic anions on the structure of water will be cited later.)

To contrast the behavior of the inorganic anions, there is a large body of evidence which indicates that quaternary ammonium cations and fatty acid anions have the ability to incite increased order in water by causing the hydrogen bonds among water molecules to either increase in magnitude or number.

Many physical methods have been used to show how the various anions and cations affect the structure of water. Although the work has been done using non-polymeric cations and anions in solution, it is believed that the conclusions can be safely transferred to the case of low-capacity anion exchangers. Some of the investigations will be discussed here in order to try to obtain a clearer understanding of how the selectivity of low-capacity anion exchangers comes about.

One of the earliest indications that quaternary ammonium ions are capable of enhancing the structure of water comes from the data of Frank and Wen (142) concerning the heat capacity of solutions of tetra-n-butylammonium bromide. The value for the apparent molal heat capacities of several aqueous solutions of this salt (below 1 m concentration) was found to be about 270 cal/deg mole. They noted that this is in excess of a reasonable prediction by about 140 cal/deg mole. They found that solutions of salts such as sodium chloride and potassium iodide have a lower heat capacity than water. The authors proposed that the reason for the exorbitantly high heat capacity of the tetra-n-butylammonium salt is that the large hydrophobic cation causes the fraction of water involved in a definite structural configuration to increase. This would explain the extra energy needed to raise the temperature of the solution to a given level in comparison to the energy needed for the same volume of water. The extra energy was believed to be necessary to dismantle the increased structure (break the stronger or more numerous hydrogen bonds) brought about by the presence of the quaternary ammonium ion.

Lindenbaum et al. (143) and Wen et al. (144) determined the osmotic coefficients for various symmetric tetraalkylammonium salts in aqueous solution. The osmotic coefficient is a correction term for non-ideal behavior of an electrolyte in dilute solutions (145) and is calculated via the isopiestic gravimetric method from vapor pressures and molalities of the solutes involved (146). It is defined in equation 2.

$$\phi = (-55.51 \ln a_a)/m_b \qquad 2$$

Here, 55.51 is the molality of pure water, $a_a$ is the activity of water (determined by the ratio of the vapor pressure of water in a solution of the salt in question to that of pure water), $m_b$ is the molality of the solute, and $\phi$ is the osmotic coefficient. One can deduce from this equation that if the molality of two different solutes is held constant, and the osmotic coefficents of the solutes differ, then the activity of water in the presence of each of the solutes must be different. Lindenbaum et al. (143) found that at 25°C, the osmotic coefficients for three tetraalkylammonium chlorides at any given molality were arranged such that the coefficient of the tetra-n-butyl salt was greater than that of the tetra-n-propyl salt which was in turn greater than the coefficient of the tetramethyl salt. This order demonstrates that the activity of water is least in the solution of the tetra-n-butylammonium salt and greatest in the solution of the tetramethyl salt. The lower activity of water in the solution of tetra-n-butylammonium chloride indicates that the intermolecular association of water (presumably hydrogen bonding) is greater than in the solution of tetramethylammonium chloride. The authors measured the osmotic coefficients at 65°C and found that the order was exactly reversed; the solution of tetra-n-butylammonium chloride displayed the lowest osmotic coefficient and, thus, the highest activity of water. Apparently, the thermal energy available in the solution at the higher temperature is enough to overcome the ability of the large quaternary ammonium cation to induce structure in water. The reason that the tetra-n-butylammonium chloride actually causes less association of water molecules than tetramethylammonium chloride at higher temperatures will be discussed later.

These authors were also able to reverse the cationic influence on the osmotic coefficient at 25°C by substituting iodide for chloride in the tetra-n-propyl and tetramethyl salts. This demonstrates that the substitution of the larger anion has the same effect on the activity of water as heating the solution, i.e., a lessening of the ability of the quaternary ammonium cation to foster the intermolecular association of water.

Wen et al. (144) determined the osmotic coefficients and the activity coefficients for the tetramethyl-, tetraethyl-, tetra-n-propyl- and tetra-n-butylammonium fluorides at 25°C. These workers found that the osmotic coefficients of the fluoride salts at equal molalities were again arranged from greatest to least in a manner which was directly proportional to the number of carbons in the quaternary ammonium ion. Even tetramethylammonium fluoride had a larger osmotic coefficient (brought about lower water activity) than tetra-n-butylammonium chloride, indicating that the fluoride salts are especially adept at causing the intermolecular association of water. (The probable reason for this facility will be made clear later during the discussion of structure.) Wen and coworkers then compared their data on the activity coefficients of tetra-n-propylammonium fluoride with the equivalent data for tetra-n-propylammonium chloride, bromide and iodide which had been obtained by Lindenbaum and Boyd (147). The order of the activity coefficients for the tetra-n-propylammonium halides was such that the fluoride had the highest activity coefficient by a wide margin. The coefficients of the chloride salt were much lower than the fluoride at any molality but were still greater than those of the bromide salt. The iodide salt, as expected, exhibited very low activity coefficients at all concentrations. This can be interpreted to mean that there is a much greater association of the quaternary ammonium cation and its counterion as the counterion becomes larger.

Gerchikova et al. (148) examined the dependence of the apparent molar volumes of tetramethylammonium, tetraethylammonium and (2-hydroxyethyl)trimethylammonium chloride on the concentration of the salts in aqueous solution. The apparent molar volume decreases substantially for tetramethylammonium chloride and to an even greater extent for tetraethylammonium chloride as the concentration of the salts increase. The value of the apparent molar volume of the (2-hydroxyethyl)trimethylammonium chloride is hardly affected by changes in concentration. These authors compared some of their data to that obtained for the corresponding bromide salts by other workers (149,150). Tetramethylammonium bromide shows essentially no change in apparent molar volume with a change in concentration, whereas the apparent molar volume decreases as the concentration of tetraethylammonium bromide is increased.

(This is in contrast to the behavior of the chlorides where both exhibit a smaller apparent molar volume with increased concentration.) The interpretation of this behavior is that the tetramethylammonium ion has only a weak ability to form the structure of water. The bromide ion is more able to disrupt the structure of water than the chloride ion because of its more diffuse charge and larger size. The power of the tetramethylammonium ion to enhance the hydrogen bonding in water can overcome the ability of chloride to disrupt the same structural feature. However, the influence of the tetramethylammonium cation is just about canceled out by the ability of bromide to disturb the prevailing water structure. The tetraethylammonium ion is apparently sufficiently able to cause order in water that it can overpower the disrupting effects of both halide ions. The (2-hydroxyethyl)trimethylammonium chloride has little effect on the water structure presumably because of the competition between the hydrophobic methyl groups and the hydrophilic hydroxyethyl group.

The spectroscopic results of Worley and Klotz (151) also support the thermodynamic evidence. These workers measured the absorbances (in the near-infrared region of the spectrum) of free and hydrogen-bonded O-H in solutions of various salts dissolved in 6 M HOD. HOD exhibits four major bands in the region of 1.4 to 1.8 micrometers. One of these bands (1.416 micrometers) was assigned by the authors (on the basis of other work) to the absorbance caused by free O-H groups, while a second band (1.556 micrometers) was judged to be the result of radiation absorbed by hydrogen-bonded O-H groups. The authors further assumed that the molar absorptivities of all free O-H absorptions are equal to each other. The analogous assumption was applied to the hydrogen-bonded O-H absorptions.

The ratios of the absorbances of hydrogen-bonded O-H groups to free O-H groups were compared for several different salt solutions. The addition of some salts to the HOD shifted the ratio of absorbances ($A_{1.556}/A_{1.416}$) to a lower value which is the same direction the ratio would move in a salt-free HOD solution which has been heated. Others shifted the ratio to a higher value indicating that more hydrogen-bonded O-H absorptions were present than in the salt-free HOD solutions. Table 25 shows a list of some of the salt solutions examined by Klotz and Worley. The list also includes the normalized ratio of absorbances of the two absorption bands. (The ratios are normalized to the ratio obtained from a salt-free HOD solution.) It is evident that the ions which are retained most strongly by the

Table 25. Normalized ratios of the absorbances of bound O-H to free O-H in solutions of various salts

| Salt | $R_{norm}$ (25°C)[a] |
|---|---|
| sodium perchlorate | 0.710 |
| sodium thiocyanate | 0.737 |
| potassium iodide | 0.773 |
| magnesium perchlorate | 0.777 |
| potassium bromide | 0.822 |
| sodium periodate | 0.825 |
| sodium formate | 0.965 |
| sodium sulfate | 0.986 |
| sodium acetate | 1.0 |
| **(salt-free 6 M HOD) | (1.0)** |
| tetramethyl ammonium bromide | 1.0 |
| tetraethyl ammonium chloride | $1.03_4$ |
| sodium n-butyrate | $1.10_6$ |
| tetra-n-butyl ammonium bromide | $1.33_9$ |

[a] Solutions were about 2 M.

benzyltrialkylammonium anion exchangers of the present study are those which reduce the ratio of hydrogen-bonded to free O-H by the greatest amount.

Solutions of sodium acetate and tetramethylammonium bromide have no effect on the ratio (competing effects of cation and anion), and salts such as sodium butyrate and tetra-n-butylammonium bromide actually increase the amount of hydrogen-bonded O-H absorbance at the expense of free O-H absorbance. These observations led the authors to the conclusion that the quaternary ammonium ions and carboxylate ions cause an increase in water structure whereas most of the other ions disrupt the structure of water. This conclusion is consistent with the thermodynamic evidence.

The only method which seems to yield equivocal evidence concerning the ability of quaternary ammonium ions to form water structure is proton NMR. A number of studies of the aqueous solutions of these salts have been carried out. The investigation of Marciacq-Rousselot et al. is a representative work (152). These workers found that the chemical shift of the proton of water is different in solutions of different tetra-n-alkylammonium halides. Only the results obtained at low molalities will be considered because these are probably most applicable to the conditions found during ion chromatography. The quaternary ammonium ions examined were the tetra-n-butylammonium, tetra-n-propylammonium and tetramethylammonium ions and the halides were fluoride, chloride and bromide. When the halide ion was fluoride, they found that the chemical shift for the proton of water (at 2°C) was moved downfield (the proton was shielded less thoroughly) in the presence of the quaternary ammonium ions with the tetra-n-butylammonium ion having the greatest effect and the tetramethylammonium ion having the least effect. This decreased shielding of the proton implies that the fluoride salts are capable of forming water structure. (The hydrogens are already covalently bound to an electronegative oxygen atom in the water molecule. An increase in the number of hydrogen bonds (structure) among the water molecules means that more hydrogens will enter secondary associations with electronegative oxygen atoms thus causing more electron density to be removed from the vicinity of the proton making it more susceptible to the energy of the applied magnetic field. Alternatively, if the lengths of the already existing hydrogen bonds are shortened, again implying increased rigidity of the arranged water molecules, there would also be greater deshielding of the involved hydrogens. The closer proximity of the oxygen to the hydrogen would allow the electronegativity of the oxygen to be felt more strongly by the electron cloud of the hydrogen atom.)

The chlorides are intermediate in behavior at 2°C with the tetra-n-butyl salt having little effect on the chemical shift of the proton and the tetra-n-propyl and tetramethyl cations causing a slight shielding (upfield movement) of the chemical shift of the water proton. The bromide salts all cause an upfield change in the chemical shift of the water proton at 2°C with the effect of the tetra-n-butyl cation being the least and that of the tetramethyl cation being greatest. The behavior of the bromides is somewhat perplexing considering the thermodynamic results already discussed.

The influence of the quaternary ammonium cations is reversed at 43°C. The fluoride salts still cause a slight downfield change, however, the tetramethyl cation unexpectedly has a more pronounced effect than the tetra-n-propyl cation, which also has a greater effect than the tetra-n-butyl cation. The chloride and bromide salts all cause pronounced upfield adjustments to the chemical shift of the water proton at 43°C with the tetra-n-butyl cation causing the greatest shielding and the tetramethyl cation bringing about the least shielding.

Lindenbaum and Levine (153) confirmed that solutions of tetra-n-butylammonium bromide cause an upfield movement of the chemical shift of the water proton even at low temperatures. (They reinforce the notion that this NMR evidence is not consistent with most other thermodynamic data which indicates that tetra-n-butylammonium bromide has an overall ability to induce structure in water.) These workers also showed that solutions of tetra-n-butylammonium butyrate cause downfield adjustments to the chemical shift of the water proton even up to 33°C which they took as an indication of a strong tendency to induce structure in the water. The chemical shifts were in fact larger than predicted suggesting that the hydration spheres of the hydrophobic cation and anion overlap and stabilize each other compared to a solution of tetra-n-butylammonium bromide where the anion and cation exert competitive effects on water.

Kreishman and Leifer (154) recently suggested that the proton NMR signal of water is composed of three components in a solution of a tetraalkylammonium salt. These components are the water near the cation, the water near the anion and the bulk water. The interchange between these states must be rapid on the NMR time scale inasmuch as only one peak is observed for water in these solutions. They use this concept of three contributions to the signal to rationalize the results of Marciacq-Rousselot et al. and to try to make sense of why NMR shows tetra-n-butylammonium bromide to be a disrupter of water structure when thermodynamic measurements indicate that it forms water structure. Kreishman and Leifer propose that the water molecules near the quaternary ammonium cation are arranged in a cage-like aggregation of some sort as intimated by Klotz (155). These ordered molecules are more tightly arranged than in bulk water and so their protons are more deshielded. These are the main contributors to the downfield movement of the chemical shift of the proton. They explain further that the hydration cage of the cation must include more water molecules as the cation becomes larger. Therefore, the ability of a tetra-n-alkylammonium salt to cause the chemical shift of the water proton to move downfield should be greater with an increasing number of carbons in the ion which is exactly what the French investigators observed at low temperature using solutions of the fluoride salts.

The likelihood of the formation of a hydration cage becomes less as the temperature increases because it is a process which decreases entropy. A local decrease in entropy becomes more improbable with increasing temperature because the entropy of pure (bulk) water becomes greater at higher temperatures. They predicted that the most ordered system would be the first to lose its hydration cage (tetra-n-butyl cation) and in fact, at 25°C, the data of the French workers confirms that the order of ability to induce a downfield movement in the chemical shift of water is changed. The tetra-n-propyl fluoride now causes the greatest shift, followed by the tetramethyl salt which is followed by the tetra-n-butyl salt. As the temperature is increased still further, Kreishman and Leifer postulate that the hydration cages break down completely and leave only simple (though undefined) "water of hydration." This is probably a radial immobilization of water molecules around a roughly spherical cation. Thus at 43°C, the order of downfield movement of the chemical shift of the water proton is such that tetramethylammonium fluoride causes the greatest change followed by tetra-n-propylammonium fluoride and finally by tetra-n-butylammonium fluoride. However, the magnitude of the changes are less than those found at a lower temperature. The authors reason that this is a result of the new hydration mechanism. Because there are now no hydration cages, the ion with the most concentrated surface charge has the greatest ability to cause a change in the chemical shift of the water proton (greater hydrogen bond polarization.) The cations are all monovalent, so the tetramethylammonium cation has the most concentrated charge because it is the smallest. The anions are assumed to have only simple "water of hydration" at all temperatures so, therefore, the smaller the ion (more concentrated surface charge), the less the upfield change should be. The observed behavior at constant temperature, concentration and cation identity is that bromide causes the greatest upfield adjustment, chloride causes a slight upfield adjustment and fluoride causes a downfield change which is in accord with the postulated mechanism.

At low molalities, these two types of water (near-cation and near-anion) should be the only contributors to the change in the chemical shift of the proton signal; the bulk water should be relatively unaffected. Qualitatively, one would expect the number of water molecules hydrating the anion and cation to be of the same order of magnitude, so Kreishman and Leifer propose that NMR happens to be quite sensitive to the contribution of the water near the anion and less sensitive to the water near the cation. They offered no concrete reason for this, but it could be that in the tetraalkylammonium cation, the charge is centered on the nitrogen which is embedded within the bulk of the hydrophobic ion. One could reasonably assume that this gives the cation less ability to influence the chemical shift of water than the more naked charge of the anion. Also, the mechanism for the change in the chemical shift of the proton must be different for the cation and the anion. (The sign of the change, either shielding or deshielding, is of course a function of the orientation of the electronic environment of the ion in relation to that of the water proton.) The anion attracts the hydrogen of a water molecule directly and so can exert a great influence on the electronic environment of the proton. The cation should polarize the hydrogen-oxygen bond of water by attracting the oxygen of the water molecule. The partial positive charge on the hydrogen atom then causes a stronger hydrogen bond with the next layer of water. It seems possible then that the change in chemical shift of the water proton caused by the cation is a secondary effect rather than a primary ion-proton interaction.

This proposed sensitivity of NMR to the anionic water then appears to make tetra-n-butylammonium bromide look like a disrupter of water structure. The authors caution that NMR data should be viewed suspiciously in this regard. Its endorsement of the ability of a given salt to form or disrupt water structure should be viewed only in the context of other available data. For example, the preponderance of thermodynamic data shows tetra-n-butylammonium bromide to be capable of forming water structure.

Let us now look at some work which describes what the actual three-dimensional structure of water might be in solutions of these salts. Klotz (155) cites several examples of the ability of hydrophobic solutes to stabilize odd conformations of water molecules. While his area of concern was the interaction of water with macromolecules, much of the evidence cited has a bearing on the phenomena observed here. Perhaps most pertinent are the data concerning apolar hydrates. These are crystalline substances which are composed of a "guest" molecule of some sort trapped within clathrate cages of water molecules linked together by hydrogen bonds. Klotz divides these into three classes based roughly on the size of the guest molecule. Class 1 apolar hydrates contain guest molecules such as argon, methane, ethane, and sulfur dioxide. The basic unit of structure in Class 1 apolar hydrates is a pentagonal dodecahedron (twelve faces, twenty vertices), the edges of which are the hydrogen bonds holding the water molecules into this form. The dodecahedra themselves are then built up into more complex structures. The water structure in these hydrates is stable because of the presence of the guest molecules within the polyhedral cavities. The guests seem to act as templates to form the water structure. These clathrate cages are stable toward conversion to regular ice structure and often toward conversion to liquid water. The Class 1 hydrates have a definite unit cell containing 8 cavities and 46 water molecules.

The Class 2 guest compounds are slightly larger species such as chloroform, bromopropane and tertiary butane. These hydrates have a unit cell consisting of 136 water molecules with 24 cavities; eight large ones and 16 small ones. Both Class 1 and Class 2 hydrates have the characteristic that each guest molecule is completely enclosed in one of the polyhedra of the unit cell.

