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EFFECT OF FUNCTIONAL GROUP STRUCTURE AND EXCHANGE CAPACITY ON THE SELECTIVITY OF ANION EXCHANGERS FOR DIVALENT ANIONS

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SUMMARY

A number of macroreticular anion-exchange resins of low capacity were prepared by chloromethylation of Rohm and Haas XAD-1 under mild conditions and reaction with the appropriate tertiary amine. The resins prepared contain a variety of substituents on the quaternary ammonium group and have varying exchange capacities. These resins are evaluated for their selectivity both for monovalent and divalent anions and for practical use in ion chromatography. Explanations are offered to help understand some of the significant changes that are observed. Several chromatograms are shown to demonstrate the advantages of some of the new resins for practical separation of anion mixtures.

INTRODUCTION

The introduction of modern ion chromatography almost ten years ago¹ has virtually revolutionized methods for the determination of inorganic anions and to some extent the determination of cations. The method brought dramatic improvements in speed of analysis, specificity and sensitivity. Numerous improvements have been made both chemically and instrumentally in the intervening decade. Variations such as single-column ion chromatography²⁻⁴ and ion interaction chromatography^{5,6} have also arisen to complement the original method.

Because of the utility of the method, there is also a renewed interest in low-capacity ion-exchange resins. The relationship of their preparation and structure to their performance is of particular interest.

A recent paper⁷ reviewed some previous research on resin structure and resin selectivity. A more detailed review of this area is also available⁸. The previous paper⁷ also examined the effect of varying the quaternary ammonium R groups on the selectivity for 17 different monovalent anions. The current investigation extends this work to cover separations of both monovalent and divalent anions. Trends in selectivity are presented along with proposed explanations for the observed behavior. Some implications for practical use of resin structure variations are outlined.

EXPERIMENTAL

Preparation of anion exchangers

Anion-exchange resins with various functional groups and exchange capacities were prepared by chloromethylation and amination of Rohm and Haas XAD-1, as described in earlier publications^{7,9}. The tertiary amines used in the amination step were better than 95% pure and were used as received. The exact procedure reported earlier⁷ was used for amination with trimethylamine, but aminations with other amines were carried out at 65–70°C in a round-bottom flask fitted with reflux condenser. The amines were added as 20–50% solutions in methanol. Aminations with trioctylamine had to be carried out in isopropyl alcohol because of solubility limitations in methanol.

Liquid chromatography

The liquid chromatograph was the same as that used in an earlier publication⁷. Chromatographic columns were packed by using the balanced-density slurry method described previously⁷.

RESULTS

Initially, resins with an average capacity of about 0.027 mequiv./g were used with 0.3 mM potassium phthalate eluent at pH 5.6. However, these conditions were so overpowering that many of the ions were eluted too quickly to discern trends in behavior. Results with resins of higher capacity were more definitive. Using resins of approximately 0.045 mequiv./g capacity, side-by-side comparisons were made of the benzyltrimethyl (TMA) quaternary ammonium structure with the benzyltriethyl (TEA) structure. These experiments showed that monovalent anions grow in relative retention (compared to chloride) and divalent anions decrease in relative retention as the size of the R groups becomes larger. Comparison of the two chromatograms in Fig. 1 shows that the TEA resin gives a better separation of the monovalent anions as well as shorten the time for separation of the divalent-monovalent anion mixture.

The effect of resin structure on the relative affinity for various anions is more clearly evident when resins of still higher capacity are compared. Resins with different functional groups but with similar capacities (about 0.09 mequiv./g) were prepared according to the procedures described earlier. These included batches containing the benzylmethyl-diethanolammonium functional group (MDEA; 0.090 mequiv./g), the benzyltrimethylammonium functional group (TMA; 0.092 mequiv./g), and the benzyltributylammonium functional group (TBA; 0.096 mequiv./g). These represent the polar, standard and non-polar functional groups, respectively. Columns were filled with a 500 × 2 mm resin bed; the eluent was 0.4 mM potassium phthalate at pH 5.0 and at 6.0. The results are shown in Tables I and II. These show even more clearly than Fig. 1 that changes in functional group structure affect the behavior of the resins toward both the highly polarizable monovalent ions, such as SCN⁻ and ClO₄⁻, 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 when benzoic acid was used as eluent⁷. That is, they are eluted at longer relative retentions as the functional group becomes more non-polar.

