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EFFECT OF FUNCTIONAL GROUP STRUCTURE ON THE SELECTIVITY OF LOW-CAPACITY ANION EXCHANGERS FOR MONOVALENT ANIONS

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SUMMARY

A number of macroreticular anion-exchange resins of low capacity were prepared by chloromethylation of XAD-1 under mild conditions and reaction with the appropriate tertiary amine. These resins were then evaluated to determine their relative selectivities for 17 monovalent anions. While the relative affinity of the resins for some anions changes very little as the resin structure is altered, other anions exhibit pronounced changes. Explanations are given as to the probable cause of these effects and the practical implications of using chemical structure as a parameter in ion chromatography are discussed.

INTRODUCTION

The question of how the chemical structure of a "strong-base" anion exchanger affects its selectivity for various anions is a very important one. However, the only resins that have been extensively used have been the Type I resins (benzyltrimethylammonium cation) and the Type II resins in which one methyl group is replaced by a hydroxyethyl group. However, the remarkable success of ion chromatography¹ has elicited a revival of interest in all aspects of anion-exchange chromatography. The anion-exchange resin used in dual-column ion chromatography is a "surface-sulfonated" styrene-divinylbenzene bead coated with a quaternized latex² that is believed to contain a Type I quaternary ammonium ion. This coated bead acts as an anion exchanger and the resulting exchange capacity is fairly low. Clifford and Weber³ state that a resin containing a benzyltriethylammonium cation is now being used in dual-column ion chromatography because of its reduced affinity for sulfate. However, the resins used in ion chromatography are proprietary and few details of their composition are available in the open literature.

A more recent variation of ion chromatography called single-column anion chromatography uses either of two types of anion exchangers. The first is a macroreticular styrene-divinylbenzene resin of very low exchange capacity that contains a benzyltrimethylammonium cation⁴⁻⁶. The second is a silica-based anion exchanger^{7,8} with a quaternary ammonium group of unknown composition.

The macroreticular poly(styrene-divinylbenzene) resins can be prepared with

any exchange capacity appropriate for ion chromatography⁶. However, the selectivity of these Type I resins for various anions is not always adequate for good separations. Some separations, such as Br^- and NO_3^- , are just not possible with Type I exchangers under the usual conditions.

There is no known published work on altering functional group structure to induce selectivity changes in the anion-exchange resins used in ion chromatography. Iskandarani and Pietrzyk⁹ studied the effect of several quaternary ammonium ions on the retention of bromide in their version of dynamic ion exchange known as ion-interaction chromatography. They settled on the tetrapentylammonium cation as the optimal counter ion for the separation of inorganic anions¹⁰.

A few investigations have been published on the effects of chemical structure on selectivity in resins of high exchange capacity, especially in the area of water treatment^{3,11-13}. However, only Type I and Type II structures were represented and very few anions were examined in these studies.

In experiments of a more controlled nature, Gózdź and Kolarz¹⁴ prepared resins containing one, two and three hydroxyethyl groups and studied their relative affinities for four different anions. Güter¹⁵ examined the behavior of some gel resins of high exchange capacity toward nitrate and sulfate. The results showed that a resin prepared with triethylamine has a greater selectivity for nitrate.

In this investigation, a number of macroreticular resins of low capacity were prepared that contain a variety of substituents on the quaternary ammonium group. These resins were systematically evaluated for their selectivities for 17 anions and for possible use in practical ion chromatography. Some explanations are offered to help understand some of the trends and selectivity changes that are observed.

EXPERIMENTAL

Materials

XAD-1 was obtained from Rohm and Haas (Philadelphia, PA, U.S.A.). The tertiary amines were obtained from either Aldrich (Milwaukee, WI, U.S.A.), Eastman Chemical (Rochester, NY, U.S.A.) or Fisher Scientific (Pittsburgh, PA, U.S.A.), and were better than 95% pure in all instances. The amines were used as received. The hydrochloric acid used was of analytical-reagent grade and was obtained from various sources. The paraformaldehyde was 96-98% pure and was also produced from more than one vendor. All solvents used in resin preparation were of laboratory grade or better. The glacial acetic acid used as a wetting agent was of analytical-reagent grade and was obtained from Fisher Scientific.