Class 3 apolar hydrates are the least symmetric and have no single unit cell for all guests. This is the class which contains quaternary ammonium salts. Feil and Jeffrey (156) obtained the crystal structure of tetraisoamylammonium fluoride hydrate. They discovered that the quaternary ammonium ion was surrounded by a clathrate structure consisting of 38 water molecules. Each "arm" of the quaternary ammonium cation projects into a polyhedral cavity of the clathrate structure. The fluoride ion and the central nitrogen atom were also found to be incorporated into the lattice, probably because of their well-known ability to form hydrogen bonds. The presence of the fluoride ion in the lattice could be part of the reason for the unusually large ability of the tetraalkylammonium fluoride salts to impart structure to water. The fluoride ion is small enough and electronegative enough to fit neatly into a position normally reserved for an oxygen atom. The water thus does not have to contend with any disruptive anionic influence and seems to act as though the quaternary ammonium ion is the only species present in solution.

Bonamico, Jeffrey and McMullan (157) determined the structure of tetrabutylammonium benzoate hydrate and found a similar cage-like structure of water around the tetrabutylammonium ion. The two carboxylate oxygen atoms were incorporated into the clathrate cage structure and the phenyl ring of the benzoate anion was housed in its own polyhedral cavity. These two structures indicate just how versatile and flexible water can be in arranging itself to suit a given guest.

One must keep in mind, however, that these arrangements of water molecules are found in the crystalline hydrates. Narten and Lindenbaum (158) point out it is unlikely that a rigid clathrate structure of the pentagonal dodecahedron type exists in solution. They suggested though that it is possible that a given ordered arrangement of water molecules coalesces around a hydrophobic solute with more frequency than other random arrangements, thereby justifying the use of the term water structure. The publication cited last also contains the determination of the x-ray diffraction pattern of tetra-n-butylammonium fluoride in aqueous solution. The analysis of the data gathered by the authors led them to the conclusion that the near-neighbor distance between water molecules decreased from 2.85 Angstroms in pure water to 2.80 Angstroms in the quaternary ammonium fluoride solution. They claim this decrease to be a direct confirmation of stronger hydrogen bonding and increased "positional correlation" (water structure) in solutions of quaternary ammonium salts. Narten and Lindenbaum attempted to match their data to models based on the clathrate type of structure and what is known as the Ice I model of water structure (159,160) and found a better fit to the Ice I model. This model proposes that the structure of water in solution is a somewhat less rigid arrangement of water molecules than found in ice, but with roughly the same geometric configuration. A good description of the geometry of the water molecules is given by Danford and Levy (160). Their description of the Ice I model states that the water molecules are arranged in layers of puckered six-membered rings which form polyhedral cavities between the layers. Some of these cavities are filled with interstitial water molecules to adjust the resulting density to the known figure. Rather than postulate a complicated clathrate structure composed of oddly shaped polyhedra, this model assumes that the alkyl chains of the quaternary ammonium salt occupy the cavities already present in the Ice I structure. The results of Narten and Lindenbaum seem to say that the hydrophobic solute has the ability to tighten this network from its normal loose configuration in water to a structure more closely resembling that of ice.

The compilation of material recorded above makes clear the fact that quaternary ammonium ions in solution cause water to attain a greater degree of hydrogen bonding (structure) than normally exists without added solute. Several of the reports also indicate that simple inorganic anions cause a disruption of water structure by decreasing the amount of hydrogen bonds relative to pure water. Both of these phenomena appear to be responsible in part for the selectivity observed in the fixed-site anion-exchange resins prepared for this study. The accumulated ion-exchange data may be interpreted as an indication that both the ordering of water caused by the quaternary ammonium ions and the disordering of the water caused by the inorganic anions work together to increase the selectivity of the resins for certain ions. Even though the capacities of the resins are fairly low, most of the functional groups should be on the surface so there is probably a high local concentration of functional groups. The cooperative effect of all of these groups which are capable of enhancing the structure of water can probably generate a good deal of short-range order at the interface between polymer and solution. Again, as the quaternary ammonium ion becomes larger, the tightening of the water structure should become greater. The water appears to try to compensate for the loss of entropy by attempting to minimize the number of excursions from the "normal" structure of pure water which are occurring in the solution. Therefore, a given anion is more easily forced to associate with the cation as the cation becomes larger.

The larger and more poorly hydrated anions cause the equilibrium structure of water to be displaced in the other direction toward a less stable configuration than in pure water. Whereas the larger quaternary ammonium ions cause increased retention of a given anion by changing the entropy of water, the inorganic anions probably have a greater effect on the enthalpy of the solution. Recall that the anions are more likely to associate with a given cation as their enthalpy of hydration becomes less exothermic. The breaking of hydrogen bonds necessary to allow the anion to be inserted among the water molecules requires the input of energy. New ion-water and water-water associations recoup some of the lost energy but the result is still a net breaking of hydrogen bonds as the inorganic anion becomes larger. The cooperative contributions of these interactions to anion-exchange selectivity are illustrated nicely in Figure 12.

It is curious that ions which cause an enhancement of water structure and ions which cause a disruption of water structure both produce the same effect, namely, increased selectivity of the ion for a given counterion. An extremely interesting parallel example is that of the thermal stability of the tertiary structure of a globular protein in aqueous solutions of various salts and non-polar molecules (161,162). These studies were carried out by von Hippel and Wong using the protein known as bovine pancreatic ribonuclease. This protein can be caused to "unfold" from its normal configuration by heating it in dilute aqueous solutions of salt at about neutral pH. This structural transition occurs at about 60°C without the influence of any outside perturbation besides the applied heat. The authors added various salts and neutral molecules to solutions of the protein and observed the affect that each solute had on the transition temperature of the protein. If the transition temperature of the protein increases, the implication is that the solute in some way stabilizes the tertiary structure of the protein, whereas if the transition temperature decreases, the conclusion is that the solute destabilizes the tertiary structure of the protein. They found that the salts potassium phosphate and ammonium sulfate actually stabilized the protein and raised the transition temperature slightly. These are well-hydrated salts that probably cause very little disruption of water structure. Salts such as KCl and NaCl affected the transition temperature very little. The authors discovered that salts such as LiBr and KSCN drastically reduced the transition temperature. (These anions are not only disruptive of water structure, but are also relatively late-eluting on a benzyltrialkylammonium anion exchanger.)

They next tested several quaternary ammonium salts which are of course capable of increasing the structure in water. They found that tetramethylammonium chloride had very little effect on the transition temperature. Tetramethylammonium bromide decreased the transition temperature slightly; tetraethylammonium bromide caused a greater decrease in transition temperature; and tetra-n-propylammonium bromide and tetra-n-butylammonium bromide caused increasingly greater destabilization of the tertiary structure of the protein. Thus, the effect of agents capable of enhancing and disrupting water structure is the same; the stability of the "native" tertiary structure of the ribonuclease is decreased by either class of solutes.

Besides the effects of the local reorganization of the water structure by the ions, there may be another influence on the system caused by the unique nature of the low-capacity anion exchangers. Because of the reaction conditions employed, it is believed that the quaternary ammonium ions are introduced into a very thin region at the surface of the macroreticular channels within the copolymer bead. Thus, in an actual chromatographic situation, there would be a layer of eluent in contact with a thin, moderately polar surface region, backed up by a non-polar bulk matrix. This is in contrast to a resin of high capacity where functional groups exist throughout the matrix and not just at the surface. At any given moment, the quaternary ammonium ion pendant on the polymer chain exists as an ion pair with either an analyte or an eluent ion. These ion pairs are in close proximity to the non-polar matrix. One must remember that on a microscopic basis, the surface is an entangled mesh of cross-linked polymer chains which have some mobility associated with them. Obviously, the interaction between the ion pair and the hydrophobic matrix will be more favorable as the charge becomes more diffuse and the ion pair thus becomes more hydrophobic. It is even possible that the ion pairs could diffuse into the bulk polymer phase to the extent allowed by the mobility of the polymer chains.

Evidence for this functional group mobility comes from the ESCA (Electron Spectroscopy for Chemical Analysis) studies of Everhart and Reilley (163,164). They examined amine functional groups on the surface of a polyethylene film which had been partially oxidized in a plasma. This film is analogous to the low-capacity anion exchangers in that the polar oxidized layer is at the surface and is backed up by the bulk phase of non-polar polyethylene. They showed that the ESCA signal for the amine nitrogen actually disappeared as the free-base amines slowly diffused from the polar surface region into the non-polar bulk of the wetted film. They found that the nitrogen signal could be regenerated by treating the film with $H_3PO_4$ or $H_2SO_4$. This implies that the ammonium phosphate and ammonium sulfate formed were not sufficiently "soluble" in the bulk phase and so migrated back to the surface. However, HCl and $HNO_3$ could not restore the nitrogen ESCA signal, thus indicating that the ammonium chloride and ammonium nitrate were able to remain in the less polar bulk phase of the film below the ESCA sampling depth. (Notice the correlation of this behavior with the effects that these ions have on the structure of water.)

It is suggested here that this sort of functional group mobility and interaction with the hydrophobic matrix perhaps contributes to the enhanced retention of the large polarizable ions. This effect is probably not as large as in polyethylene because of the high degree of cross-linking found in macroreticular resins. The cross-linking would have a retarding effect on the diffusion of the functional groups within the matrix. Besides the work of Everhart and Reilley, there are other contributions which suggest this sort of mobility of polymer surfaces (165,166).

### Selectivity of resins with hydroxyalkyl substituents

When the behavior of the hydroxyalkyl resins in Table 20 is examined, one does not see the same smooth variation of properties that occurred with the trialkyl resins in Table 19. If the TMA (Type I) resin is compared to the DMEA (Type II) resin, very little change in relative retention is observed for any ion except $BF_4^-$, which elutes slightly earlier in relation to chloride. Moving to the MDEA resin, $I^-$ and $BF_4^-$ now decrease in relative retention. The decrease for $BF_4^-$ is so great that the elution order of $I^-$ and $BF_4^-$ becomes inverted. Also, $ClO_3^-$ and $NO_3^-$ appear to sustain a significant loss of retention relative to chloride. This trend does not, however, continue with the TEA resin. The first fact of note is that the retention time for chloride on the TEA resin is roughly twice that of either the MDEA or DMEA resins. Also, the relative retentions of the polarizable anions increase slightly compared to the DMEA resin. These results are believed to be a consequence of the long chloromethylation time needed to produce this resin. Because the resin has a capacity similar to the others, there obviously must be a great excess of unreacted chloromethyl groups on the surface. There may also be hydroxymethyl groups resulting from the hydrolysis of the chloromethyl groups. The heavy surface modification somehow influences the retention of ions by making the stationary phase more favorable an environment for the presence of an ion. It is interesting to note that although the retention times of the ions are drastically increased on this resin, the relative retentions are not affected strongly.

It is not known why TEA is so unreactive toward the chloromethylated substrate. The low reactivity may be related to the viscosity of the reagent and its considerable ability to form hydrogen bonds in a hydroxylated solvent such as methanol which was employed in the amination step.

The data of Gozdz and Kolarz (105) show some agreement with that obtained here. Moving from a TMA resin to a TEA resin by replacing methyl groups with hydroxyethyl groups, they observed a decrease in the selectivity of the resins for bromide and iodide compared to chloride. However, they found an increase in the selectivity for fluoride, which is also marginally visible in the MDEA resin shown in Table 20. The main inconsistency is that Gozdz and Kolarz observed larger differences, probably because of the high capacity of their resins. Their TEA resin showed a continuation of the trend in the other resins rather than the slight reversal of properties noted in the TEA resin prepared in this study. This probably resulted from two factors. Because their resins were of high capacity, all of the polymers needed to be chloromethylated heavily so the effects on the matrix were probably similar in each case. Also, they ran the amination reactions for five days at 50°C and so forced the transformation of a higher percentage of chloromethyl groups into anion-exchange sites which would cause the influence of the surface to be less than in the resin of low capacity.

Excluding the TEA resin, the results acquired here seem to be in line with what might be expected. Although the size of the quaternary site increases as the methyl groups are substituted by hydroxyethyl groups, the new substituents can participate in hydrogen bonding with water. This causes less disruption of the water structure (compared to a trialkyl resin) and thus provides less impetus for the formation of a water-structure enforced ion pair. The hydrophilic nature of the ion-exchange site also helps to preclude an extensive interaction with the non-polar matrix.

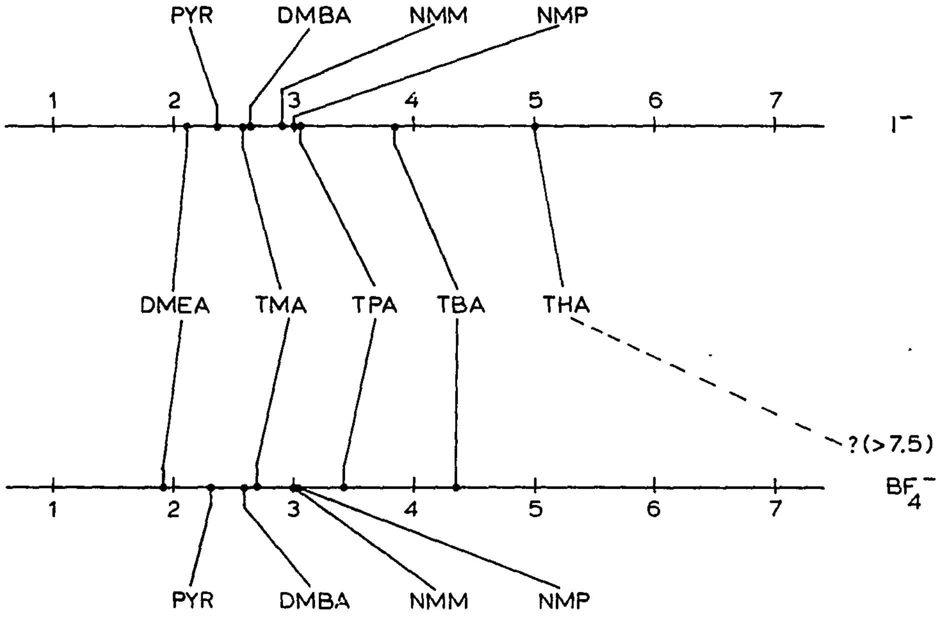
## Selectivity of resins with cyclic substituents

Selectivity data for these resins are shown in Table 21. Many anions show no remarkable selectivity changes compared to the other resins. The resin containing the benzylpyridinium ion is perhaps most similar to the TMA resin. This is a surprising result in light of the fact that the nitrogen is in an aromatic ring. It shows a slight decrease in relative retention of $I^-$ and $BF_4^-$ compared to the TMA resin. This indicates that it is similar to the MDEA resin in its behavior. The resins prepared from the other three tertiary amines show some slight increases in relative retention of the polarizable ions $I^-$ and $BF_4^-$, but it does not appear that they offer any distinct advantages over a trialkyl resin in ion chromatography.

## Conclusions concerning monovalent selectivity

Caution must be used in the interpretation of all of these results. First, if resins of higher capacity are prepared, selectivity changes related to chemical structure may very well be amplified as indicated by the results of Gozdz and Kolarz (105). The capacity of these resins could probably be increased by a factor of 4-6 without becoming too high for use as a stationary phase in single-column ion chromatography. It would be of interest to prepare some batches of resin with fairly high capacities and some of the more unusual functional groups such as benzylpyridinium or benzyl-N-methylmorpholinium to see what surprises are concealed by the low capacities of the present resins. Also, the use of a different eluent (either weaker or stronger) would tend to change selectivity somewhat (167). Changes in pH would also cause differences because weak acids would be shifted in accordance with their degree of ionization. This compilation of data is meant to be used only as an indication of trends in behavior caused by changes in chemical structure.

It appears that the behavior of a resin containing any quaternary ammonium ion can be related to a standard scale based on the behavior of the trialkyl and hydroxyalkyl resins. The scheme would use the relative retention of an ion such as $ClO_3^-$, $I^-$ or $BF_4^-$ to categorize the behavior of the resin. These polarizable ions are quite sensitive to changes in the structure of the quaternary ammonium ion. A scale of relative retention for these ions could be drawn up as shown in Figure 13. Then the general behavior of a resin which is not a member of these series (such as one prepared with N-methylmorpholine) could be estimated by noting where the relative retentions of the test ions fall in relation to the members of the series with regular structural variation.



Numbers are relative retentions for the ion listed

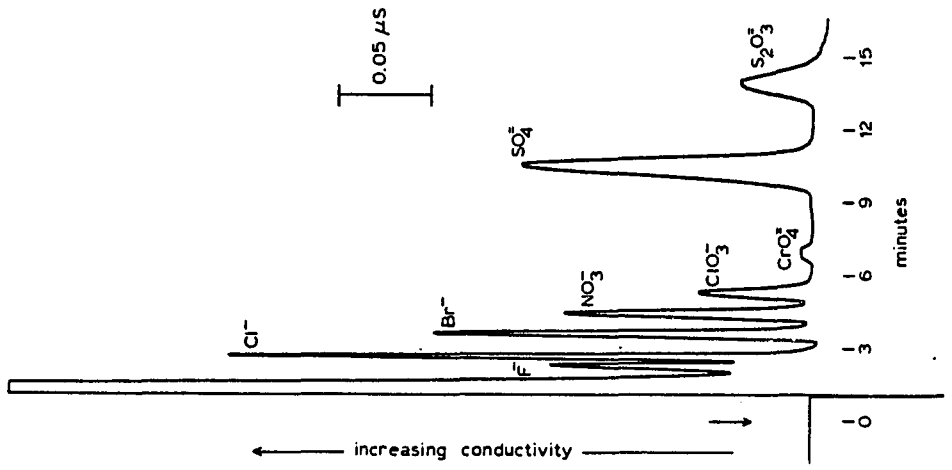
Figure 13. The use of iodide and tetrafluoroborate to classify unusual strong-base anion exchangers.