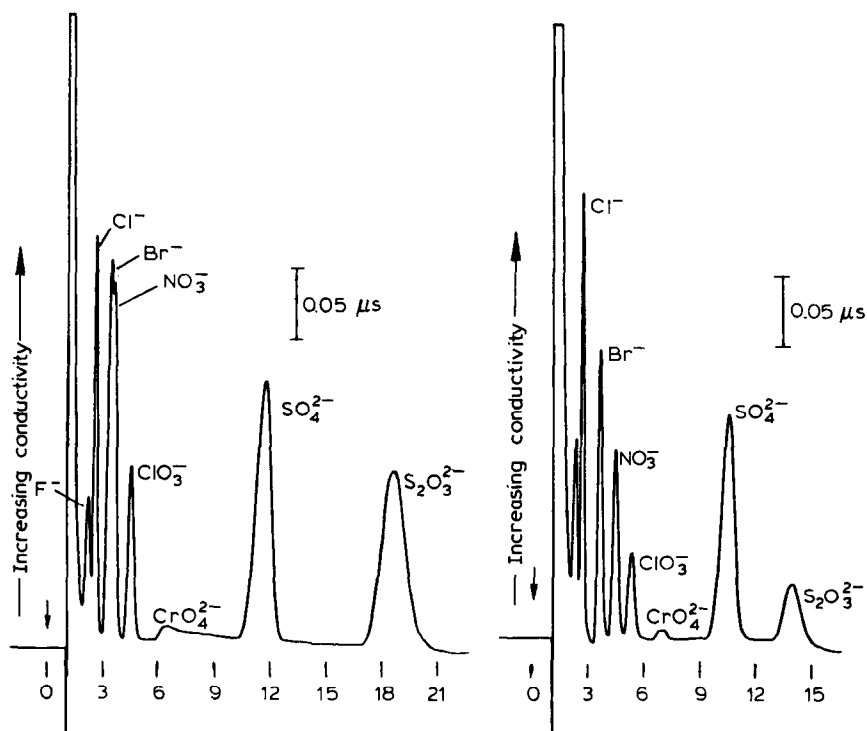


Fig. 1. The comparison of the separation of mixed monovalent and divalent anions on two resins with different functional groups. The resin on the left is a TMA resin with a capacity of 0.046 mequiv./g. The resin on the right is a THA resin with a capacity of 0.043 mequiv./g. The eluent is 0.4 mM KHP at a pH of 5.0 and a flow-rate of 1.0 ml/min. The resins are packed into 500 × 2.0 mm I.D. glass columns.

The behavior of divalent ions, such as sulfate and thiosulfate, seems more complex. The relative retentions of these ions are quite similar on the MDEA and TMA resins, but they are eluted more rapidly from the TBA resin. Raising the eluent pH from 5.0 to 6.0 increases the relative retention of monovalent anions on the TMA and TBA resins but decreases the relative retention of the divalent anions (compared to chloride). Figs. 2, 3 and 4 show the relative retention behavior of Cl^- , NO_3^- , and SO_4^{2-} on the MDEA, TMA, and TBA resins at pH 6.0. The alteration of behavior is great enough to cause NO_3^- to be eluted after SO_4^{2-} on the TBA resin.

The preceding data 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 III shows the relative retentions for several anions on two Type I (TMA) resins. 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 seen clearly, because the ratios of each of the eluent species to the number of functional groups will be constant for both resins.

TABLE I

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

The values are expressed as $t_{R \text{ anion}}/t_{R \text{ Cl}^-}$.

<i>Ion</i>	<i>MDEA</i> *	<i>TMA</i> **	<i>TBA</i> ***
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 ²⁻	7.31	7.29	6.36
S ₂ O ₃ ²⁻	15.75	16.6	9.23
C ₂ O ₄ ²⁻	7.41	7.18	6.30
MoO ₄ ²⁻	9.50	9.92	8.72
WO ₄ ²⁻	—	—	—
$t_{R \text{ Cl}^-}$ (min)	3.20	3.80	3.90

* Capacity 0.090 mequiv./g.

** Capacity 0.092 mequiv./g.

*** Capacity 0.096 mequiv./g.

TABLE II

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

The values are expressed as $t_{R \text{ anion}}/t_{R \text{ Cl}^-}$.