Ion chromatography was carried out using an instrument built from several components. The pump was a Milton Roy Mini-Pump manufactured by Laboratory Data Control (Riviera Beach, FL, U.S.A.). A LiChromaDamp II pulse damper manufactured by Handy and Harman Tube (Norristown, PA, U.S.A.) was used to remove some of the flow fluctuation introduced by the reciprocating piston of the pump. A Model 7010 injection valve manufactured by Rheodyne (Berkeley, CA, U.S.A.) was fitted with a 20- μl loop and was used to introduce samples into the system. The glass chromatographic columns had dimensions of 500 \times 2.0 mm I.D. and were made by the glass shop at Iowa State University. The column ends were obtained from Rainin (Woburn, MA, U.S.A.).

The detector used was a Model 213A conductivity detector with a 3- μ l flow cell, both of which were manufactured by Wescan Instruments (Santa Clara, CA, U.S.A.). A dual-pen strip-chart recorder manufactured by Curken Scientific (Danbury, CT, U.S.A.) was used to record chromatograms.

The benzoic acid used to prepare eluents was of analytical-reagent grade and was recrystallized from water before use. The analyte solutions were prepared from analytical-reagent grade sodium and potassium salts.

The 0.45- μ m membranes used to filter the eluents were obtained from Rainin.

The water used to prepare all solutions was distilled and further deionized by a dual-bed ion-exchange column.

Procedures

The XAD-1 resin was prepared by first subjecting it to Soxhlet extraction with methanol, acetonitrile and diethyl ether for at least 24 h each. The resin was dried overnight at 70°C, then ground in a shear mill or a ball mill and passed through U.S. standard sieves to separate size fractions of the copolymer.

The preliminary reactions were carried out on resins with a size range of 75–150 μ m as it had been determined earlier that particle size had no bearing on the reaction⁶. The resins used for chromatography were prepared from the material that passed through a 38- μ m sieve. This material was slurried in methanol and allowed to settle for 10 min, then any resin that remained suspended was poured off. This procedure was repeated until the supernatant liquid was almost devoid of particles. The remaining resin was then used to prepare low-capacity anion-exchange resins for chromatography.

Chloromethylations were carried out with hydrochloric acid and paraformaldehyde using glacial acetic acid as a wetting agent as previously described⁶. *Caution:* Because of the possibility of the *in situ* formation of bischloromethyl ether, the chloromethylation reaction should be carried out in a good fume hood and the reaction vessel should be vented to a water trap. This should cause any bischloromethyl ether that may be evolved to be hydrolyzed.

After washing, the resin was aminated with an excess of tertiary amine in methanol. Aminations with trimethylamine were carried out in an unstirred solution at room temperature for 24 h. All other aminations were carried out at 65–70°C for the same time period. The aminated resins were then washed and air dried as described earlier⁶.

The strong-base ion-exchange capacity of the resins was determined in the manner described earlier⁶.

The chromatographic columns were packed using the upward packing method with a balanced density fluid consisting of 40% ethylene glycol in water. The packing pressure was usually about 9650 kPa (1400 p.s.i.) and the operating pressure was generally less than 2100 kPa (about 300 p.s.i.).

RESULTS AND DISCUSSION

Preparation of resins

The purpose of this investigation was to determine how structural changes in the fixed quaternary ammonium ion affect the selectivity of low-capacity macroporous anion-exchange resins when they are used in ion chromatography.

To ascertain the effect of functional group structure on selectivity, the various resins should be of a similar capacity so that identical elution conditions can be used for each resin. For the same reason, only one substrate was used to prepare the anion exchangers. With only one substrate, the physical properties of the exchangers should remain constant.