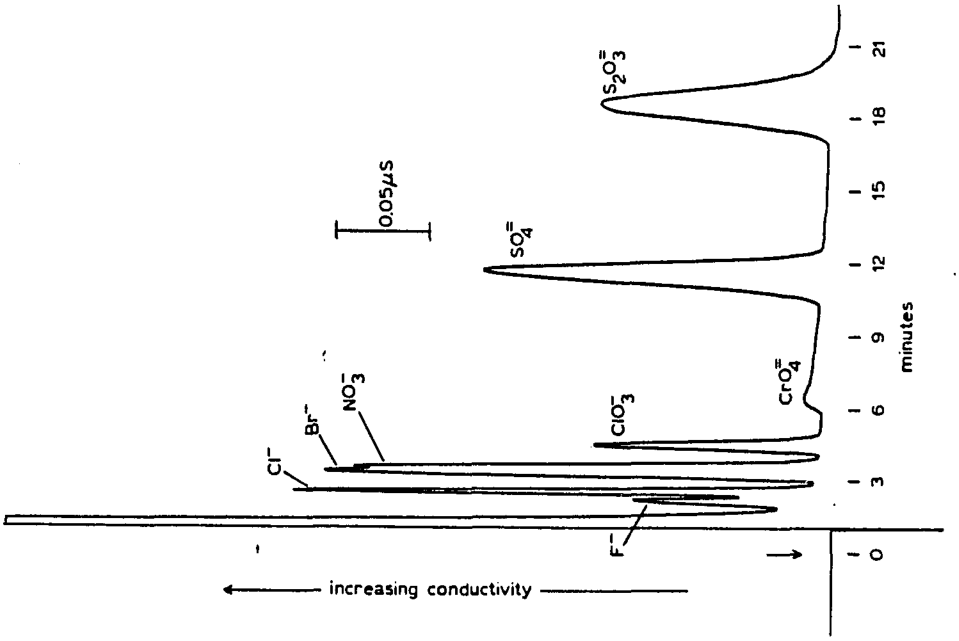
This is not unlike the use of the McReynolds number in gas chromatography as an indicator of the polarity of the stationary phase. To give an example, the NMM resin is similar to the TPA resin in its behavior toward both $I^-$ and $BF_4^-$ as shown in Figure 13.

## Separation of mixed monovalent and divalent ions

Recall that one of the reasons for carrying out the study of functional group structure was to determine if a resin could be prepared that would be more appropriate than a Type I resin for separating mixtures of monovalent and divalent ions. A resin based on a trialkyl amine of high molecular weight seemed to be a good preliminary choice. This type of resin retains monovalent ions more strongly than the Type I resin and so should narrow the gap between the monovalent and divalent ions provided that the effect on the divalent ions is not similar. Several experiments were performed with various resins and the results indicate that not only do the monovalent ions grow in relative retention (compared to $Cl^-$), but the divalent ions suffer a loss in relative retention as the functional group becomes more hydrophobic. Figure 14 shows a side-by-side comparison of two resins under equivalent conditions. The only difference in the resins is their functional group. It is evident that the THA resin performs a better separation of the monovalent

Figure 14. The comparison of the separation of mixed monovalent and divalent anions on two resins with different functional groups. The resin on the left is a TMA resin with a capacity of 0.046 meq/g. The resin on the right is a THA resin with a capacity of 0.043 meq/g. The eluent is 0.4 mM KHP at a pH of 5.0 and a flow rate of 1.0 mL/min. The resins are packed in 500 x 2.0 mm i.d. glass columns.


0.05 $\mu S$
$Cl^-$
$Br^-$
$NO_3^-$
$F^-$
$ClO_3^-$
$CrO_4^=$
$SO_4^=$
$S_2O_3^=$
increasing conductivity
0
3
6
9
12
15
minutes


0.05$\mu S$
$Cl^-$
$Br^-$
$NO_3^-$
$F^-$
$ClO_3^-$
$CrO_4^=$
$SO_4^=$
$S_2O_3^=$
increasing conductivity
0
3
6
9
12
15
18
21
minutes

ions as well as shortening the analysis time for this particular mixture of anions.

After these results were obtained, a more systematic investigation of the selectivities of some representative resins toward a few divalent ions was undertaken. Given the orderly behavior of the trialkylammonium and hydroxyalkylammonium resins toward monovalent ions, the decision was made to use only certain of the members of these series to see how the structure of the functional groups affects the selectivities of the resins toward divalent ions.

Initially, the same resins used for the monovalent study were employed to study the selectivities of the divalent ions. However, the conditions chosen were not extremely appropriate. The eluent chosen was potassium hydrogen phthalate (0.3 mM) at a pH of 5.6. The resins had an average capacity of only about 0.027 meq/g, so these conditions were slightly overpowering. The ions were driven off the column so quickly that it was difficult to discern trends in behavior. Another problem was the choice of the pH of the eluent. Table 26 shows that at a pH of 5.0, 28% of the phthalic acid exists as the divalent ion and at pH 6.0, 80% of the acid is in the divalent form. This indicates that even slight errors in the pH adjustment in this region could have drastic effects on the elution of

Table 26. Ionization of *o*-phthalic acid at selected pH values

| pH | 3.00 | 3.50 | 4.00 | 4.50 |
|---|---|---|---|---|
| $H_2A$ | 45.4% | 20.7% | 7.4% | 2.3% |
| $HA^-$ | 54.4 | 78.4 | 89.1 | 87.0 |
| $A^=$ | 0.2 | 0.9 | 3.5 | 10.7 |

| pH | 5.00 | 5.50 | 6.00 | 6.50 |
|---|---|---|---|---|
| $H_2A$ | 0.6% | 0.12% | 0.017% | 0.002% |
| $HA^-$ | 71.5 | 44.7 | 20.4 | 7.50 |
| $A^=$ | 27.9 | 55.18 | 79.6 | 92.5 |

anions. Unfortunately, by the time that this data was reduced and the difficulties were diagnosed, many of the original resins had been used up or were depleted to the point that there was not enough remaining to pack a column.

Therefore, a decision was made to prepare three batches of resin with fairly high, but similar capacities (about 0.09 meq/g) to better evaluate trends in selectivity with changes in functional group. The resins prepared included batches containing the benzylmethyldiethanolammonium functional group (MDEA; 0.090 meq/g), the benzyltrimethylammonium functional group (TMA; 0.092 meq/g), and the benzyltributylammonium functional group (TBA; 0.096 meq/g.) These represent the polar, standard and non-polar functional groups respectively. These resins were prepared according to the procedures described earlier with the appropriate adjustments to the chloromethylation time, etc.

The eluent chosen for use with these resins was 0.4 mM potassium hydrogen phthalate at two pH values, 5.0 and 6.0. The eluent was pumped through the columns at the rate of 1.0 mL/min and the columns used were the 500 x 2.0 mm columns used earlier. The results are shown in Tables 27 and 28. Several trends emerge from this data. This study corroborates the results in Figure 14 and shows even more

Table 27. The relative retentions of certain monovalent and divalent ions on three anion exchangers of differing polarity at pH 5.0, 0.4 mM KHP, 1.0 mL/min ($t_{r\ anion}/t_{r\ Cl^-}$)

| Ion | MDEA[a] | TMA[b] | TBA[c] |
|---|---|---|---|
| $Cl^-$ | 1.0 | 1.0 | 1.0 |
| $NO_3^-$ | 1.47 | 1.79 | 2.77 |
| $ClO_3^-$ | 1.78 | 2.42 | 3.18 |
| $I^-$ | 3.81 | 6.16 | 13.9 |
| $SCN^-$ | 7.50 | 14.5 | ---- |
| $ClO_4^-$ | 9.12 | ---- | ---- |
| | | | |
| $SO_4^=$ | 7.31 | 7.29 | 6.36 |
| $S_2O_3^=$ | 15.75 | 16.6 | 9.23 |
| $C_2O_4^=$ | 7.41 | 7.18 | 6.30 |
| $MoO_4^=$ | 9.50 | 9.92 | 8.72 |
| $WO_4^=$ | ---- | ---- | ---- |
| | | | |
| $t_r$ $Cl^-$ | 3.20 min | 3.80 min | 3.90 min |

[a] Capacity = 0.090 meq/g.

[b] Capacity = 0.092 meq/g.

[c] Capacity = 0.096 meq/g.

Table 28. Relative retentions of certain monovalent and divalent ions on three anion exchangers of differing polarity at pH 6.0, 0.4 mM KHP, 1.0 mL/min ($t_{r\ anion}/t_{r\ Cl^-}$)

| Ion | MDEA[a] | TMA[b] | TBA[c] |
|---|---|---|---|
| $Cl^-$ | 1.0 | 1.0 | 1.0 |
| $NO_3^-$ | 1.48 | 1.93 | 4.32 |
| $ClO_3^-$ | 1.92 | 2.83 | 5.76 |
| $I^-$ | 4.24 | 8.00 | 35. |
| $SCN^-$ | 8.72 | ---- | ---- |
| $ClO_4^-$ | 10.8 | ---- | ---- |
| | | | |
| $SO_4^=$ | 4.64 | 4.77 | 4.21 |
| $S_2O_3^=$ | 9.68 | 11.3 | 7.65 |
| $C_2O_4^=$ | 4.96 | 5.10 | 4.80 |
| $MoO_4^=$ | 6.72 | 7.27 | 6.94 |
| $WO_4^=$ | 7.20 | 6.30 | 6.70 |
| | | | |
| $t_r$ $Cl^-$ | 2.50 min | 3.00 min | 3.40 min |

[a] Capacity = 0.090 meq/g.

[b] Capacity = 0.092 meq/g.

[c] Capacity = 0.096 meq/g.

clearly that the changes in functional group structure have an effect on the behavior of the resins toward both the highly polarizable monovalent ions such as $SCN^-$ and $ClO_4^-$ and the divalent ions. The effects on selectivity are amplified by the higher capacity as predicted earlier. The monovalent ions, as expected, show the same behavior as they did using the benzoic acid eluent. That is, they elute at longer relative retentions as the functional group becomes more non-polar. To contrast the behavior of the monovalent ions, the relative retentions of the divalent ions such as sulfate and thiosulfate seem to be more complex. The relative retentions of these ions are quite similar on the MDEA and TMA resins at pH 5.0. There is a barely noticeable maximum in relative retention at the TMA resin when the pH is adjusted to 6.0. Figures 15, 16 and 17 show separations of $Cl^-$, $NO_3^-$ and $SO_4^=$ on each of the three resins under identical elution conditions to give a more graphic representation of their behavior.

The eluent characteristics also affect the behavior of the monovalent ions. Changes in pH cause somewhat unanticipated effects. Intuitively, one might expect that as the pH (therefore the ionic strength) increases, the relative retention of the monovalents would decrease, but

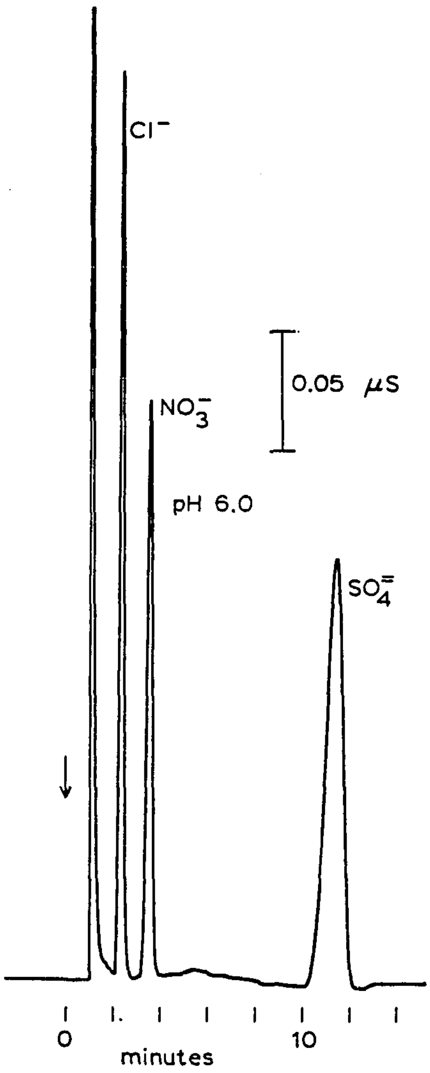


Figure 15. The separation of chloride, nitrate and sulfate on MDEA anion exchanger of capacity 0.090 meq/g. The eluent is 0.4 mM KHP at pH 6.0; flow rate 1.0 mL/min. The column is 500 x 2.0 mm i.d.

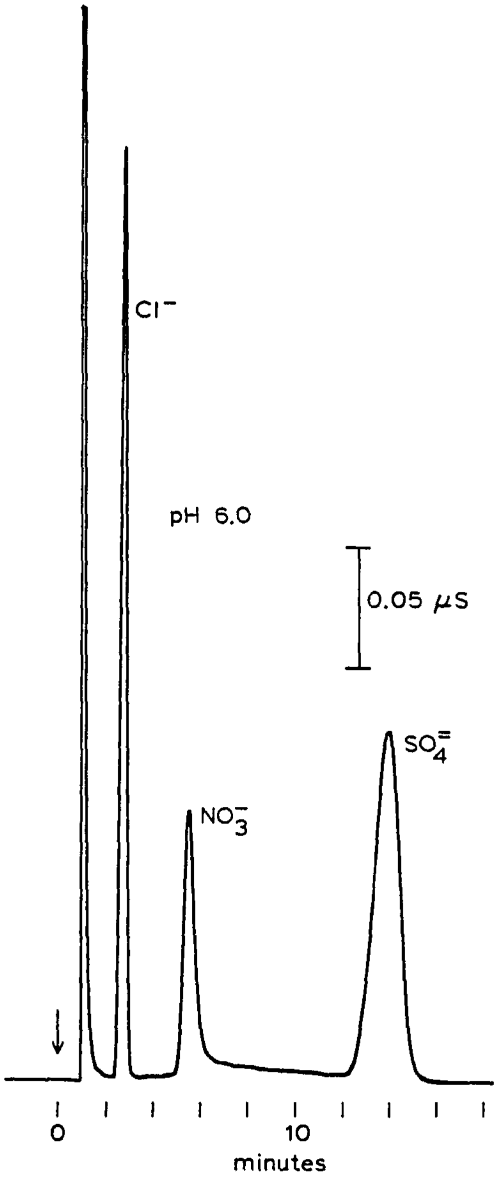


Figure 16. The separation of chloride, nitrate and sulfate on TMA anion exchanger of capacity 0.092 meq/g. Conditions as in Figure 15.

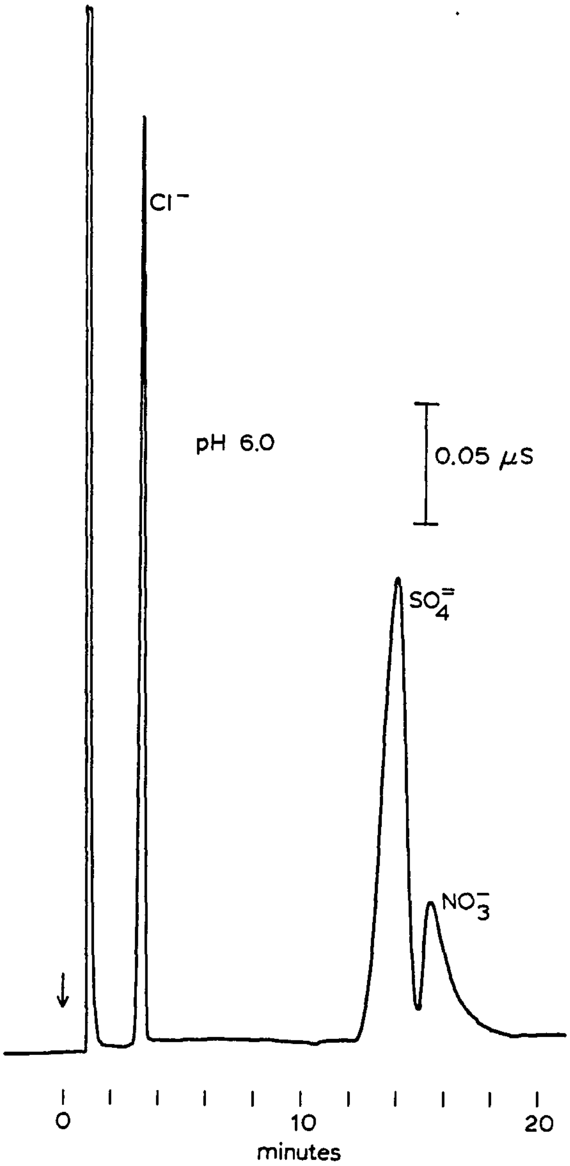


Figure 17. The separation of chloride, nitrate and sulfate on TBA anion exchanger of capacity 0.096 meq/g. Conditions as in Figure 15.

the change is in the opposite direction. (Note that the absolute retention times do decrease slightly.) An increase in pH has the anticipated effect on most of the divalent ions; that is, as the pH increases, the relative retentions of the divalent ions decrease. The behavior of three ions on the TBA column over an expanded pH range is shown in Figures 18 and 19. All conditions are the same except the pH. Note that at pH 6.55, the retention time of nitrate increases enough so that it elutes well after sulfate. The large jump in relative retention for nitrate between pH 5.0 and pH 6.0 will be explained later.

The five preceding figures show that the relative elution behavior of the monovalent and divalent ions depends on both functional group identity and eluent pH. The capacity also has an effect on the relative elution behavior. Table 29 shows the relative retentions for several anions on two Type I resins. Resin A is the same one used in Figure 16. Resin B is one prepared so that it has exactly half of the capacity of Resin A. The eluent used for Resin A is 0.4 mM potassium hydrogen phthalate at pH values of 5.0 and 6.0. The eluent used for Resin B is 0.2 mM potassium hydrogen phthalate at pH values of 5.0 and 6.0. The same column was used to hold both resins. These conditions should allow the importance of the capacity to be

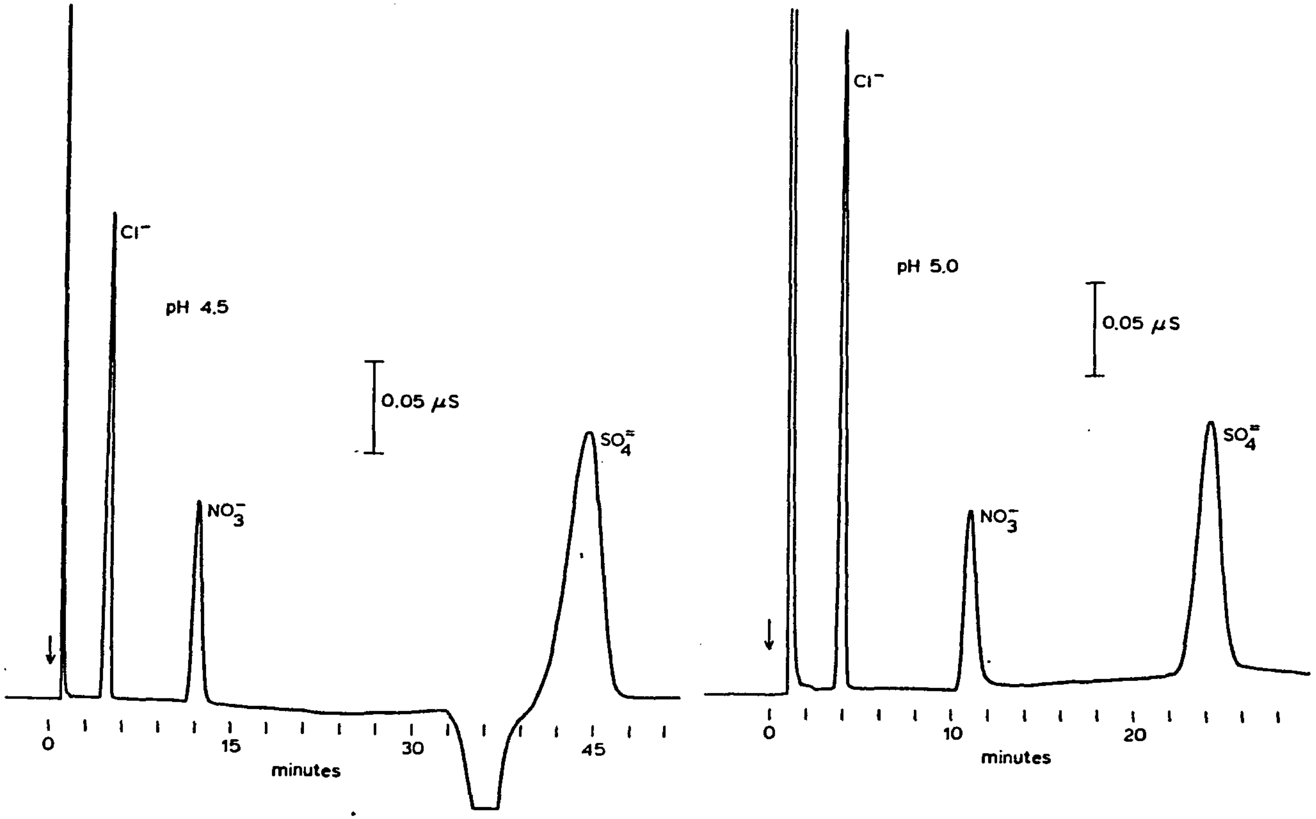


Figure 18. The comparison of the separation of chloride, nitrate, and sulfate on a TBA resin of capacity 0.096 meq/g at different pH values. The eluent is 0.4 mM KHP at a flow rate of 1.0 mL/min and the pH indicated in the Figure. The column is a 500 x 2.0 mm i.d. glass column.