<i>Ion</i>	<i>MDEA</i> *	<i>TMA</i> **	<i>TBA</i> ***
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 ²⁻	4.64	4.77	4.21
S ₂ O ₃ ²⁻	9.68	11.3	7.65
C ₂ O ₄ ²⁻	4.96	5.10	4.80
MoO ₄ ²⁻	6.72	7.27	6.94
WO ₄ ²⁻	7.20	6.30	6.70
$t_{R \text{ Cl}^-}$ (min)	2.50	3.00	3.40

* Capacity 0.090 mequiv./g.

** Capacity 0.092 mequiv./g.

*** Capacity 0.096 mequiv./g.

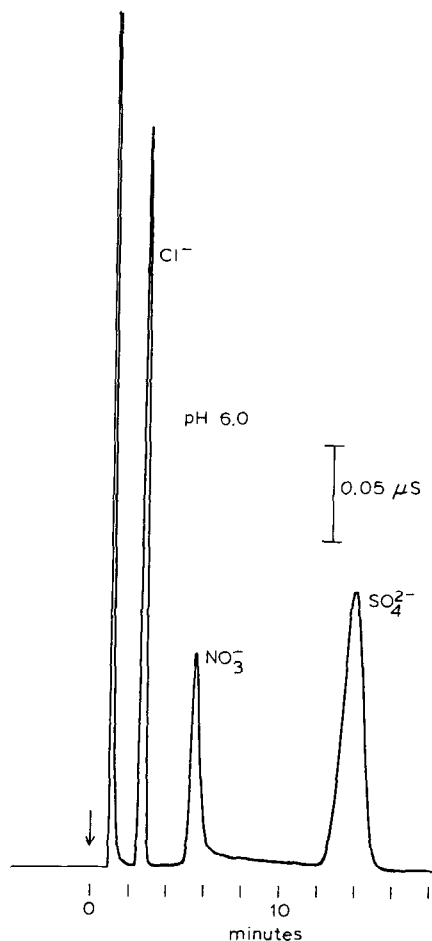
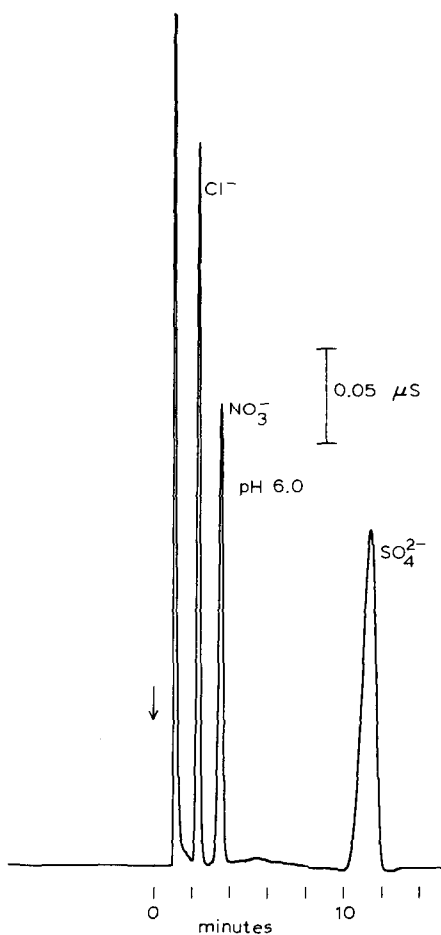


Fig. 2. Separation of Cl^- , NO_3^- and SO_4^{2-} on MDEA resin of a capacity of 0.090 mequiv./g. Eluent: 0.4 mM KHP at a pH of 6.0 and a flow-rate of 1.0 ml/min.

Fig. 3. Separation of Cl^- , NO_3^- and SO_4^{2-} on TMA resin of a capacity of 0.092 mequiv./g. Eluent: same as Fig. 2.

The data definitely show that as the capacity becomes greater, the monovalents and divalents draw closer together, with the exception of thiosulfate.

We have seen that the chemical nature of the quaternary ammonium group on the resin, the resin capacity, and the eluent pH are all variables that affect the retention times of monovalent and divalent anions. Specifically, polarizable monovalent ions will be retained longer in relation to chloride with greater hydrophobicity of the anion-exchange site, with higher capacity at a given hydrophobicity, or with higher concentrations of a divalent eluent salt. Divalent ions exhibit behavior which is roughly opposite that of the monovalent anions.