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* hydrochloric acid, 2.2 *M* formaldehyde, 1 g of XAD-1 and a 20-min reaction time at room temperature⁶. Each batch of the chloromethylated copolymer

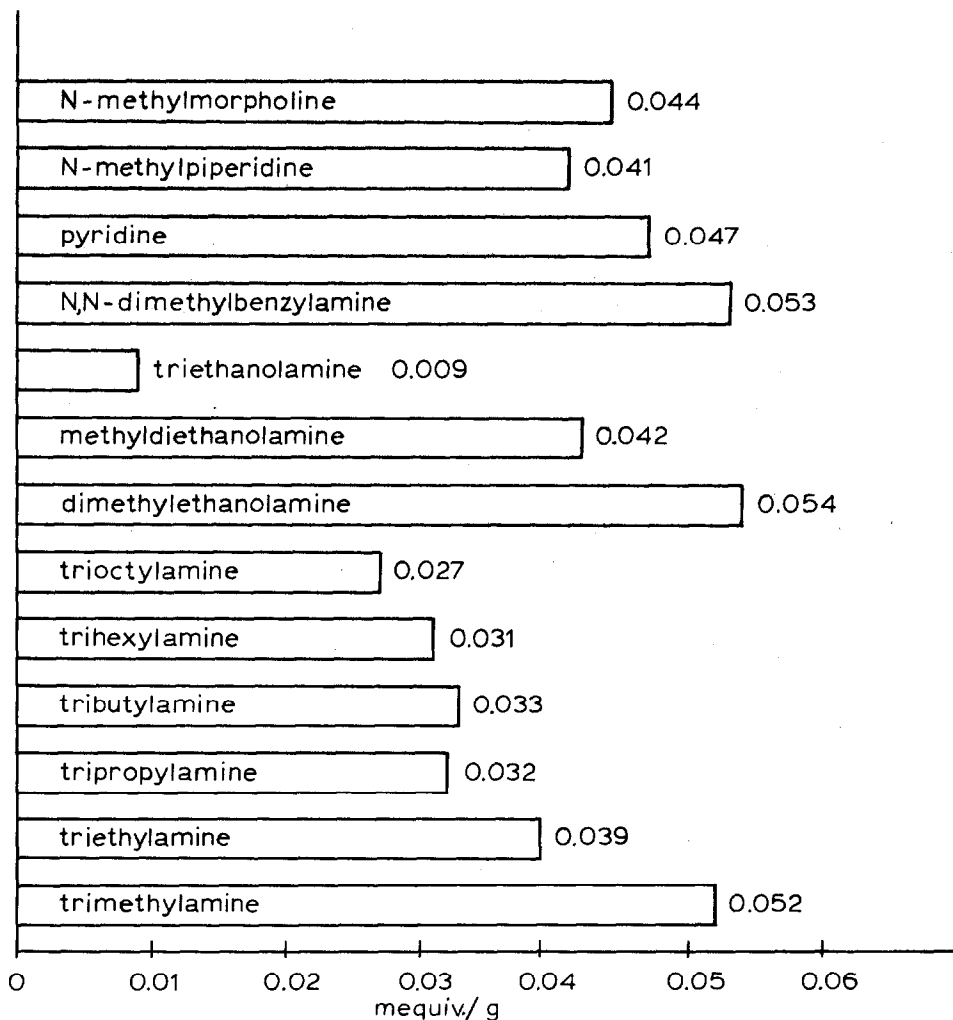


Fig. 1. Relative reactivities of tertiary amines. All of the amines were reacted with chloromethylated copolymer prepared under the same set of conditions. The resulting capacities are listed near the appropriate bars. See text for details.

was then aminated for 24 h with one of the chosen tertiary amines. The strong-base ion-exchange capacity of each batch of resin was then determined. The results are shown in Fig. 1.

Once the relative reactivities were known, it was simple 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 mequiv./g was chosen as a target for the resins to be prepared 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 h. Most of the calculated chloromethylation times fell in the range 8–20 min, except for the resin prepared with triethanolamine, for which a reaction time of about 3.5 h was necessary to produce a resin of 0.031 mequiv./g capacity. This long reaction time was a result of the low reactivity of triethanolamine towards the chloromethylated substrate. The consequences of this extended chloromethylation time will be pointed out later.

The capacities of all resins produced for the selectivity study are listed in Table I. The average capacity of these resins was 0.027 mequiv./g with a standard deviation of 0.002 mequiv./g. The capacities are on a dry-weight basis with all resins originally in the chloride form. It should be pointed out that the chloromethylation process was reliable enough for the correct capacity to be achieved at the first attempt with nearly every amine.

Evaluation of resin selectivity

The next step was to evaluate selectivity differences that could be attributed to the structural changes in the functional groups. A true selectivity coefficient for an anion exchanger is normally obtained by shaking a weighed portion of resin in a given ionic form (usually Cl^-) with a solution of the ion of interest until the resin and 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.