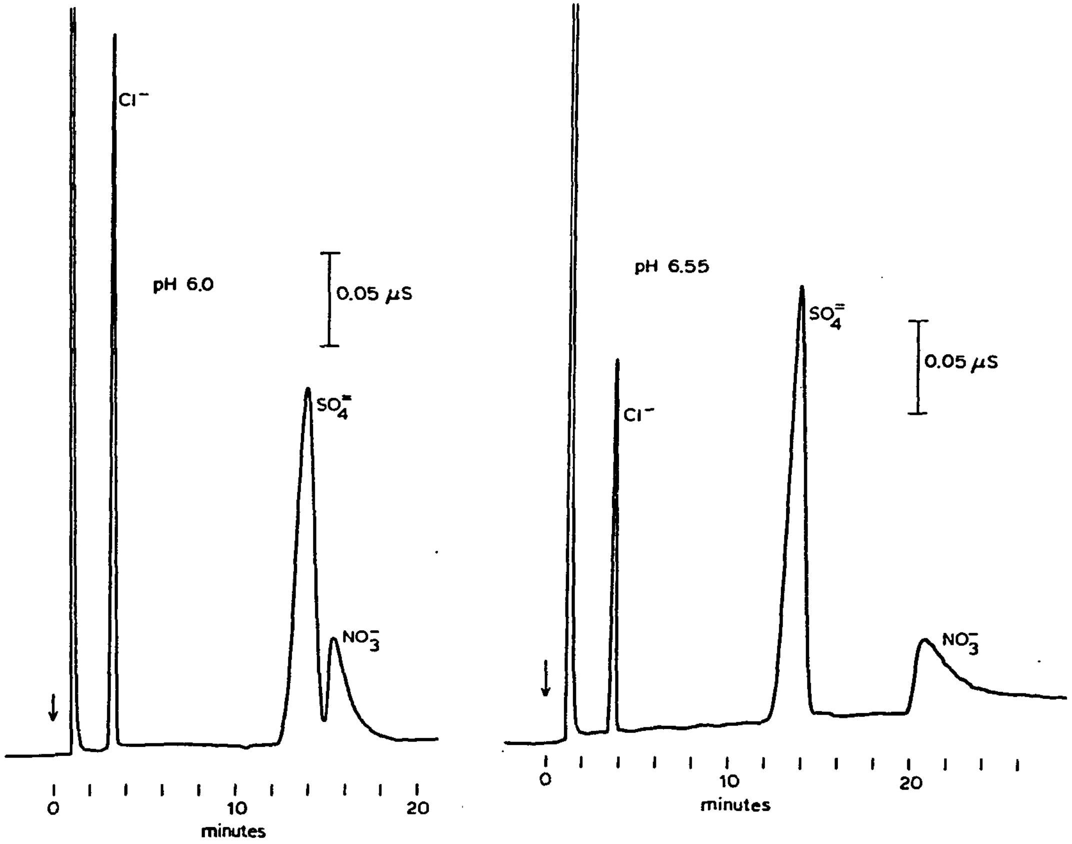


Figure 19. The comparison of the separation of chloride, nitrate and sulfate on a TBA resin of capacity 0.096 meq/g at different pH values. The eluent is 0.4 mM KHP at a flow rate of 1.0 mL/min and the pH indicated in the Figure. The column is a 500 x 2.0 mm i.d. glass column.

Table 29. Effect of capacity on the relative retentions of monovalent and divalent ions on two Type I resins ($t_r$ anion/$t_r$ $Cl^-$)

| Ion | "A"<br>0.4 mM KHP<br>pH 5.0<br>0.092 meq/g | "B"<br>0.2 mM KHP<br>pH 5.0<br>0.046 meq/g | "A"<br>0.4 mM KHP<br>pH 6.0<br>0.092 meq/g | "B"<br>0.2 mM KHP<br>pH 6.0<br>0.046 meq/g |
|---|---|---|---|---|
| $Cl^-$ | 1.0 | 1.0 | 1.0 | 1.0 |
| $NO_3^-$ | 1.79 | 1.42 | 1.93 | 1.56 |
| $ClO_3^-$ | 2.42 | 1.80 | 2.83 | 1.97 |
| $I^-$ | 6.16 | 3.25 | 8.00 | 3.61 |
| $SCN^-$ | 14.5 | 7.00 | ---- | 7.87 |
| $ClO_4^-$ | ---- | 8.50 | ---- | 9.42 |
| | | | | |
| $SO_4^=$ | 7.29 | 8.40 | 4.77 | 5.68 |
| $S_2O_3^=$ | 16.6 | 14.2 | 11.3 | 9.65 |
| $C_2O_4^=$ | 7.18 | 8.05 | 5.10 | 6.03 |
| $MoO_4^=$ | 9.92 | 10.1 | 7.27 | 7.68 |
| $WO_4^=$ | ---- | ---- | 6.30 | 7.22 |
| | | | | |
| $t_r$ $Cl^-$ | 3.80 min | 4.00 min | 3.00 min | 3.10 min |

seen clearly because the ratios of each of the eluent species to the number of functional groups will be constant for both resins. The data definitely show that as the capacity becomes greater, the monovalents and divalents draw closer together with the exception of thiosulfate.

Therefore, if one wishes to have a resin which will allow nitrate to elute after sulfate, for example, certain conditions need to be observed. The functional group has to be highly hydrophobic or the capacity has to be quite high if a Type I resin is to be used or the concentration of the eluent salt has to be quite high. Obviously, a combination of the above conditions would also be effective. Such a combination is undoubtedly why the recently introduced S-2 separator column from Dionex Corporation will allow nitrate to elute after sulfate. Clifford and Weber (100) reveal that the resin contains a benzyltriethylammonium functional group which is not very hydrophobic. However, the salt concentration of even the standard eluent (0.0024 M $Na_2CO_3$ + 0.003 M $NaHCO_3$) employed by Dionex is higher than any of the eluents used here and the pH is about 9.85. Technical information published by Dionex recommends that the S-2 column be used with an eluent which is made up of 0.003 M $Na_2CO_3$ + 0.002 M NaOH. The salt concentration is similar to that of the standard eluent but the pH of this eluent is even higher at about 11.2. The capacity of the S-2 resin is unknown, but is assumed to be in the range of about 0.03 to 0.06 meq/g.

To illustrate the interplay of these factors, a batch of benzyltriethylammonium resin of fairly high capacity was prepared according to the procedures which were described earlier. The chloromethylation was carried out at 55°C for 60 minutes (12 M HCl, 2.2 M formaldehyde) and the amination was carried out for about 36 hours in warm methanol. This resulted in a capacity of 0.184 meq/g. A column with dimensions 250 x 2.0 mm i.d. was packed with this resin. The column therefore has the same total capacity as the one packed with the Type I resin used in Figure 16 even though the capacity per gram is twice as high for the TEtA resin. An eluent of 0.4 mM potassium hydrogen phthalate at pH 9.2 was pumped through the column at 1.0 mL/min. Figure 20 shows the separation of $Cl^-$, $Br^-$, $SO_4^=$ and $NO_3^-$ under these conditions. The nitrate does indeed elute after sulfate, even at pH 9.2, thus demonstrating that the assessment by the author of the factors involved in the ion-exchange behavior is accurate.

The peak shapes of the bromide and nitrate are poor, as they are on the S-2 column. This is a function of the high

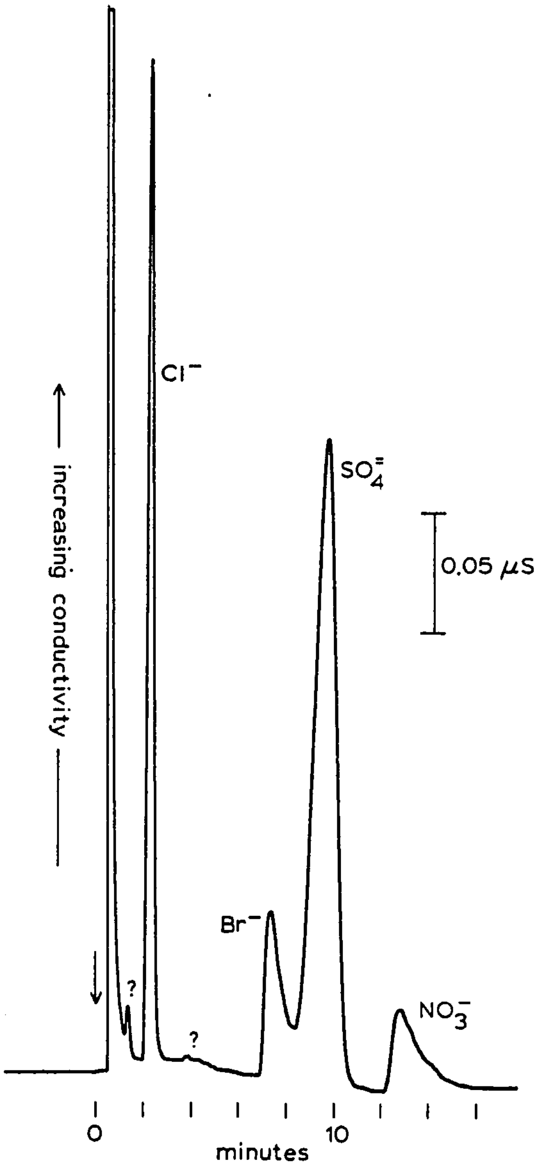


Figure 20. The separation of chloride, bromide, nitrate and sulfate on a TEtA resin with a capacity of 0.184 meq/g. The resin is packed into a 250 x 2.0 mm i.d. column. The eluent is 0.4 mM KHP at a pH of 9.2 and a flow rate of 1.0 mL/min.

capacity and the affinity of the ions for the functional groups. Peak shapes generally improve for the late-eluting monovalent ions as one changes functional group in the more hydrophilic direction, but the ions also elute much earlier. Conversely, the peak shapes for the well-hydrated ions improve as one moves toward more hydrophobic functional groups. Ions such as oxalate and molybdate exhibit prominent tailing on a MDEA resin of moderately high capacity but yield symmetric, normally shaped peaks on resins with a functional group such as TBA.

The concentration of the eluent must also affect the manner in which the ions elute from the column. Figure 21 is a comparison of the same THA column operated at the same pH but different concentrations of potassium hydrogen phthalate. The lower concentration tends to allow the entire chromatogram to be spread out somewhat.

### Explanation of the observed selectivity behavior

The behavior reported above can be easily sorted out by considering some information related to ion exchange and by keeping in mind the earlier discussion of how various classes of ions affect the structure of water. The information in Table 26 will also be called into play.

Consider that in many of the examples cited earlier in this section, it was reported that $SO_4^=$ was a well-hydrated

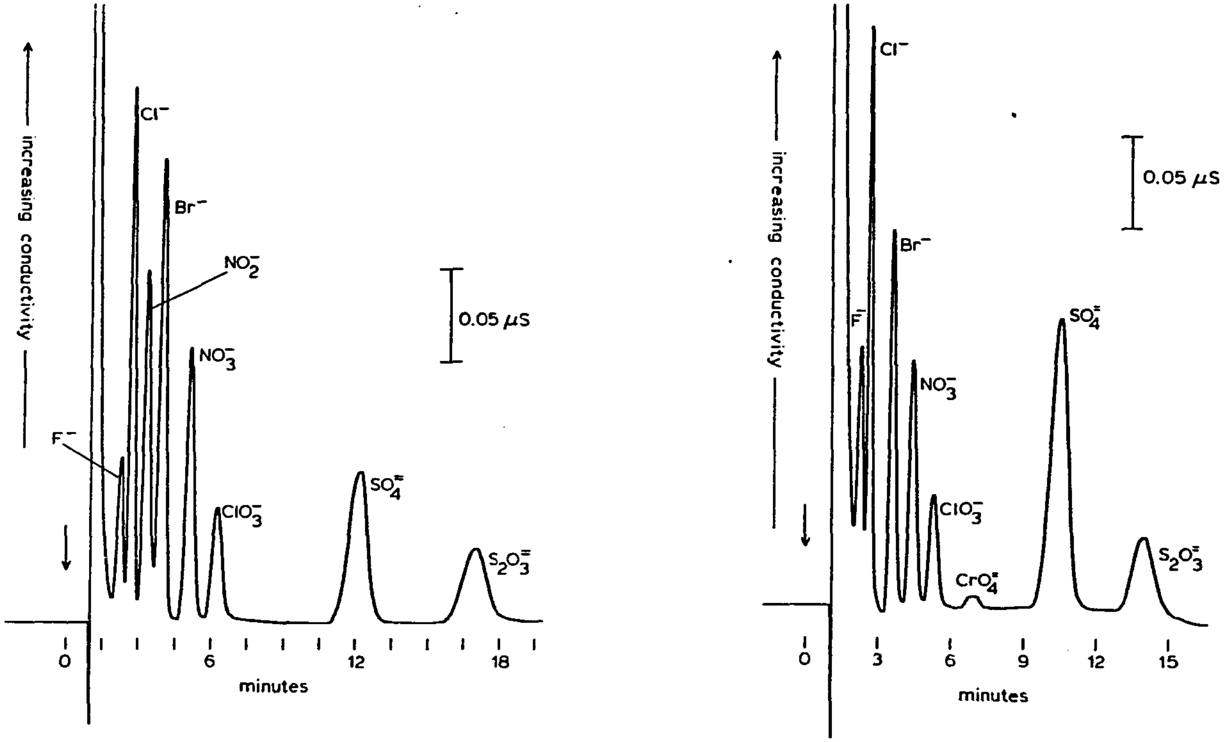


Figure 21. The effect of eluent concentration on the separation of mixed monovalent and divalent ions on a THA resin. The resin has a capacity of 0.043 meq/g and is packed into a 500 x 2.0 mm i.d. column. The eluent used in the left half of the Figure is 0.3 mM KHP at a pH of 5.0. The eluent used in the right half of the Figure is 0.4 mM KHP at a pH of 5.0. Both separations are run at 1.0 mL/min.

ion that seemed to have little effect on the structure of water. Why then does it normally elute after ions such as $Br^-$, $NO_3^-$ and $ClO_3^-$ which are strong disrupters of water structure? The reason for its late elution is commonly referred to as electroselectivity. Electroselectivity alludes to the fact that a solid anion-exchange resin will usually prefer a divalent ion to a monovalent ion, all other conditions being equal. The preference increases as the external solution becomes more dilute and the internal molality of the resin increases. Electroselectivity is usually explained in terms of the Donnan potential which is a potential difference caused by the imbalance between the concentration of ions in solution and the concentration of ions in the resin bead (168). The amount of electroselectivity observed is directly proportional to the Donnan Potential. One might conclude that in this version of ion chromatography, where the resins are porous and of low capacity and the solutions are dilute, the importance of electroselectivity would be diminished. The fact that it is still operative seems to indicate that there is a rather high local concentration of functional groups at the polymer-solution interface. One of the reasons that electroselectivity comes about is related to the entropy of the solution in a manner similar to the so-called chelate effect. Consider an anion exchange resin in the chloride form suspended in a solution of sodium sulfate. Both anions are similar in their effects on water structure and are fairly well-hydrated. The anion exchange resin has a fixed number of ion-exchange sites, x, available. Assume that the solution also contains x $SO_4^=$ ions. If the resin retains only chloride ions, there will be x anionic particles in solution. If the resin retains only sulfate, however, there will be x + x/2 anionic particles in solution because only half the number of sulfate ions are needed to preserve electroneutrality in the resin compared to the number of chloride ions needed. To restate the matter, the Donnan Potential is reduced if the molality of the external solution becomes more similar to that of the resin phase; hence, the divalent ions are preferred by the exchanger.

Electroselectivity is obviously a powerful effect because much other data show that $SO_4^=$ should not be where it is in the order of elution from a Type I anion exchange resin. Glasstone (169) cites the early work of Hofmeister (ca. 1891) concerning the imbibation of water by gelatin. Hofmeister tested a number of ions and their effects on the ability of gelatin to absorb water. He found that sulfate and acetate inhibit the swelling of gelatin but that several other ions enhance the ability of gelatin to absorb water.

The ions which cause gelatin to swell heavily are $SCN^-$, $I^-$, $NO_3^-$, $Br^-$, $ClO_3^-$ and $Cl^-$ to some extent. This categorization of ions is called the lyotropic (Greek, meaning "change to liquid") series. Hofmeister found that an ion such as $I^-$ causes such a great effect that gelatin would often disperse to a sol ("change to liquid") spontaneously without the need for heating.