To illustrate the generality of these observations and to prove that there is nothing inherently special about the TBA functional group, another batch of resin was prepared. The amination was carried out with triethylamine, which was shown

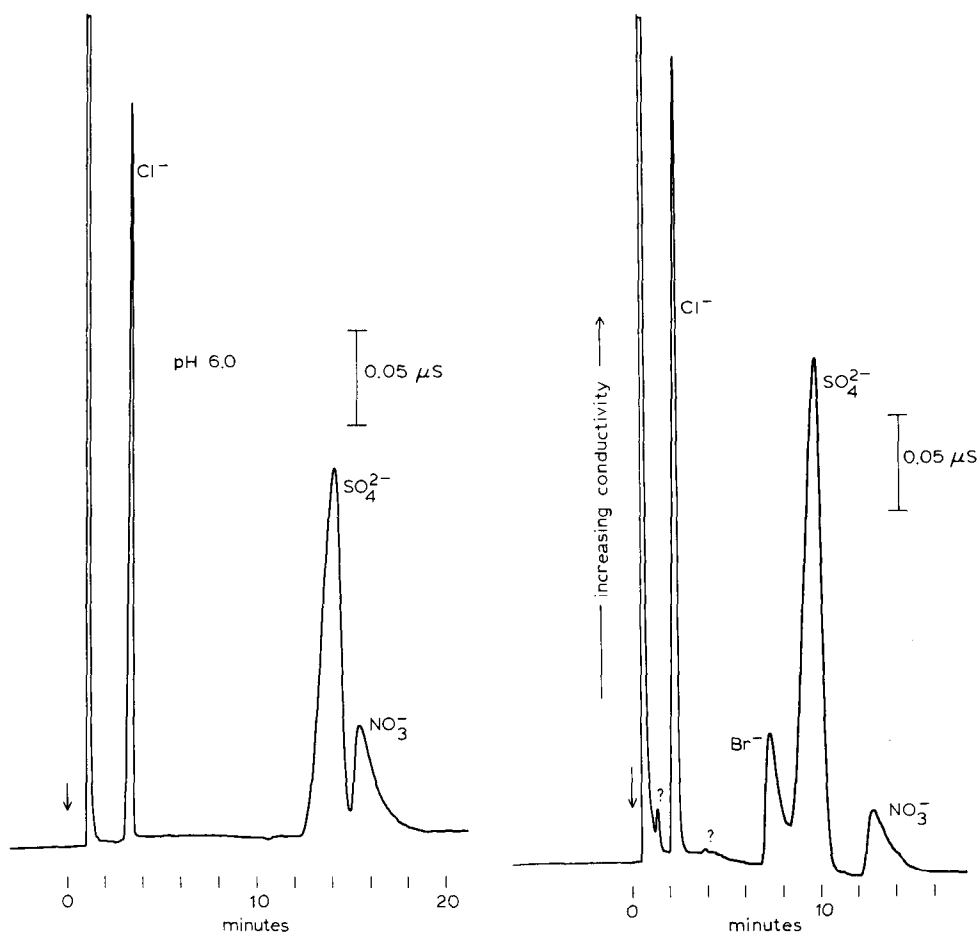


Fig. 4. Separation of Cl^- , NO_3^- and SO_4^{2-} on TBA resin of a capacity of 0.096 mequiv./g. Eluent: same as Fig. 2.

Fig. 5. Separation of Cl^- , NO_3^- , Br^- and SO_4^{2-} on a benzyltriethylammonium anion exchanger with a capacity of 0.184 mequiv./g. The eluent is 0.4 mM KHP at pH 9.2 and a flow-rate of 1.0 ml/min. The column is 250×2.0 mm.

to be almost identical to trimethylamine at low capacities⁷. The goal was to use the benzyltriethylammonium functional group and yet allow nitrate to be eluted after sulfate. The chloromethylation was carried out at 55°C for 60 min (12 M hydrochloric acid, 2.2 M formaldehyde) and the amination was carried out for about 36 h in warm methanol. This resulted in a strong-base capacity of 0.184 mequiv./g. A column with dimensions 250×2.0 mm I.D. was packed with this resin. The column therefore has the same total capacity as the columns used to produce the data in Table I, even though the capacity per gram is twice as high for the new resin. An eluent of 0.4 mM potassium hydrogen phthalate at pH 9.2 was pumped through the column at 1.0 ml/min. Fig. 5 shows the separation of chloride, bromide, sulfate and nitrate under these conditions. The nitrate is indeed eluted after sulfate, thus demonstrating that