TABLE I

STRONG-BASE EXCHANGE CAPACITY OF RESINS PREPARED FOR SELECTIVITY EVALUATION

<i>Tertiary amine</i>	<i>Capacity (mequiv./g)</i>
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)	0.026
N-Methylmorpholine (NMM)	0.029
N-Methylpiperidine (NMP)	0.029
N,N-Dimethylbenzylamine (DMBA)	0.024
Av.: 0.027 ± 0.002	

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. The dynamic method consisted of packing each resin into a 500×2.0 mm I.D. column and determining the retention time of the analyte anions under identical elution conditions for each resin. The current study encompassed only singly charged anions and used a singly charged eluent, the benzoate ion. The retention times of seventeen different anions were determined on each column. The data were then tabulated as relative retention times compared with that of 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 the small differences in capacity that exist between the resins.

Tables II-IV give these relative retention times. Each table contains the data for the TMA resin (Type I) as a point of reference. Table II contains the resins that have trialkylammonium functional groups, Table III those which have hydroxyalkylammonium functional groups and Table IV those which have rings associated 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 V, which shows the relative retentions of glycolate and chlorate for four separate injections of each ion plus chloride on a column containing TEtA resin. This

TABLE II
RELATIVE RETENTIONS OF ANIONS ON TRIALKYLAMMONIUM RESINS

Anion	TMA	TEtA	TPA	TBA	THA	TOA
Cl ⁻	1.0	1.0	1.0	1.0	1.0	1.0
F ⁻	0.66	0.70	0.69	0.71	0.68	0.69
Br ⁻	1.20	1.19	1.25	1.34	1.32	1.41
I ⁻	2.51	2.48	3.05	3.82	5.00	> 5.0
H ₂ PO ₄ ⁻	0.84	0.85	0.84	0.85	0.83	0.83
NO ₂ ⁻	0.82	0.82	0.86	0.90	0.89	0.98
NO ₃ ⁻	1.30	1.32	1.38	1.54	1.63	1.72
Acetate	0.25	0.28	0.23	0.25	0.22	0.22
Formate	0.52	0.54	0.51	0.52	0.51	0.53
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
Nicotinate	0.31	0.32	0.31	0.31	0.31	0.33
ClO ₃ ⁻	1.53	1.55	1.56	1.73	1.92	2.15
BrO ₃ ⁻	1.05	1.06	1.03	1.08	1.08	1.14
N ₃ ⁻	0.36	0.39	0.34	0.37	0.35	0.37
BF ₄ ⁻	2.70	2.58	3.41	4.34	> 7.5	-
CH ₃ SO ₃ ⁻	1.00	1.06	1.01	1.06	1.01	1.07
<i>t_R</i> Cl ⁻ (min)	8.3	8.0	9.5	8.9	10.6	9.4

TABLE III
RELATIVE RETENTIONS OF ANIONS ON HYDROXYALKYLAMMONIUM RESINS

Anion	TMA	DMEA	MDEA	TEA
Cl ⁻	1.0	1.0	1.0	1.0
F ⁻	0.66	0.67	0.74	0.64
Br ⁻	1.20	1.22	1.19	1.30
I ⁻	2.51	2.60	2.11	2.95
H ₂ PO ₄ ⁻	0.84	0.83	0.88	0.88
NO ₂ ⁻	0.82	0.91	0.82	0.79
NO ₃ ⁻	1.30	1.28	1.22	1.38
Acetate	0.25	0.22	0.24	0.14
Formate	0.52	0.52	0.55	0.44
Lactate	0.44	0.46	0.49	0.38
Glycolate	0.45	0.42	0.45	0.38
Nicotinate	0.31	0.30	0.33	0.22
ClO ₃ ⁻	1.53	1.53	1.43	1.58
BrO ₃ ⁻	1.05	1.05	1.10	1.05
N ₃ ⁻	0.36	0.35	0.36	0.22
BF ₄ ⁻	2.70	2.44	1.93	2.29
CH ₃ SO ₃ ⁻	1.00	1.05	1.07	0.95
<i>t_R</i> Cl ⁻ (min)	8.3	9.4	8.4	18.6