Glasstone discusses the reverse process, that is, the salting out of solution of lyophilic sols (gelatin) by various ions (170). The ability of an ion to salt gelatin out of solution occurs in the order $SO_4^=$, $C_2H_3O_2^-$, $Cl^-$, $NO_3^-$, $ClO_3^-$, $I^-$ and finally $SCN^-$. This arrangement of ions looks very similar to the order of elution of these anions from a Type I anion exchanger except for the anomalous presence of sulfate at the beginning of the list. This behavior may be interpreted such that the ions which impede swelling or easily salt out the colloid interact so strongly with water that there is less of it available to solubilize the gelatin.

More recent examples from the field of solvent extraction give results similar to this early work. The analogy of ion exchange to solvent extraction is a compelling one and was recognized quite some time ago (171). Navtanovich et al. (172) cite the work of Ivanov and coworkers (173) who established the selectivity of extraction of various anions into toluene by tetraoctylammonium cation. The order of increasing selectivity for monovalent anions found by these workers is $OH^-$, $F^-$, $C_2H_3O_2^-$, $HCO_3^-$, $HSO_4^-$, $Cl^-$, $Br^-$, $C_6H_5COO^-$, $NO_3^-$, $I^-$, and $ClO_4^-$. (Note the position of bisulfate.)

The work of Navtanovich and coworkers in the publication cited above concerns establishment of the positions of $SCN^-$, $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ in the solvent extraction of these and other anions using benzyltrialkylammonium cations with alkyl chains of 7-9 carbons. The solvent used was xylene. They found the order of decreasing selectivity to be $ClO_4^-$, $SCN^-$, $I^-$, $Fe(CN)_6^{3-}$, $NO_3^-$, $Br^-$, $Fe(CN)_6^{4-}$, $Cl^-$, and finally $C_2H_3O_2^-$. This shows that ions such as ferricyanide and ferrocyanide, which should disrupt water structure on the basis of size, actually cause little disruption by virtue of their high charge and act more like slightly polarizable monovalent ions during solvent extraction. Ferrocyanide in fact falls in a position very similar to where sulfate would probably occur in the extraction series. One can easily deduce that ions such as ferricyanide and ferrocyanide would probably be held very tightly on a Type I anion exchanger explicitly because of their high charges.

Ion-selective electrodes based on liquid anion exchangers (174,175) show roughly the same order of selectivity as established in the solvent extraction work discussed in the paragraph above. Nowhere is there a mention of sulfate as an interference in the determination of such anions as nitrate or perchlorate, chiefly because the enthalpies of hydration of the anions are the main causes of selectivity in these electrodes. Many pieces of evidence have demonstrated that $SO_4^=$ is hydrated enough so that it is not attracted preferentially by long-chain quaternary ammonium cations in the absence of the Donnan potential. (As a sidelight, Reinsfelder and Schultz (176) note that these electrodes are really a losing proposition for any ions other than the most hydrophobic such as $ClO_4^-$, because the liquid quaternary ammonium ion exchangers inherently prefer these ions. The evidence presented in this section suggests that a nitrate-selective electrode based on a liquid ion exchanger is more myth than reality.)

Let us reconsider the elution behavior on the anion exchangers of low capacity. Recall that the relative retention of the monovalent ions becomes greater as the ion exchange group becomes more hydrophobic, as the capacity is increased and as the pH of the eluent becomes more alkaline. The relative retentions of divalent ions such as sulfate are a little more complicated in behavior. These anions have similar relative retentions on the TMA and MDEA resins and decrease in relative retention as the anion-exchange site becomes more hydrophobic. The pH changes affect the divalent ions in a manner opposite that of the monovalent ions. The slightly lower affinity of the sulfate (and other divalent ions) for the MDEA resin compared to the TMA resin at pH 6.0 is puzzling. One would expect the affinity to vary smoothly from polar to non-polar resins in complete reversal of the behavior of the monovalent ions. A satisfactory explanation for the maximum in the data is not available at this time.

Now, let us use the sulfate ion as an example to explain the results of varying functional group and pH. The adjustments to the experimental conditions are apparently overcoming electroselectivity and forcing sulfate to take its place in the hydration energy series. First, the sulfate ion presumably has less affinity for an ion-exchange site as the site becomes more hydrophobic by virtue of the favorable interaction that the sulfate ion has with water. Meanwhile, the affinity of the exchanger increases for the monovalent ions as the quaternary ammonium ion becomes more hydrophobic.

Changes in pH also contribute to the change in relative retention of the monovalent and divalent ions. The percentage of divalent phthalate ion increases and the percentage of monovalent phthalate decreases as the pH increases. The exact behavior is shown in Table 26. Apparently, hydrophobic monovalent analyte ions are only eluted well by monovalent eluent ions and so are retained longer and longer (relatively, but not necessarily absolutely) as the percentage of monovalent eluent ion decreases. Concomitantly, the divalent ions can only be eluted efficiently by divalent eluent species and so are retained less as the percentage of divalent ion increases. (This can be explained in another way by noting that the increase in ionic concentration in solution decreases the Donnan potential which will then likewise decrease electroselectivity.)

### Practical implications of the structure of functional groups

The use of anion-exchange resins with different functional groups offers a valuable parameter for improving the separation of some anions. One practical example is shown in Figure 22. Here, a mixture of five anions is injected onto each of three columns containing resins of approximately the same capacity, but with increasingly larger alkyl groups on the quaternary nitrogen. Identical elution conditions were used for each column. The THA resin can perform a baseline separation of the five anions, while

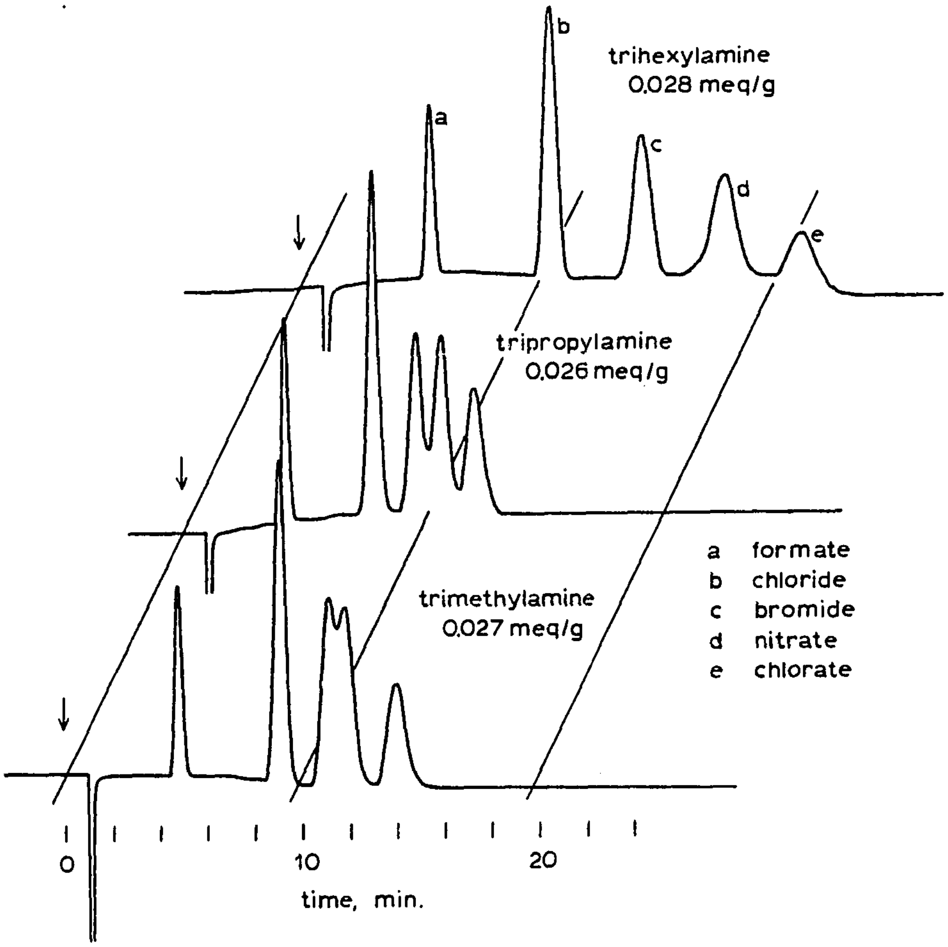


Figure 22. Separation of a mixture of five anions on three resins of similar capacity but different functional group identity. The eluent is 0.001 M benzoic acid at a flow rate of 0.93 mL/min. The resins are all packed in columns which are 500 x 2.0 mm i.d.

the TPA resin gives a less convincing separation and the TMA resin gives poor resolution of bromide and nitrate. The use of the more hydrophobic functional group allows the eluent to remain acidic so that high sensitivity is retained. It is possible to speed up the flow rate when using the THA resin so that the total separation time can be reduced while still retaining the integrity of the separation.

The increased relative retention of monovalent ions can be useful in other situations. Because a resin such as THA spreads the ions out quite a bit, it would be useful for the qualitative analysis of solutions of unknown composition. There would be more "windows" available where ions could appear because differences in selectivity are maximized. Figure 23 shows a separation of several ions on a THA resin. This Figure should be compared to the separation shown in Figure 6 on a Type I resin. Resolution on a Type I resin can be increased somewhat by increasing capacity, but in order to use a conductimetric detector, there are limits to the eluent concentration and hence limits to the capacity of the resins which may be used to achieve reasonable analysis times.

A second situation where these resins would be useful is in separating a small amount of an early-eluting component from a large excess of a late-eluting component or vice

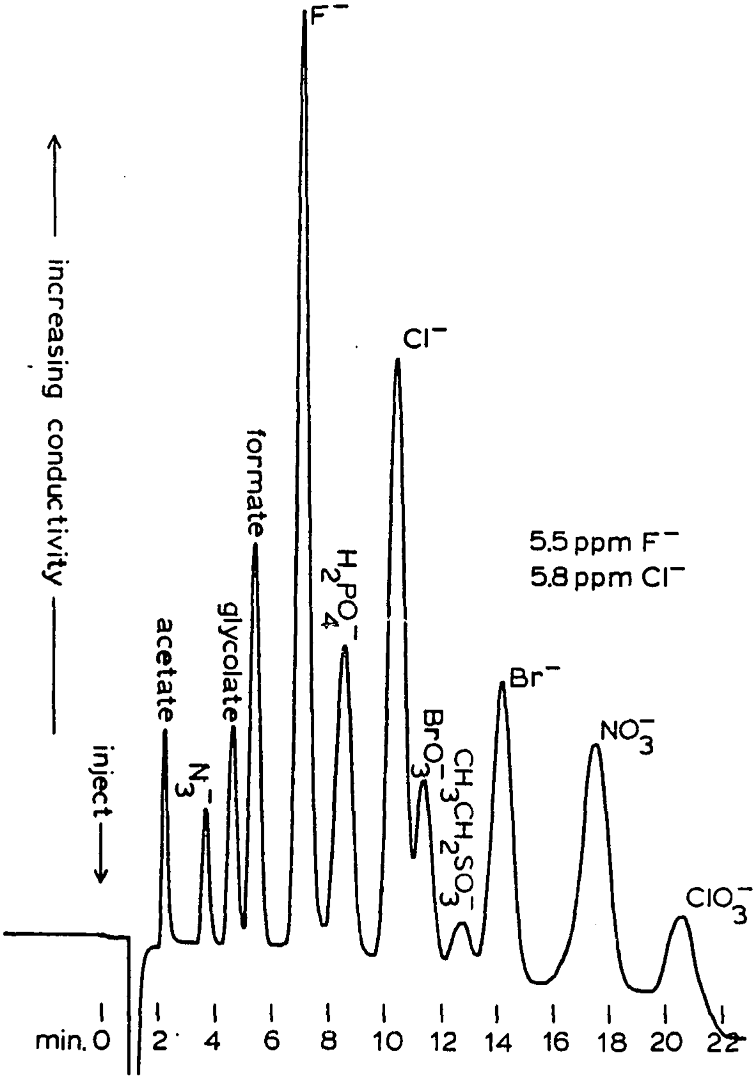


Figure 23. Separation of a mixture of monovalent ions on a THA resin. The capacity of the resin is 0.028 meq/g and the eluent is 0.001 M benzoic acid at a flow rate of 0.93 mL/min. A 500 x 2.0 mm glass column was used.

versa. Again, by using a resin with a naturally high selectivity for late-eluting components, the capacity of the resin can be kept in the usual range, the eluent concentration can remain low and sensitivity will be retained while allowing the minor component to elute well away from the major component. A good example would be the use of a short column of MDEA resin in a system used for dedicated sulfate analysis in natural water samples. This resin has an affinity for monovalent ions which is lower than a Type I resin and an affinity for divalent ions which is similar to a Type I resin. A 10.0 cm x 2.0 mm column packed with MDEA resin of about 0.09 meq/g could be operated with an eluent consisting of 0.3 mM potassium hydrogen phthalate at a pH of 4.5-5.0. The combination of low pH and resin affinity should allow most common monovalent ions to elute shortly after the injection peak and allow sulfate to elute in five or six minutes. The only serious interference for sulfate is oxalate, but this ion is not commonly found in natural waters.

Figures 24 through 27 show a number of practical separations obtained on resins containing a functional group other than a Type I cation. Note that the separation of sulfate and oxalate is virtually impossible to perform on a Type I resin in this pH range.

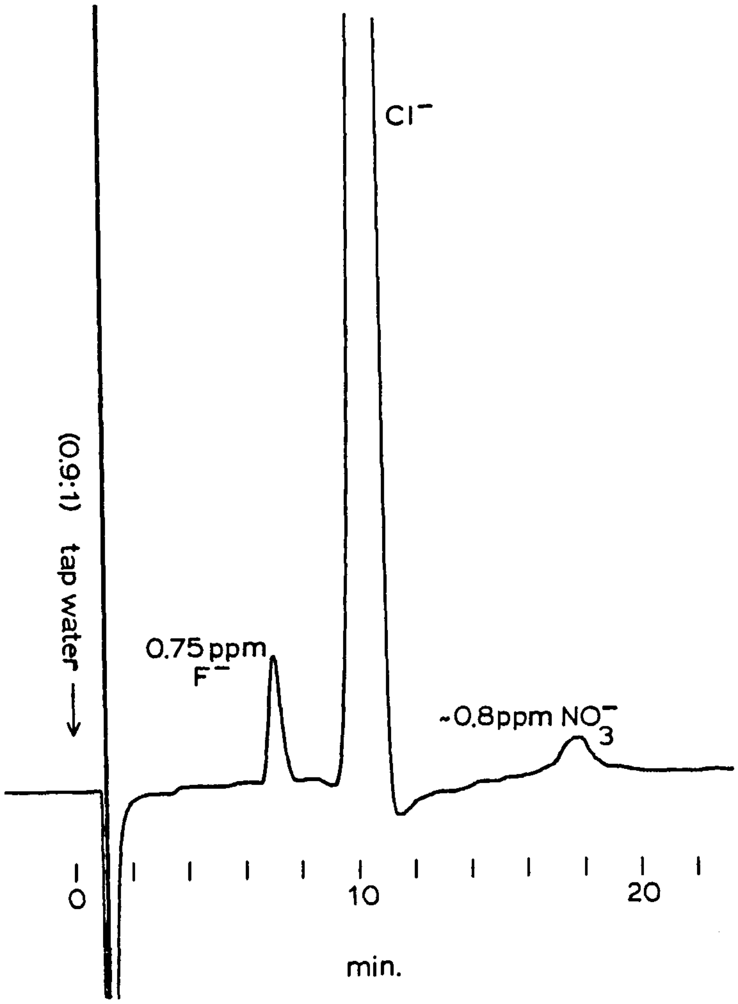


Figure 24. Analysis of tap water for fluoride content. The resin contains a THA functional group and has a capacity of 0.028 meq/gm. The eluent is 0.001 M benzoic acid at a flow rate of 0.93 mL/min. An aliquot of more concentrated benzoic acid was added to the sample to allow the final benzoic acid concentration to equal that of the eluent.

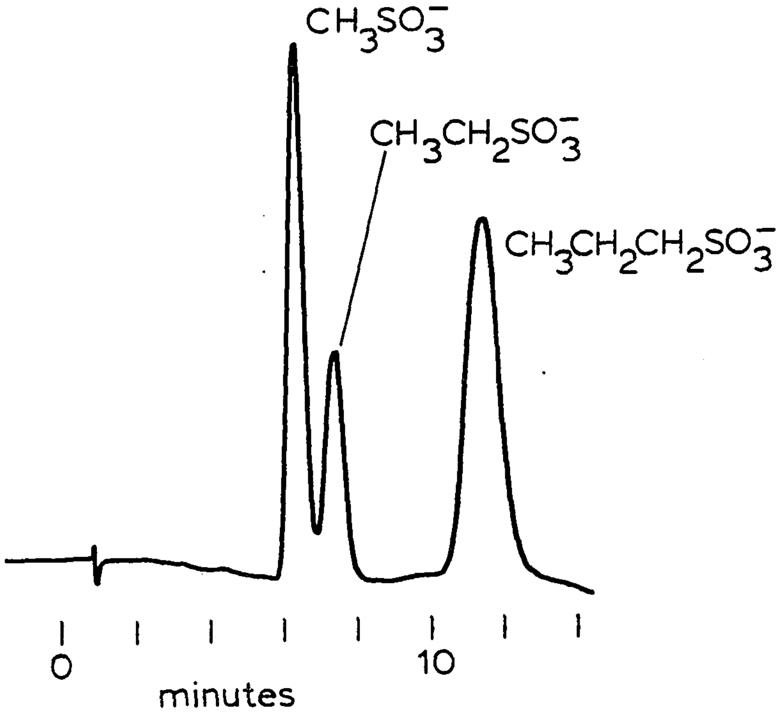


Figure 25. Separation of methanesulfonate, ethanesulfonate, and propanesulfonate on a TEtA resin of capacity 0.026 meq/g. The eluent is 0.001 M benzoic acid at a flow rate of 1.0 mL/min. A 20-microliter sample loop was used and the concentrations of the ions are 15, 20 and 26 ppm, respectively.