TABLE III

EFFECT OF CAPACITY ON THE RELATIVE RETENTIONS OF MONOVALENT AND DIVALENT IONS ON TWO TYPE I RESINS

The values are expressed as $t_{R \text{ anion}}/t_{R \text{ Cl}^-}$.

Ion	A	B	A	B
	0.4 mM KHP, pH 5.0, 0.092 mequiv./g	0.2 mM KHP, pH 5.0, 0.046 mequiv./g	0.4 mM KHP, pH 6.0, 0.092 mequiv./g	0.2 mM KHP, pH 6.0, 0.046 mequiv./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 ²⁻	7.29	8.40	4.77	5.68
S ₂ O ₃ ²⁻	16.6	14.2	11.3	9.65
C ₂ O ₄ ²⁻	7.18	8.05	5.10	6.03
MoO ₄ ²⁻	9.92	10.1	7.27	7.68
WO ₄ ²⁻	—	—	6.30	7.22
$t_{R \text{ Cl}^-}$ (min)	3.80	4.00	3.00	3.10

the assessment of the factors involved in the ion-exchange behavior is probably accurate.

The concentration of the eluent will, of course, also exert a profound effect. Fig. 6 compares the elution of a complex mixture of anions from a THA column under identical conditions except for the eluent concentration. The higher concentration of phthalate gives a faster elution and a more compact chromatogram. Note that an excellent separation of a sample containing both monovalent and divalent cations is possible in a single chromatogram.

DISCUSSION

In our previous paper⁷ the effect of larger resin R groups on the greater relative retention of poorly hydrated anions, such as bromide, iodide, and nitrate, was attributed to stronger ion pairing, resulting from disruption of the water structure by these anions and by tightening of the water structure surrounding the ion pair by the larger R groups. A more thorough discussion of these causes may be found in another source⁸.

Considering the above arguments, why is a well-hydrated anion such, as sulfate, normally eluted after such ions as bromide, nitrate, and chlorate, which are strong disrupters of water structure? The explanation commonly given for the late elution of sulfate is based on 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. One might conclude that in ion chromatography, where the resins are porous and of low capacity