TABLE IV
RELATIVE RETENTIONS OF ANIONS ON MISCELLANEOUS RING-CONTAINING QUATERNARY AMMONIUM RESINS

Anion	TMA	PYR	NMP	NMM	DMBA
Cl ⁻	1.0	1.0	1.0	1.0	1.0
F ⁻	0.66	0.69	0.68	0.69	0.72
Br ⁻	1.20	1.18	1.24	1.26	1.22
I ⁻	2.51	2.39	2.99	2.90	2.62
H ₂ PO ₄ ⁻	0.84	0.83	0.82	0.85	0.89
NO ₂ ⁻	0.82	0.85	0.88	0.82	0.86
NO ₃ ⁻	1.30	1.25	1.33	1.34	1.30
Acetate	0.25	0.25	0.24	0.24	0.26
Formate	0.52	0.50	0.49	0.49	0.56
Lactate	0.44	0.47	0.46	0.44	0.48
Glycolate	0.45	0.45	0.44	0.42	0.46
Nicotinate	0.31	0.32	0.31	0.30	0.35
ClO ₃ ⁻	1.53	1.49	1.58	1.60	1.52
BrO ₃ ⁻	1.05	1.04	1.05	1.06	1.10
N ₃ ⁻	0.36	0.36	0.35	0.34	0.42
BF ₄ ⁻	2.70	2.31	3.02	3.00	2.58
CH ₃ SO ₃ ⁻	1.00	1.05	1.02	1.03	1.06
<i>t_R</i> Cl ⁻ (min)	8.3	8.4	9.2	9.6	7.2

TABLE V

EXPERIMENTAL VARIATION OF RELATIVE RETENTION TIMES FOR TWO REPRESENTATIVE ANIONS

Run	$t_{R \text{ glycolate}}/t_{R \text{ Cl}^-}$ *	$t_{R \text{ ClO}_3^-}/t_{R \text{ Cl}^-}$ **
1	0.48	1.35
2	0.50	1.42
3	0.52	1.37
4	0.52	1.40

* Average $t_{R \text{ glycolate}}/t_{R \text{ Cl}^-} = 0.51 \pm 0.02$.** Average $t_{R \text{ ClO}_3^-}/t_{R \text{ Cl}^-} = 1.38 \pm 0.03$.

shows that for an ion such as glycolate a relative retention range of 0.49–0.53 might be expected. For chlorate, a range of 1.35–1.41 is probably normal.

Selectivity of resins with alkyl substituents

The data in Table I show that the relative retentions of the weak-acid anions are virtually independent of the size of the R groups. However, as the size of the R groups increases, large changes begin to occur with the more polarizable anions such as NO_3^- , BF_4^- , ClO_3^- and I^- . A clear trend towards greater relative retention occurs for these ions as the size of the quaternary ammonium ion increases.

This increase in relative retention as the hydrophobicity of the ion-exchange site increases is paralleled by the recent work of Iskandarani and Pietrzyk using ion interaction chromatography⁹. They showed that at a given solvent composition, the retentions of a series of quaternary ammonium bromides on a poly(styrene-divinylbenzene) column (Hamilton PRP-1) were dependent on the number of carbon atoms in the quaternary ammonium ion. Their data seem to imply a liquid-liquid partition phenomenon with the copolymer acting as the hydrophobic phase.

All of these facts seem to be explained by the phenomenon of "water-structure induced ion pairing", which was suggested by Diamond¹⁶ and Diamond and Whitney¹⁷. With large polarizable anions, electrostatic ion pairing with the quaternary ammonium cation is minimized because, as Diamond pointed out, electrostatic ion pairing requires small, highly charged ions and solvents of low dielectric constant. However, water-structure induced ion pairing occurs most readily with large univalent ions in aqueous solutions. The pairing of ions results because the large ions with diffuse charge have trouble orienting an adjacent shell of water molecules and thus do not fit smoothly into the prevailing water structure. This causes the water molecules closest to the ion to become more tightly bound to the next layer of water. This is in effect a decrease in entropy, which is not a favorable situation. Thus, the larger and more polarizable the ion, the more disruption of the local water structure it causes and the more easily it associates with a given quaternary ammonium ion.