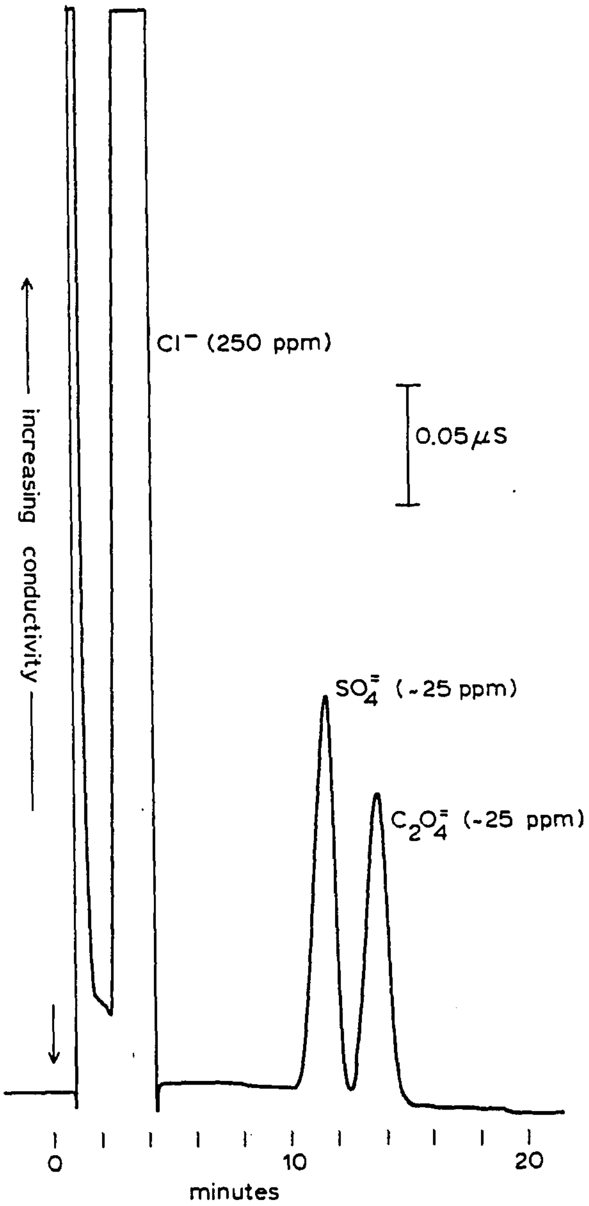


Figure 26. Separation of oxalate and sulfate in the presence of a tenfold excess of chloride. The resin contains a TPA functional group and has a capacity of 0.082 meq/g. The resin is packed in a 500 x 2.0 mm i.d. column. The eluent is 0.4 mM KHP, pH 6.7 at a flow rate of 1.0 mL/min. A 50-microliter sample loop was used.

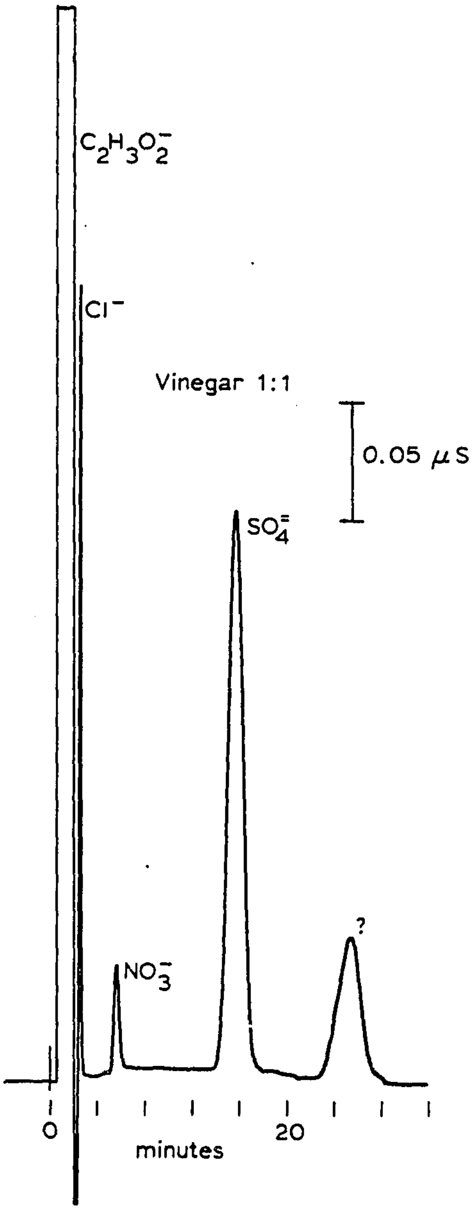


Figure 27. Separation of late-eluting ions in vinegar diluted 1:1. The column is the same as used in Figure 26. The eluent is 0.4 mM KHP, pH 5.0 at a flow rate of 1.5 mL/min. A 50-microliter sample loop was used.

It is difficult to give suggestions for the "optimum" functional group, capacity, eluent conditons and column size. The analyst would be better off deciding what the problem requires and then tailoring the experimental conditions to the problem by using the information in this section as a guideline. The suggestion which makes the most sense is to have available resins which span the range of functional group polarity. Resins such as MDEA, TMA and TBA would be good choices. Each of these resins should probably be available in capacities of about 0.02, 0.045 and 0.09 meq/g. The 500 x 2.0 mm column would be a good universal choice. The nine different resins combined with variations in eluent concentration and pH should allow most anionic separation problems to be solved using single-column ion chromatography. Because the process of resin preparation is so simple, extraordinary situations could be accommodated by preparing a special batch of resin uniquely suited to the particular problem.

### Effect of adding carbonyl groups to the copolymer matrix

Even though this section has been primarily concerned with the variation of functional group structure, the experiments to be reported next could turn out to be important also.

A batch of resin was prepared according to the procedure described in the Experimental section. The resin contained a Type I functional group and had a capacity of about 0.026 meq/g. This acylated resin was compared to a plain Type I resin of 0.027 meq/g under identical conditions. The results are shown in Table 30. The addition of carbonyl groups to the copolymer matrix seems to have an effect similar to increasing the hydrophobicity of the functional group. The weak acids are largely unaffected by the change but the hydrophobic anions show longer relative retentions. Nitrite is one ion which does not respond to changes in functional group but yet actually inverts order of retention with chloride because of the presence of the carbonyl groups. (The assumption is that the residual aluminum is present in too small a concentration to affect the behavior of the resin. This assumption should be valid because the relative retention of $F^-$ is similar on both resins and $F^-$ has a great affinity for aluminum.) The acylated resin seems to give slightly broader peaks than the plain resin but would be useful for a separation of ions such as nitrite and phosphate which are inseparable using an acid eluent with most anion exchangers.

This resin is not that important by itself, but it demonstrates that the addition of neutral functional groups

Table 30. Relative retentions of various monovalent ions on plain and acylated Type I anion exchangers
Eluent: 1 mM benzoic acid, 1.0 mL/min
($t_r$ anion/$t_r$ $Cl^-$)

| Ion | Plain[a] | Acylated[b] |
|---|---|---|
| $F^-$ | 0.66 | 0.67 |
| $Cl^-$ | 1.0 | 1.0 |
| $Br^-$ | 1.19 | 1.47 |
| $I^-$ | 2.37 | ---- |
| $NO_2^-$ | 0.90 | 1.21 |
| $NO_3^-$ | 1.26 | 2.10 |
| $H_2PO_4^-$ | 0.83 | 0.81 |
| acetate | 0.22 | 0.22 |
| glycolate | 0.44 | 0.43 |
| formate | 0.51 | 0.33 |
| lactate | 0.46 | 0.42 |
| nicotinate | 0.30 | 0.26 |
| $N_3^-$ | 0.34 | 0.56 |
| $ClO_3^-$ | 1.51 | 2.53 |
| $BrO_3^-$ | 1.04 | 1.10 |
| $IO_3^-$ | 0.82 | 0.79 |
| meth-$SO_3^-$ | 1.0 | 0.96 |
| eth-$SO_3^-$ | 1.15 | 1.06 |
| prop-$SO_3^-$ | 2.0 | 1.39 |
| $BF_4^-$ | 2.57 | ---- |
| $t_r$ $Cl^-$ | 8.9 min | 11.6 min |

[a] Capacity = 0.027 meq/g.

[b] Capacity = 0.026 meq/g.

to the copolymer can influence selectivity in an unexpected manner, such as in the case of nitrite and dihydrogen phosphate. A careful study of specific interactions of ions with neutral functional groups could yield suggestions for resins which are specific or highly selective for ions in a fashion which is not predictable on the basis of the identity of the functional group.

# INTERACTION OF ELUENT ACIDS WITH THE COPOLYMER MATRIX

## Introduction

The eluents that have been used for the ion chromatography of anions are few in number. The standard eluent used in the dual-column system is a mixture of carbonate and bicarbonate salts (7). Other eluents that have been used in this system include borate ion (177) and sodium hydroxide (178). Single-column ion chromatography originally employed salts of phthalic acid and benzoic acid as eluents (17,18). Book (179) examined a number of salt eluents and their behavior in single-column ion chromatography. The salts work well as eluents, but do not yield excellent sensitivity because of the relatively high background signal which they generate. Recently, the Toyo Soda Co. introduced a single-column ion chromatograph which, according to their promotional literature, makes use of phthalate, gluconate, borate, tartrate and hydroxide as eluent anions. There has been no opportunity to evaluate the sensitivity of this instrument with the recommended eluents.

Gjerde and Fritz (180) showed that benzoic acid could be used as an eluent because it is partially ionized to provide eluent anion and supplies hydronium ion as the counterion which increases sensitivity to a level very close to that of a dual-column instrument. Glatz and Girard (181) showed that the choice of the phthalic acid isomer used as an eluent has an effect on the separation of ions. Ivey (182) recently published a note suggesting the use of methanesulfonic acid as an eluent in single-column ion chromatography. He points out that it is especially useful when conductimetric and UV detectors are coupled in series because the molecule has a low molar absorptivity in the ultraviolet region of the spectrum in comparison to an eluent such as phthalate.

Despite the fact that the sensitivity is so good, the use of benzoic acid as an eluent causes operational difficulties. Baseline drift increases to an excessive level unless the system is well-insulated. Also, unless the analyte solutions are prepared in eluent, large baseline perturbations occur which have been dubbed "acid dips". These cause problems in quantification and slow down analyses because of the need to wait for the baseline to restabilize.

It was thought that much of this behavior could be caused by the adsorption of the acid onto the copolymer matrix. If acid is adsorbed onto the copolymer, then small fluctuations in room temperature could cause relatively large quantities of material to be adsorbed and desorbed thus resulting in a drifting baseline. Also, if a sample made up in pure water (without added eluent) were to be injected, it would cause some acid to be stripped from the column as the plug of water passed through the bed. Then, more acid would have to be removed from the eluent stream to restore the equilibrium between the column and the eluent, thus causing a baseline perturbation.

These problems led to the idea that if an acid could be found which had limited interaction with the copolymer matrix, it might prove to be a better eluent than benzoic acid for routine use in ion chromatography.

## Experimental

### Materials and apparatus

The weak acids were obtained from a number of sources and were used as received. The phosphate salts and phosphoric acid were reagent grade. A Tracor Model 970 ultraviolet-visible variable wavelength spectrophotometric detector was used to monitor the elution of the weak acids. All other materials and apparatus were the same as described in earlier sections.

### Procedures

All procedures for resin preparation and column packing have been described previously. The retention time study was carried out by injecting samples of each acid into a flowing stream consisting of phosphoric acid at pH 2.1 or phosphate buffer at pH 6.7. This stream flowed through a 500 x 3.0 mm i.d. column packed with plain (without functional groups) XAD-1 copolymer. The low pH and high pH were used to make sure that the weak acids were largely in their molecular or ionized forms respectively when interacting with the copolymer.

## Results and Discussion

### Interaction of acids with the XAD-1 copolymer

The results of the study are shown in Table 31. The acids are loosely grouped into classes along the length of the Table. The retention times prefaced by "greater than" are conservative. Most of these compounds were monitored for longer times but the analyte was never observed to elute from the column. Some interesting trends may be picked out. Note that benzoic acid is probably one of the worst choices possible in terms of its strength of interaction with the copolymer. Surprisingly, the molecular form of the acid is

Table 31. Interaction of potential eluent acids with plain XAD-1 copolymer

| | Retention Time (min) | |
|---|---|---|
| Acid | pH 2.1 | pH 6.7 |
| benzoic acid | (80)[a] | 3.6 |
| *o*-sulfobenzoic acid | 5.0 | 2.6 |
| *o*-phthalic acid | 29.3 | 2.6 |
| 1,3,5-benzenetricarboxylic acid (trimesic acid) | 13.5 | >40 |
| 1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid) | 5.5 | >40 |
| salicylic acid | (102) | 6.8 |
| 5-sulfosalicylic acid | 10.0 | 10.5 |
| *o*-aminobenzoic acid | 11.5 | 3.5 |
| *p*-aminobenzoic acid | 3.9 | 2.4 |
| *o*-nitrobenzoic acid | 35.0 | 3.2 |
| *m*-nitrobenzoic acid | >60 | 7.5 |
| *p*-nitrobenzoic acid | >60 | 7.5 |
| 3,5-dinitrobenzoic acid | (130) | 19.5 |
| *m*-chlorobenzoic acid | >60 | 11.5 |
| *m*-bromobenzoic acid | >60 | 18.6 |
| benzenesulfonic acid | 5.4 | 4.1 |
| *p*-toluenesulfonic acid | 12.8 | 11.1 |
| *p*-sulfanilic acid | 2.3 | 2.4 |
| α-furoic acid | 8.0 | 2.4 |
| phenylacetic acid | >60 | 4.6 |
| 2,4-hexadienoic acid (sorbic acid) | (86) | 3.7 |
| fumaric acid | 2.6 | 2.4 |
| citric acid | 2.6 | 2.3 |
| phenylphosphinic acid | 7.1 | 3.3 |
| phenylphosphonic acid | 4.6 | 2.3 |
| 2-pyridinecarboxylic acid (picolinic acid) | 3.7 | 21.7 |
| 3-pyridinecarboxylic acid (nicotinic acid) | 2.4 | 2.5 |
| 2,3-pyridinedicarboxylic acid (quinolinic acid) | 3.3 | 2.4 |
| 2,6-pyridinecarboxylic acid (dipicolinic acid) | 3.0 | 2.5 |

[a] Parentheses indicate an extremely broad elution profile.

retained less and less as more carboxylic acid groups are added to the aromatic ring. (Even though the pH was kept at 2.1, the first ionization constants of trimesic acid and pyromellitic acid are large enough, $pK_{1\ trimesic} = 2.12$ and $pK_{1\ pyromellitic} = 1.92$, so that there is significant ionization of these acids.) Several of the acids such as fumaric, citric, nicotinic, quinolinic and dipicolinic have low retention in either the molecular or ionized forms.

### Evaluation of nicotinic acid as an eluent

Potassium hydrogen phthalate is an adequate eluent for separating divalent ions or mixtures of monovalent and divalent ions as demonstrated in the last section. It gives reasonable sensitivity and its use does not result in an unstable baseline. The main need is a replacement for benzoic acid to elute monovalent ions, especially those which elute early from an anion exchanger.

The decision was made to concentrate on evaluating 3-pyridinecarboxylic acid (nicotinic acid) as a replacement for benzoic acid. This acid was chosen because it is available in good purity, it is structurally easy to relate to benzoic acid and has limited interaction with the copolymer in either its molecular or ionized form. Nicotinic acid was found to give good sensitivity and very stable baselines as expected. Figure 28 shows a comparison

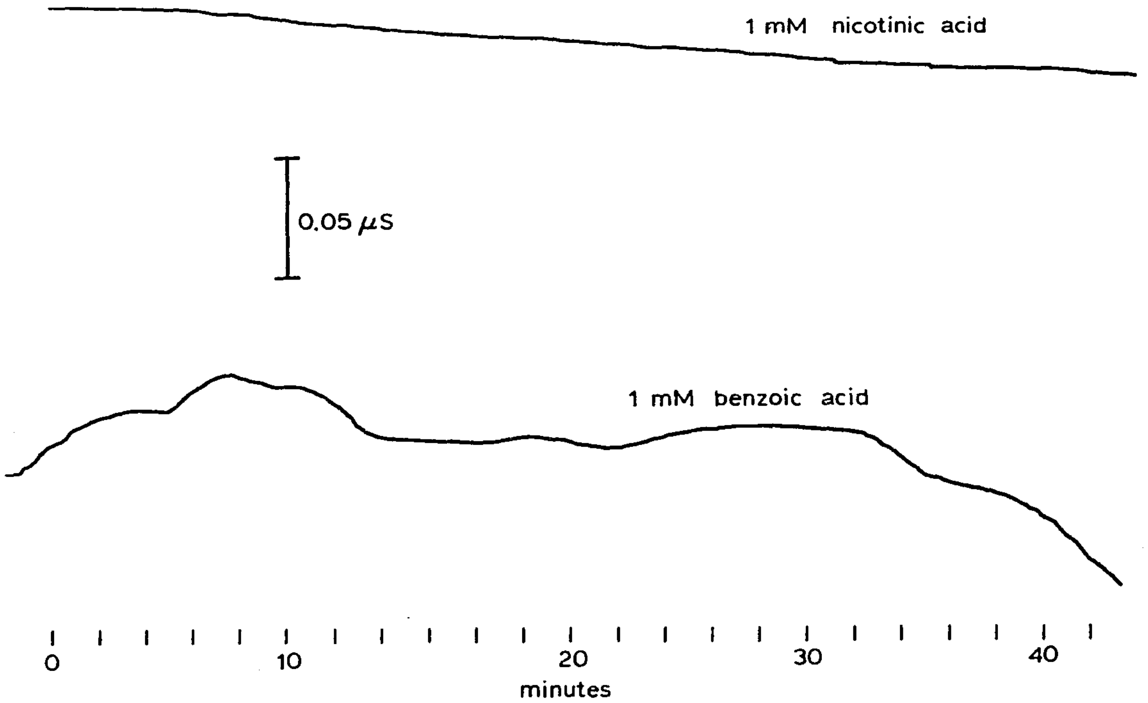


Figure 28. •Comparison of the baselines obtained using 0.001 M nicotinic acid and 0.001 M benzoic acid. The acids were pumped through the same column at the same flow rate. (MDEA resin; 0.030 meq/gm, 500 x 2.0 mm i.d., 1.0 mL/min.)

of a baseline obtained with 0.001 M nicotinic acid and one obtained with 0.001 M benzoic acid. The sensitivity of the detector was set at a higher level than used in routine separations, but the comparison shows the relative stability well.