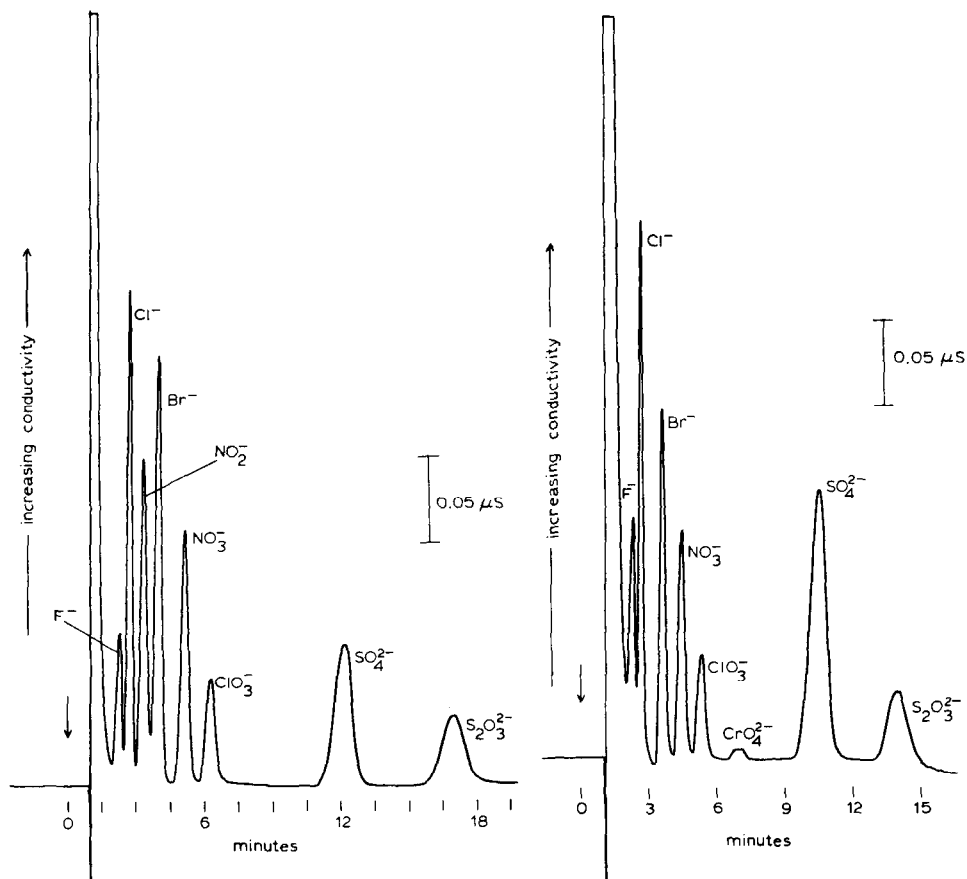


Fig. 6. The effect of eluent concentration on the separation of mixed monovalent and divalent ions on a THA resin. The resin has a capacity of 0.043 mequiv./g and is packed into a 500×2.0 mm I.D. column. The eluent used in the left half is 0.3 mM KHP at a pH of 5.0. The eluent used in the right half is 0.4 mM KHP at a pH of 5.0. Both separations are carried out at 1.0 ml/min.

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.

Electroselectivity in ion exchange is obviously a powerful effect, because much other data show that SO_4^{2-} should not be where it is in the order of elution from a Type I anion-exchange resin. Glasstone¹⁰ cites the early work of Hofmeister (*ca.* 1891) concerning the imbibition 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 ions¹¹. The ability of an ion to salt gelatin out of solution occurs in the order SO_4^{2-} , $\text{C}_2\text{H}_3\text{O}_2^-$, 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 ago¹². Navtanovich *et al.*^{13,14} cite the work of Ivanov and co-workers^{15,16}, who established the selectivity of extraction of various anions into toluene by tetractylammonium cation. The order of increasing selectivity for monovalent anions found by these workers is OH^- , F^- , $\text{C}_2\text{H}_3\text{O}_2^-$, HCO_3^- , HSO_4^- , Cl^- , Br^- , $\text{C}_6\text{H}_5\text{COO}^-$, NO_3^- , I^- and ClO_4^- . (Note the position of bisulfate.)

The work of Navtanovich and co-workers in the publication cited above concerns establishment of the positions of SCN^- , $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ in the solvent extraction of these and other anions when benzyltrialkylammonium cations with alkyl chains of 7-9 carbons are used. The solvent used was xylene. They found the order of decreasing selectivity to be ClO_4^- , SCN^- , I^- , $\text{Fe}(\text{CN})_6^{3-}$, NO_3^- , Br^- , $\text{Fe}(\text{CN})_6^{4-}$, Cl^- and finally $\text{C}_2\text{H}_3\text{O}_2^-$. 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.

Now, let us look at the reasons for the observed effects of varying functional group and eluent pH on the elution of sulfate in ion chromatography. 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. These effects are clearly visible in Tables I and II.

TABLE IV
IONIZATION (%) OF *o*-PHTHALIC ACID AT SELECTED pH VALUES

	<i>pH</i>							
	3.00	3.50	4.00	4.50	5.00	5.50	6.00	6.50
H_2A	45.4	20.7	7.4	2.3	0.6	0.12	0.017	0.002
HA^-	54.4	78.4	89.1	87.0	71.5	44.7	20.4	7.50
A^{2-}	0.2	0.9	3.5	10.7	27.9	55.18	79.6	92.5

Changes in pH also contribute to the change in relative retention of the mono-valent and divalent ions. The percentage of doubly charged phthalate ion increases and the percentage of biphthalate (singly charged) decreases as the pH is increased (see Table IV). Apparently, hydrophobic monovalent analyte ions are only eluted well by monovalent eluent ions and so they 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 they are retained less as the percentage of divalent ion increases.

While many more elucidative experiments could be carried out, the present investigation provides an outline of the important variables that should be changed in order to change selectivity in anion-exchange chromatography with low-capacity resins.

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