This also explains the behavior of the quaternary ammonium bromides in the work of Iskandarani and Pietrzyk⁹. As the quaternary ammonium ion becomes larger, it more easily forms the water-structure induced ion pair with bromide. This neutral moiety is then more easily sorbed by the poly(styrene-divinylbenzene) resin, resulting in greater retention for the larger ions.

It is believed that an analogous effect occurs in the fixed-site ion-exchange resins prepared for this study. The quaternary ammonium ions are thought to be at the surface of the macroreticular channels of the resin and thus must contact the aqueous eluent within the pores. The quaternary ammonium ion is then capable of disrupting the water structure near the interface of the polymer and the solution. Again, the larger the quaternary ammonium ion, the greater this disruption should be. As the water structure is tightened up more and more, there is a greater impetus to form an ion pair with any given anion. This is exactly the effect observed in Table II.

In addition to this effect caused by the local tightening of the water structure, 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 polymer bead⁶. 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 anion. These ion pairs are in close proximity to the non-polar matrix. It must be remembered 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 non-polar 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 studies of Everhart and Reilley^{18,19}. They examined amine functional groups on the surface of a plasma-oxidized polyethylene film. This film is analogous to the low-capacity anion exchanger in that the polar oxidized layer was at the surface and was backed up by the bulk phase of non-polar polyethylene. They showed that the nitrogen ESCA signal 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 orthophosphoric or sulfuric acid. 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, hydrochloric and nitric acids 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.

We suggest 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 diffusion of the functional groups within the matrix.

Selectivity of resins with hydroxyalkyl substituents

When the behavior of the hydroxyalkyl resins in Table III is examined, one

does not see the same smooth variation of properties that occurred with the trialkyl resins in Table II. Going from the TMA resin to the DMEA resin, very little change in relative retention is observed for any ion except BF_4^- , which elutes earlier in relation to Cl^- . 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 decrease in retention relative to chloride. Therefore, a resin prepared from MDEA would be a good candidate for separating a mixture of early- and late-eluting ions of similar concentration because the relative retention of the late-eluting ions is reduced by this functional group.

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 with 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 those of the others, there must obviously 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 for the presence of an ion. 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 Gózdź and Kolarz¹⁴ show some agreement with those 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 with chloride. However, they found an increase in the selectivity for fluoride, which is also marginally visible for the MDEA resin shown here in Table III. The main inconsistency is that Gózdź 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 with 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 instance. Also, their aminations were run from five to seven days, thus allowing for more of the chloromethyl groups to react in a given polymer.

Excluding the TEA resin, the results acquired here seem to be logical. The size of the quaternary site increases as the methyl groups are substituted by ethanol groups, but the new substituents can participate in hydrogen bonding with water. This causes less disruption of the water structure (compared with a trialkyl resin) and thus provides less impetus for the formation of a water-structure induced 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 IV. Many anions show no

remarkable selectivity changes compared with the other resins. The resin containing a benzylpyridinium ion is perhaps most similar to the TMA resin. This is surprising as the nitrogen is in an aromatic ring. It shows a slight decrease in relative retention of I^- and BF_4^- compared with a TMA resin, which indicates a diminished tendency to form water-structure induced ion pairs. The resins prepared from the other three tertiary amines show slight increases in relative retention of the polarizable ions I^- and BF_4^- , but it does not appear that they would offer any distinct advantages over a trialkyl resin in ion chromatography.

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 well be amplified, as indicated by the results of Góźdz and Kolarz¹⁴. The capacity of these resins could probably be increased by a factor of 4-5 without becoming too