There is more than a correlation of baseline stability with copolymer interaction. The effectiveness of the eluent also seems to be related to the affinity of the particular acid for the copolymer. Thus, nicotinic acid is a much weaker eluting agent than benzoic acid at comparable concentrations. Table 32 shows a comparison of the retention times of monovalent ions on a Type I resin using solutions of 0.001 M benzoic acid and 0.001 M nicotinic acid as eluents. The flow rate used was 0.93 mL/min and the resin was packed in the usual 500 x 2.0 mm i.d. column. Part of the reason for the feeble strength of nicotinic acid is the fact that its $pK_a$ is 4.82 compared to that of benzoic acid which is 4.20. Another experiment was performed using 0.001 M nicotinic acid which had been neutralized enough to give the same percentage of ionization as a 0.001 M solution of unadulterated benzoic acid. The retention times for the monovalent ions using this eluent are shown in the column on the right of Table 32. There is a decrease in the elution times overall, but it is plain that this molecule has an

Table 32. Comparison of the retention times of monovalent anions on a Type I column using benzoic acid and nicotinic acid as eluents

| Ion | $t_r$ 0.001 M benzoic (acid) | $t_r$ 0.001 M nicotinic (acid) | $t_r$ 0.001 M nicotinic (part. neut.) |
|---|---|---|---|
| $C_2H_3O_2^-$ | 2.0 min | 6.3 min | 5.9 min |
| $CHO_2^-$ | 4.5 | 20.8 | 10.9 |
| $F^-$ | 5.8 | 23.8 | 10.7 |
| $Cl^-$ | 8.7 | 38.2 | 14.8 |
| $Br^-$ | 11.1 | 55.0 | 20.8 |
| $I^-$ | 23.1 | 100 | 60 (broad) |
| $H_2PO_4^-$ | 7.4 | 31.2 | 13.1 |
| $NO_2^-$ | 8.1 | 37.2 | 16.4 |
| $NO_3^-$ | 11.8 | 61.0 | 23.0 |

eluting strength that is inherently weaker than benzoic acid. Figure 29 shows a separation of several monovalent ions on a column packed with MDEA resin. (Recall that this resin has a lower affinity for late-eluting monovalent ions.) The resolution is good, but the elution times are inconveniently long.

Because the only difference between benzoic acid and nicotinic acid is the pyridine nitrogen, there is only one place to fix the cause for its weak eluting capability. Apparently, the pyridine nitrogen keeps the acid from adhering strongly to the column and also prevents a strong interaction of the carboxylic acid with the ion-exchange sites. This may be caused by an association between acid molecules in solution or by a repulsion of the pyridine nitrogen by the positively charged surface of the anion exchanger. The situation may be aided by using a resin with a lower capacity as shown in Figure 30. However, as the capacity is lowered to these levels, the resolution begins to deteriorate. Another solution is to use a much greater concentration of eluent and a resin with an MDEA functional group. An example of this combination is shown in Figure 31. The background conductivity is still not unreasonably high at this concentration and the sensitivity remains good. Figure 32 shows the separation of the early-eluting

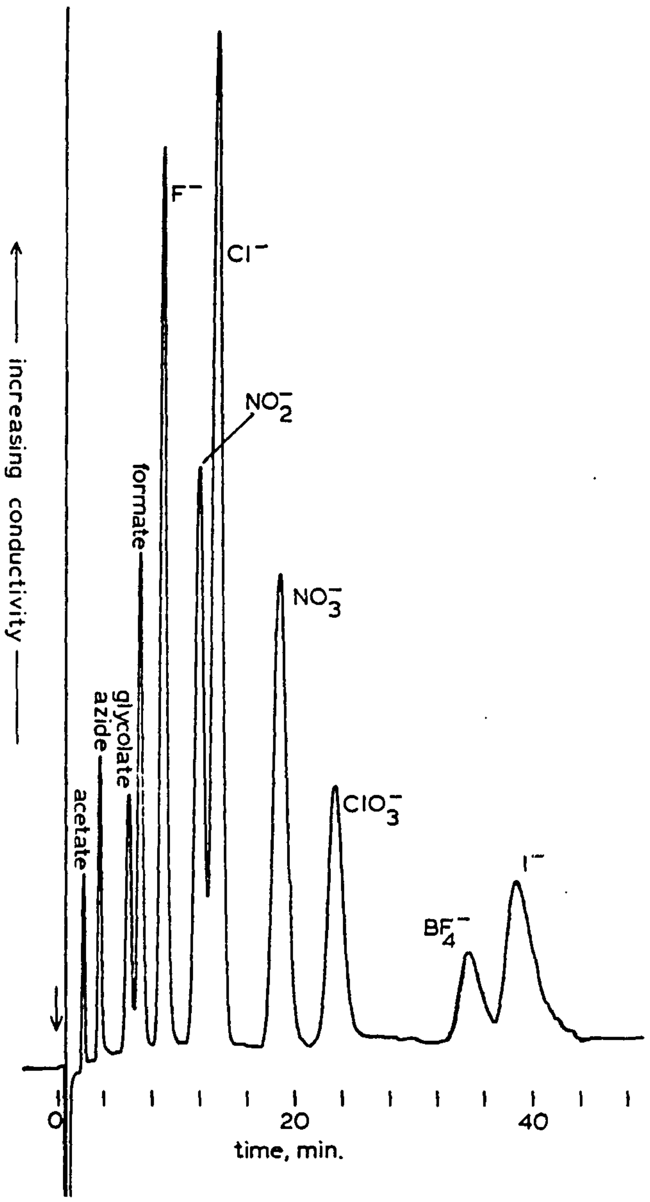


Figure 29. Separation of several monovalent ions on a MDEA resin of capacity 0.026 meq/g. The eluent is 0.002 M nicotinic acid at a flow rate of 1.5 mL/min. The column is 500 x 2.0 mm i.d.

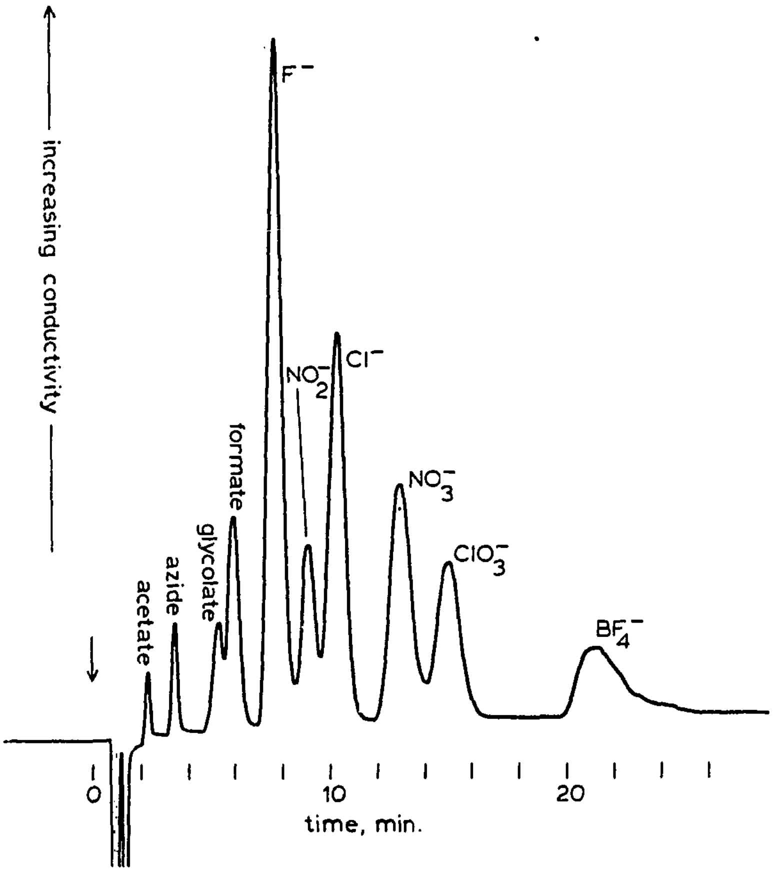


Figure 30. Separation of several monovalent ions on a MDEA resin of capacity 0.012 meq/g. The column size and eluent concentration are the same as in Figure 29, but the flow rate is 1.0 mL/min.

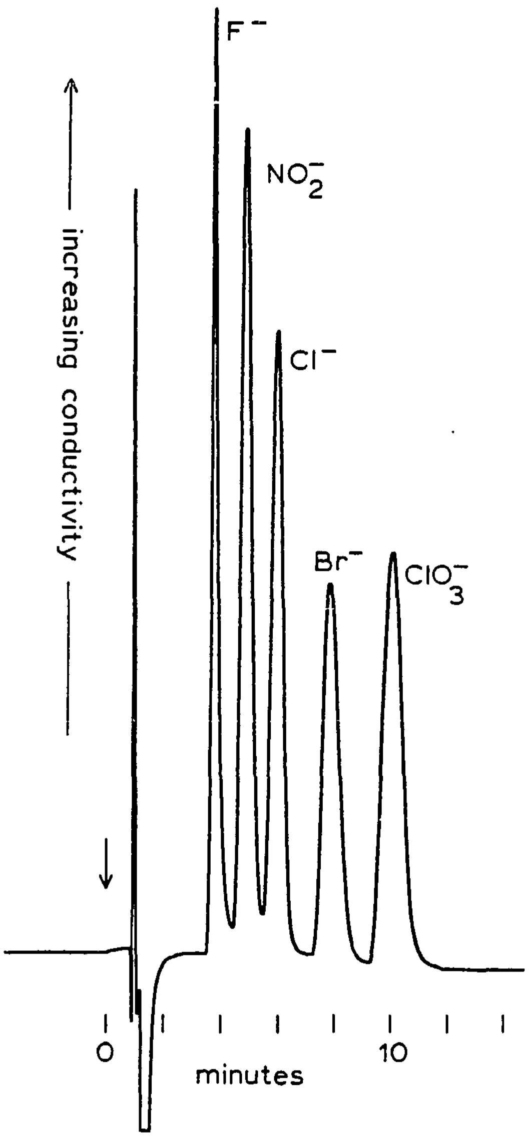


Figure 31. Separation of five monovalent ions on a MDEA column of capacity 0.030 meq/g. The column is again the same size as the column used in the preceding two figures. The eluent is 0.015 M nicotinic acid at a flow rate of 1.0 mL/min.

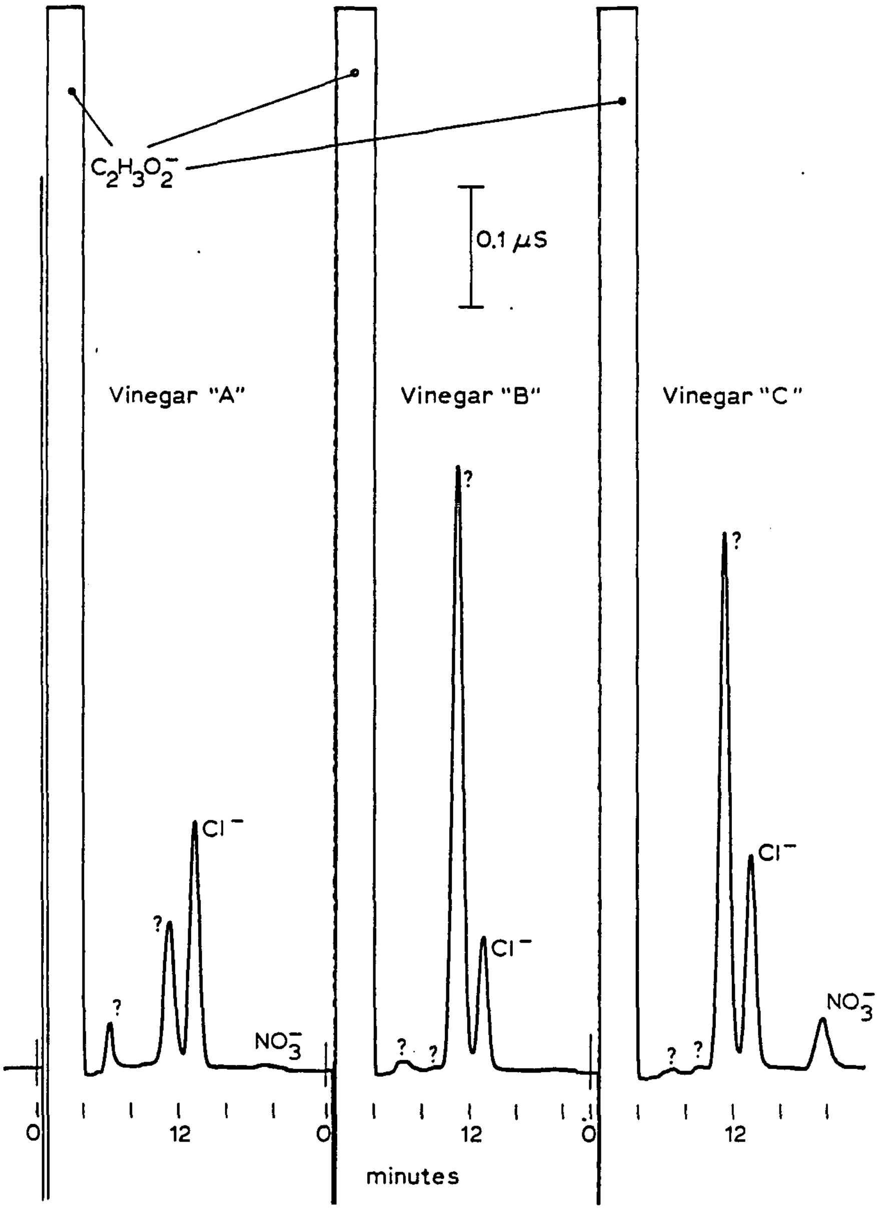


Figure 32. The separation of early-eluting impurities in three brands of vinegar. The column is the same one used in Figure 31. The eluent is 0.002 M nicotinic acid at a flow rate of 1.5 mL/min. The sample size is 20 microliters of vinegar diluted 1:1 with deionized water.

impurities in three brands of vinegar arranged in order of decreasing price from left to right. These are injections of vinegar which were diluted 1:1 with deionized water. Even though there is about 2 1/2% acetic acid present, the baseline is not disrupted. An injection of such a sample (without added eluent) when using benzoic acid causes such disruption of the system that a clear chromatogram cannot be obtained. The vinegar on the right contains about 14 ppm nitrate.

Because it seems that the pyridine nitrogen is the cause of the low eluting strength of nicotinic acid, it was thought that inserting a methylene group between the pyridine ring and the carboxylate group might give some improvement. The addition of this group would put more distance between the anionic moiety and the pyridine nitrogen. It would also increase the distance of closest approach of the pyridine nitrogen to the polymer surface assuming that the molecule approaches the ion-exchange site stretched out with the carboxylate end first. The influence of the ring on the $pK_a$ is different though and so the $pK_a$ of 3-pyridylacetic acid is higher at about 5.4. A similar, but not so drastic difference occurs between the analogous molecules benzoic acid ($pK_a = 4.20$) and phenylacetic acid ($pK_a = 4.31$). Table 33 shows the comparison of retention

Table 33. Comparison of 0.015 M nicotinic acid and 0.015 M 3-pyridylacetic acid as eluents on a MDEA column

| Ion | 0.015 M nicotinic acid | 0.015 M 3-pyridylacetic acid |
|---|---|---|
| $F^-$ | 3.8 min | 3.7 min |
| $Cl^-$ | 5.9 | 4.9 |
| $Br^-$ | 7.5 | 6.2 |
| $I^-$ | 16.3 | 13.5 |
| $NO_2^-$ | 5.0 | 5.1 |
| $NO_3^-$ | 8.3 | 6.8 |
| $H_2PO_4^-$ | 5.0 | 4.1 |
| $N_3^-$ | 2.6 | 3.6* |
| glycolate | 2.7 | 3.5* |
| formate | 2.9 | 3.8* |
| $CH_3SO_3^-$ | 6.2 | 5.0 |
| $CH_3CH_2CH_2SO_3^-$ | 15.1 | 11.5 |
| $BrO_3^-$ | 6.4 | 5.3 |
| $ClO_3^-$ | 10.0 | 8.3 |

times of several anions using a resin with a MDEA functional group (capacity 0.030 meq/g) and solutions of 0.015 M nicotinic acid and 0.015 M 3-pyridylacetic acid as eluents. Despite the higher $pK_a$ of 3-pyridylacetic acid, it still elutes the strongly retained ions better than nicotinic acid thus confirming the effectiveness of adding the methylene group. The anions marked with asterisks elute later than with nicotinic acid. These are weak acids and undoubtedly elute later because of the difference in ionization between the two eluents.

The effectiveness of 3-pyridylacetic acid drops off quickly with decreasing concentration which is apparently another manifestation of its higher $pK_a$. Nicotinic acid becomes the stronger eluent by far as the concentration is lowered to about 0.005 M.

## Conclusion

It has been shown that using an eluent which has less attraction to the copolymer is beneficial in terms of improving the stability of the baseline. Adjustments of the functional group and capacity of the resin and the eluent concentration are necessary in order to make use of the acids containing a pyridine ring. Additional work (167) has shown that other non-adsorbed acids such as succinic, fumaric and citric acid can also be useful as eluents. The discovery of an eluent that could be used to separate polyvalent ions while in its acid form would be useful, but so far this goal has been elusive. An acid such as pyromellitic acid is very strong, but produces unexplained perturbations in the baseline during chromatograms. It also seems to have a degrading effect on the ion-exchange resin. Book (179) preferred to use the salt of trimesic acid as an eluent; it may also be useful in its acid form.

Most polyvalent acids seem to produce such baseline perturbations. Even citric acid which seems to have very little interaction with the copolymer gives an "acid dip" when a sample is injected unless the eluent is predominantly in its salt form. This is a mystifying phenomenon that will require more study in a careful fashion in order to elucidate the mechanism of the problem. It may be that the "acid dip" is partly caused by carbonic acid. The carbonic acid is much less conductive than the divalent acid and would register as a decrease in conductivity as the carbonic acid peak passes through the detector.

As the pH increases and the eluent molecule becomes more salt than acid, the carbonic acid would, in turn, be changed into bicarbonate which has a much greater conductance and would not be noticeable as a sharp decrease in conductivity. It would also be held up by the anion exchanger and may elute in a broad band rather than a sharp peak. Until the "acid dip" is explained definitively, and then ameliorated, the use of divalent acids in their acid form will not be possible.

## FUTURE WORK

One of the most constant unwritten rules of research is the one which holds that no scientific investigation is a closed, self-contained unit with all of the original questions answered and no new revelations encountered along the way. It is the experience of the author that when engaged in research, one finds many sidelights and interesting offshoots that are worth at least a preliminary experiment or two. However, when one is involved in a project with a time limit, one must have some self-discipline concerning these new directions lest one never accomplish the original goal. The present investigation suggested many possible projects; some of the more interesting ones are recorded below for the benefit of those who may continue to work in this area.

The literature of ion exchange makes clear the fact that most of the work in the field has been done with resins of high exchange capacity. The success of ion chromatography indicates that there may be other interesting uses for resins of low capacity. While the basic principles of ion exchange should be the same for resins of high capacity and resins of low capacity, it would be dangerous to conclude that their behavior would be the same in all respects. One must always be cautious when extrapolating from one scale to another. Even though one cannot transfer conclusions directly from resins of high capacity to resins of low capacity, the current accumulation of knowledge in the literature of ion exchange will undoubtedly serve as a useful starting point. Also, there may already have been examinations of exchangers which have interesting properties and which can only be prepared with a low capacity for reasons of reactivity. While low capacity would have been the death knell of a resin many years ago, recent experience shows that it need not be considered a fatal drawback.

There is still much work that may be pursued profitably in the area of chemically bonded polymeric stationary phases of low capacity. The main objectives that should be sought are improved efficiency (in chromatography), and more methods of manipulating selectivity. What is needed is a collection of methods for varying the selectivity in unique, abrupt ways rather than the smooth, regular fashion reported in this dissertation, although that too is useful.

To illustrate the scope of the work remaining, this investigation has focused solely on strong-base anion-exchange resins of low capacity which are prepared from a macroreticular styrene-divinylbenzene copolymer.

This is a very narrow category of anion exchanger compared to all of those which may be envisioned. One specific suggestion for moving out of this category is to start with an acrylic amide polymer and partially reduce the amide groups to amines via the use of the reagent diborane (183). The amine groups can then be easily quaternized by the use of methyl iodide. This will provide a strong-base resin with a completely different matrix than that of a styrene-divinylbenzene copolymer. Alternatively, the methods of Inman and Dintzis (52) may also be used to alter the functionality of an acrylic amide polymer.

As noted earlier, Clifford and Weber (99,100) concluded that the two most important factors in monovalent vs. divalent selectivity are matrix and functional group. Keeping this conclusion in mind, the next suggestion is that a reliable method for preparing microspherical polymer beads be sought out in the literature or worked out in the lab. The production of small, spherical beads is necessary for good efficiency in chromatography and is still something of a mystical art rather than a well-defined technique. Once the method of preparing polymer beads with reproducible physical characteristics is in place, many formulations of polymers may be tried out. This type of a program should include a careful examination of the relationship between polymerization conditions, bead morphology and chromatographic performance. Such a study should allow some definite answers to be obtained concerning the optimum surface area, pore shape, pore size and pore content of a porous ion exchanger. The ability to prepare polymer beads would allow one to carry out research at a much faster pace. It would also eliminate the dependence on commercially available products which are often a poor compromise compared to what is desired. The final goal of this program of polymer production is obviously the introduction of ionic groups into the various matrices so that they might be used in ion chromatography to provide separations which are currently impossible or difficult.

An alternative to the preparation of beads of varying chemical composition is to modify the surface of an existing polymer. This approach has the advantage that one can use a polymer with well-known physical properties which behaves well in chromatography. By modifying the surface, one alters the polarity of the solid and thus changes its interaction with the solvent and the hydrated ions. This idea was shown to have some merit in this report. There are undoubtedly many other neutral functional groups which could be added to polymers in order to vary the selectivity observed in the unmodified particles. One group which can be easily added to styrene-divinylbenzene copolymers is the nitro group. This can also be reduced and converted into a number of other functional groups.

The other most important factor in selectivity is functional group identity. This conclusion was confirmed for different quaternary ammonium groups in this report. Several other suggestions concerning resins of low capacity come to mind. Even though weak-base resins have the disadvantages of required operation at low pH and slow kinetics, it may be useful to examine one or two weak-base anion exchangers of low capacity to see if they show any promise at all. These resins can be prepared in a manner analogous to that used for the strong-base resins discussed in this report. One would merely need to treat the chloromethylated intermediate with ammonia, a primary amine or a secondary amine to arrive at a weak-base resin.

Also, instead of using only amines to create the ionogenic group, phosphines, sulfides, and stibines could be used to prepare the corresponding phosphonium, sulfonium, and stibonium anion-exchange sites. These resins would also be of a strong-base nature, and given the results of the current study, they almost certainly would exhibit selectivities different from the quaternary ammonium strong-base resins.

An additional idea for functional group variation consists of altering the position of the functional group in relation to the matrix. When an amine is reacted with a chloromethylated substrate, the ion-exchange site which results is very close to the main polymer chain. There seems to be no evidence that anyone has tried to use quaternary ammonium ions attached to long "spacer arms" in the ion-exchange chromatography of common ions. The use of "spacer arms" is often seen in affinity chromatography when large biogenic substances such as proteins are being separated. While the steric constraints are not present in ion chromatography, the long attached arm would allow the ion-exchange site to be away from the influence of the polymer surface, especially in a macroreticular polymer. It is conjectured that this separation would cause a different set of ionic interactions than those observed in conventional ion-exchange resins. There are a few synthetic approaches shown in Figures 33 to 35. The first is one that Hefferman and coworkers (184) have used to prepare polymers to be used as phase transfer catalysts. These employ extremely long chains in the range of eleven carbons. However, the process should also be usable for the shorter chains recommended in the figure as starting points. The last two approaches have been tried in a preliminary fashion

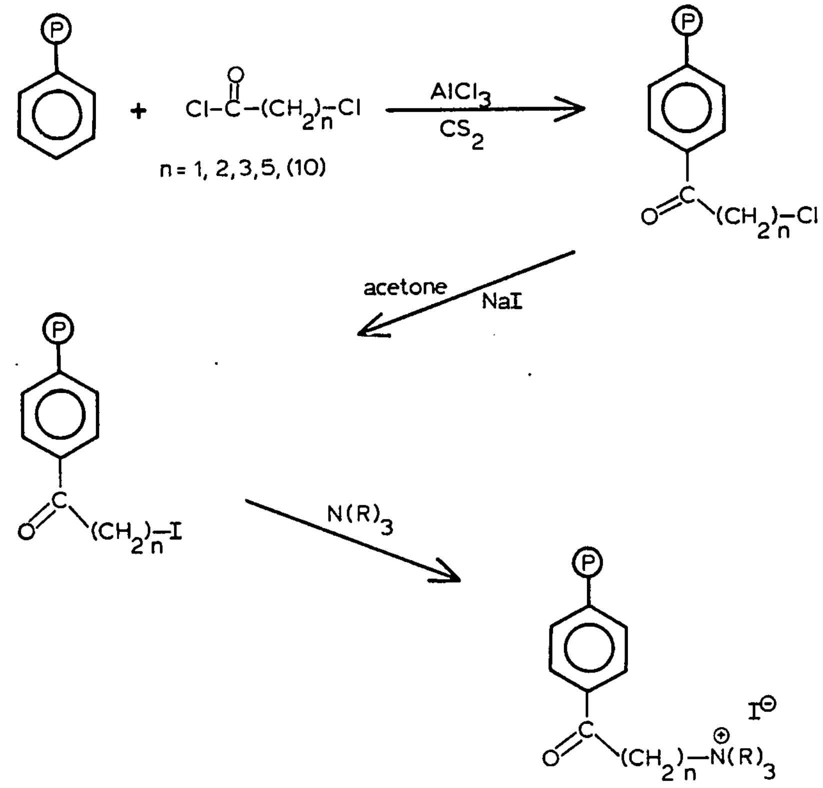


Figure 33. Possible synthetic route for a "spacer-arm" resin.

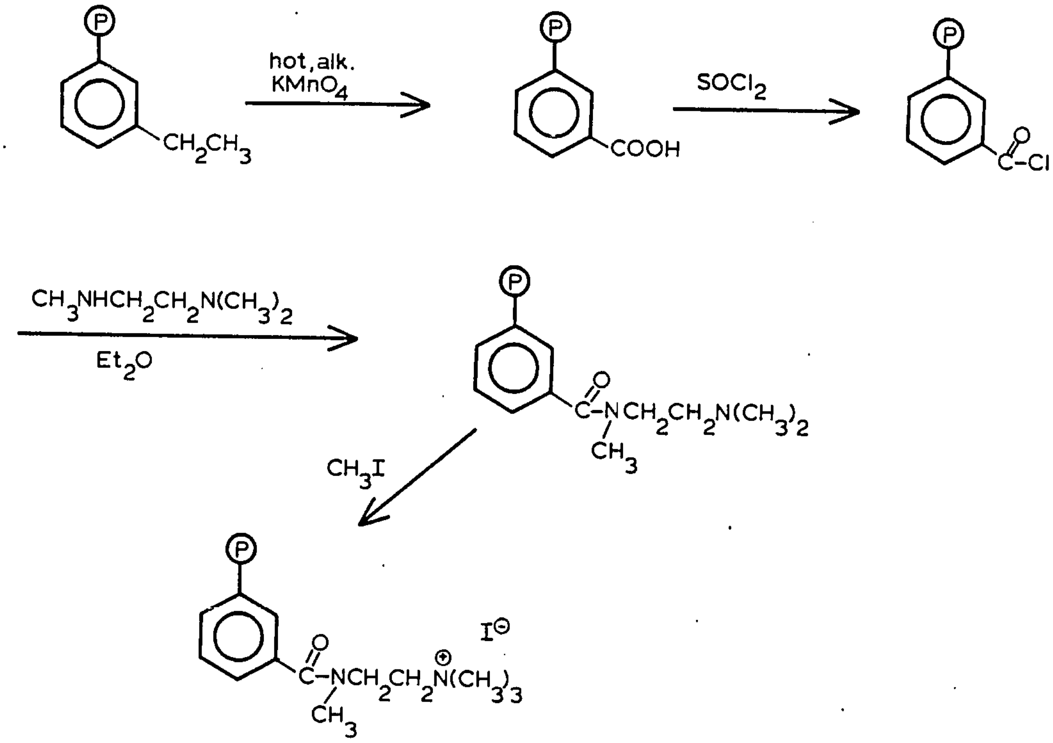


Figure 34. Possible synthetic route for a "spacer-arm" resin.

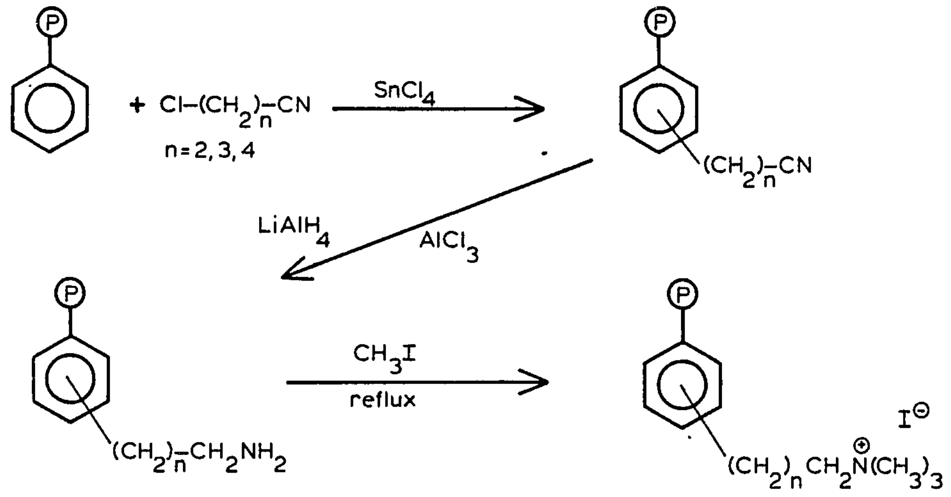


Figure 35. Possible synthetic route for a "spacer-arm" resin.

and appear to yield strong-base anion exchangers, but much more work is needed to confirm the initial results. It is not known how the ion-exchange properties will be affected by the use of "spacer-arms", but it should be interesting to synthesize and characterize these resins. It is recommended that a model compound study first be carried out. The molecules tentatively identified as models for styrene and divinylbenzene as they appear in the polymer chain are cumene and _m_-diisopropylbenzene. The alkyl chains on these molecules should allow the aromatic nucleus to feel some of the steric hindrance that it might be subject to in the polymer. The reason that a model compound study is recommended is that functionalized polymers, particularly of low capacity, are difficult to characterize by known methods. The reactions could be run on the model compounds where the products could be fully characterized and then the reactions could be run on linear polystyrene which allows some characterization. Finally, the reactions could be run on the insoluble polymer beads with some assurance that the product obtained is the one which was originally sought.

A final idea concerning stationary phase modification is the nature of the chloromethylation reaction. It produces a very useful intermediate but is generally looked upon as dangerous to carry out because of the carcinogenic nature of the bis(chloromethyl) ether impurity in the chloromethylmethyl ether. If methods are used to generate the haloethers in situ, the danger from direct handling is removed and with careful precautions, the reaction should not be that hazardous. However, the latent danger perceived by many workers probably prevents many small-scale users from employing the reaction. A possible replacement for the chloromethylation reaction is shown in Figure 36. This is a simple sequence using known reactions and non-exotic reactants. It seems likely, based on the work of Nazarov (80) and Ziegler (83), that the sequence should work. The resultant product is that which would be achieved by direct chloro*ethyl*ation, but again, haloethers are avoided. This should react in the same fashion as a chloromethylated intermediate would when reacted with amines, though it may react more slowly because of the presence of the methyl group.

Instead of modifying the stationary phase, one may also modify the mobile phase, and indeed, this is usually the rule in other forms of high performance liquid chromatography. The variety of mobile phases that can be used is almost limitless. However, in ion-exchange chromatography, one does not see mobile phase modification used nearly as often, especially for common anions. The

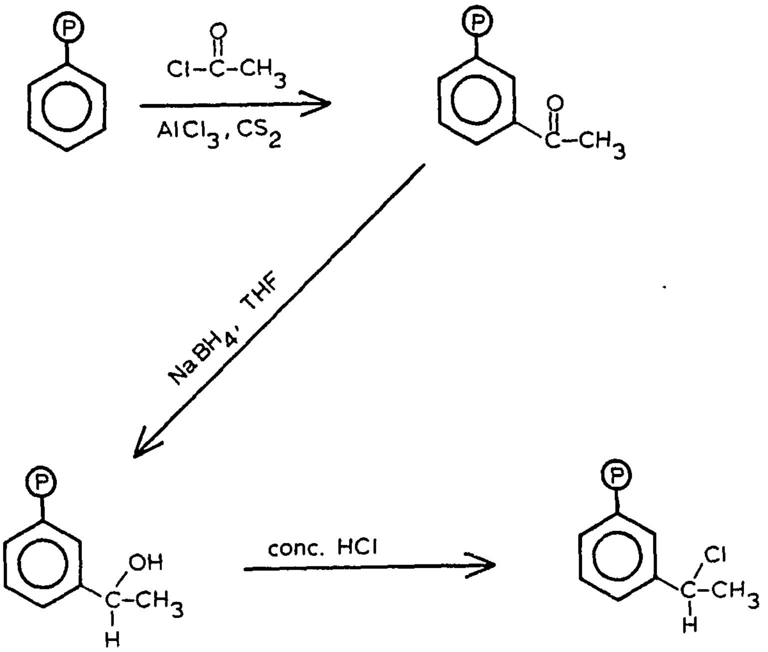


Figure 36. Possible route to use as an alternative to the chloromethylation reaction.

literature of ion chromatography shows only one account of the use of non-aqueous solvents to aid the separation of common ions (185). Non-aqueous solvents have been used to good advantage in the column chromatography of anionic metal complexes (186), but solvent effects in the separation of common anions have not been heavily investigated. Most often, a simple acid, base or buffer solution is all that is used for the purposes of elution. Part of the reason for this may be that concentrated eluents are needed for high capacity resins and the presence of organic solvents may limit the amount of ionic substance that will go into solution.

Some polymeric resins cannot tolerate organic solvents because they shrink and swell and eventually deteriorate from the mechanical stress induced by the contraction and expansion. However, macroreticular resins are particularly resistant to this phenomenon and should allow the use of organic solvents. Moreover, small amounts of various organic solvents in the mobile phase for ion chromatography do not cause serious deterioration of the signal from the conductimetric detector. Experiments carried out in this laboratory showed that up to 10% of a number of common organic solvents could be added to the eluent solution without reducing the peak height of a fully dissociated salt by more than a few percent (187). Acetonitrile caused very little change in the signal throughout the range of 10-100% water.

The use of organic modifiers may also help in another area. Small and Miller (188) and Barron (189) showed that an ultraviolet-visible spectrophotometric detector may be used as an indirect monitor for analytes in ion chromatography. One monitors the absorbance of an eluent which contains a chromophore and detects and quantifies analytes by the loss of eluent signal they cause as they pass through the flow cell. The author thought that this idea could be extended to provide a method for producing a gradient in ion chromatography. The idea consists of finding an eluent which does not interact very much with the polymer matrix and which also has an isosbestic point in its ultraviolet spectrum. The absorbance of a given concentration of eluent should always be constant at the isosbestic point no matter what the pH value of the eluent. The eluent strength of the acid increases as the pH increases because the acid becomes more ionized at high pH values. The reasoning is that if one monitors the absorbance at the isosbestic point while going from a low eluent pH value to a high eluent pH value, one would in effect have gradient elution without the baseline shift which would occur with a conductimetric detector. This scheme was tried out with nicotinic acid which shows very little interaction with the copolymer in either its molecular or ionic form. However, the results were somewhat disappointing. There was a small, but significant, baseline perturbation upon changing pH which is attributed to a minor interaction of the eluent with the stationary phase. It is possible that the use of an organic modifier would eliminate the last vestiges of adsorption of the acid and allow the gradient to work as it was conceived.

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# APPENDIX

## Bibliography of Ion Chromatography from 1975 through September 1983

This bibliography is a fairly complete compilation of all non-commercial publications which concern ion chromatography and closely related techniques. The bibliography contains no references to abstracts of papers presented at meetings because it is expected that most of these results appeared in print in a journal or monograph at some time after their oral presentation. The review by Smith and Chang and the books by Fritz, Gjerde and Pohlandt and Smith and Chang contain many references to presentations given at various meetings. Unfortunately, a number of the references listed in the book by Smith and Chang contain serious errors. The reader is advised to cross-reference any citations from that book against those in this compilation in order to save time when attempting to locate the publication.

The bibliography is also devoid of references to technical notes from manufacturers. Only patents that have been granted are included in the list; pending patents are not listed.

There can be no guarantee that this collection is comprehensive; inadvertent omissions can probably be found by examining the references of the individual publications cited in this bibliography.

The entries are presented first by year of publication. Patents, books and monographs are listed at the head of the citations for each year. These are followed by papers which are presented alphabetically by journal. The entries for each journal are listed according to increasing volume and page number. All publications are in English unless otherwise noted. Papers with the title "Ion Chromatography" are usually reviews, with the quality being highly variable. A few of the better reviews are marked with an asterisk in parentheses; (*).

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