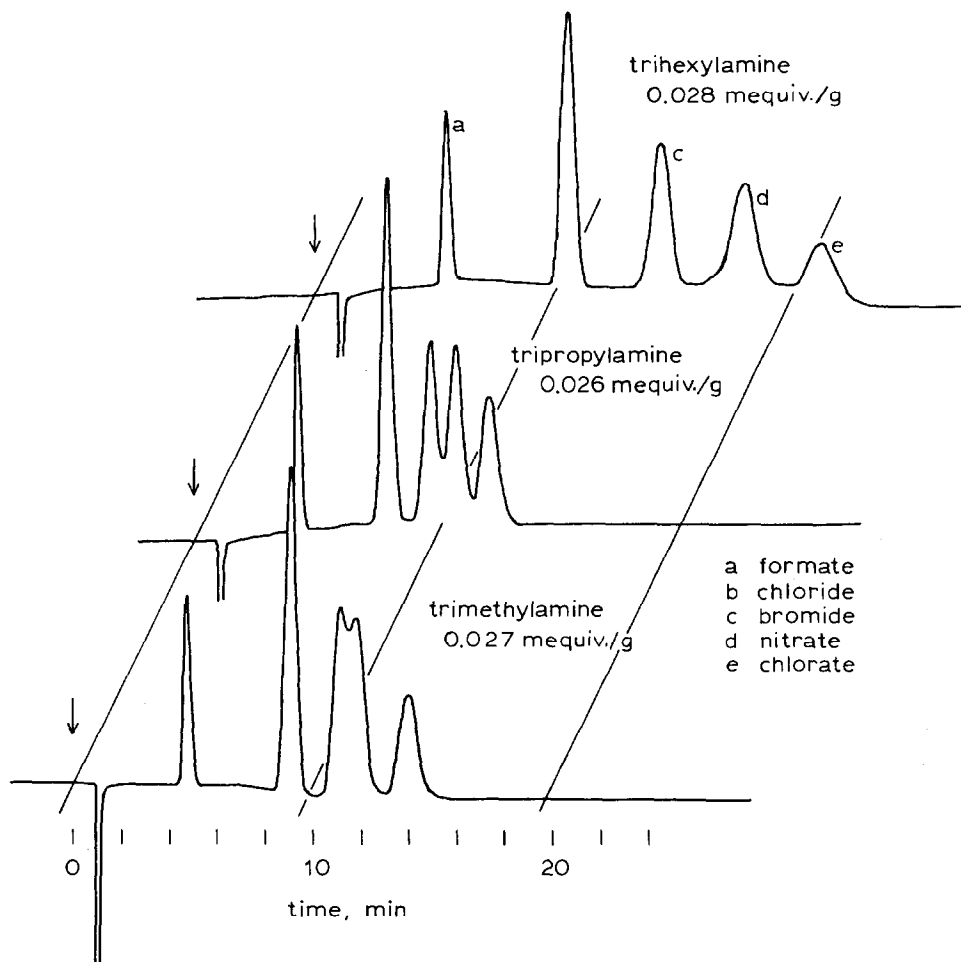


Fig. 2. Separation of five anions on three different resins of similar capacity. The resins were packed in a 500×2.0 mm I.D. column and a solution of $0.001 M$ benzoic acid was used as the eluent at a flow-rate of 0.93 ml/min.

high for use as a stationary phase in single-column ion chromatography. Also, the use of a different eluent (either weaker or stronger) would tend to change the selectivity²⁰. Changes in pH would also cause differences because weak acid anions 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.

Practical application of new resins in ion chromatography

The use of anion-exchange resins with different substituents offers a useful parameter for improving the separation of some anions. One practical example is shown in Fig. 2. Here a mixture of five anions was injected into 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, whereas the TPA resin gives a less convincing separation and the TMA resin gives poor resolution of bromide and nitrate. It is possible to increase 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 the monovalent ions can be useful in two other general situations. Because a resin such as THA spreads the ions out, 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. Of course, the resolution can be increased on a conventional Type I resin by increasing the capacity. However, in order to use a conductimetric detector, there are limits to the eluent concentration and hence limits to the capacity of the resins that may be used.

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 versa*. Again, by using a resin with a naturally high selectivity for late-eluting components, the capacity can be kept in the usual range, the eluent concentration can remain steady and sensitivity will still be retained while allowing the minor component to elute well away from the major component.

CONCLUSION

It has been shown that the identity of the quaternary ammonium ion in anion exchangers of low capacity has an influence on selectivity, especially for large polarizable anions. The observed behavior seems to fit the pattern outlined by the mechanism of water-structure induced ion pair formation.

A few suggestions for the use of functional group changes have been given; there are undoubtedly other specific instances where this procedure would be useful. It will be necessary for other workers to provide such cases from within the context of their own research.

The data from an analogous study of divalent ions is currently being compiled and will appear in a separate publication. The changes in functional group structure have a greater impact on the separation of mixtures of monovalent and divalent ions than they do for the separation of monovalent ions alone.

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