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## ANION-EXCHANGE SELECTIVITY IN LATEX-BASED COLUMNS FOR ION CHROMATOGRAPHY

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### SUMMARY

The anion-exchange columns employed in suppressed ion chromatography contain packings which are agglomerations of anion-exchange latexes and functionalized polymeric substrate. Differences in anion-exchange selectivity studied here are achieved through variations of the properties of the ion-exchange sites and charge density. Column capacity is influenced by the particle sizes of the latexes and substrate. Efficiency is most strongly effected by size of the substrate resin. This paper discusses selectivity variations that are associated with differences in the nature of the quaternary ammonium ion-exchange sites of the latexes and their relationships with various eluents employed in suppressed ion chromatography. Hypotheses are proposed to explain retention behavior of model analyte anions.

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### INTRODUCTION

Selectivity in a ion-exchange system is often quantified through use of the selectivity coefficient,  $K_{A/B}$ , as described by a number of authors<sup>1-3</sup>. The selectivity coefficient  $K_{A/B}$  is defined as

$$K_{A/B} = \frac{[A]_r[B]_s}{[B]_r[A]_s} \cdot \frac{\gamma_{A,r}\gamma_{B,s}}{\gamma_{B,r}\gamma_{A,s}} \quad (1)$$

where the brackets represent concentration terms for two monovalent ions, A and B, “ $\gamma$ ” represents the activity terms for ions A and B, “r” represents the resin phase, and “s” represents the solution phase.

When the selectivity coefficient of eqn. 1 is greater than unity, preference is expressed for ion A over ion B in the resin phase *versus* the solution phase in the concentration range studied. Discussions of parameters that affect the selectivity coefficient deal with the parameters that affect the activity coefficients of the ions in the one phase relative to the other. The selectivity coefficient expresses the net effect of all parameters operating in both phases that are responsible for creating selectivity.

In a chromatographic process, the ionic components of the eluent determine the form of the ion exchanger, *e.g.*, ion B, against which selectivity for the analyte, A, is

measured. Selectivity between two analyte ions, A and C, is usually expressed as the ratio

$$a = \frac{V_A - V_0}{V_C - V_0} \quad (2)$$

where  $V_A$  and  $V_C$  are the retention volumes of ions A and C, respectively and  $V_0$  is the void volume. Implicit in this relationship is the affinity of the resin phase for each analyte ion relative to that for the eluent ion.

The capacity factor in chromatography is expressed as  $k'$  where

$$k' = \frac{V_A - V_0}{V_0} \quad (3)$$

$V_A$  is the retention volume of the analyte A, and  $V_0$  is the void volume of the column. Capacity factors are used to compare relative selectivities of chromatographic systems for the different analyte ions.

Some authors<sup>2-4</sup> have discussed various models for explaining ion-exchange selectivity in resins. Diamond and Whitney<sup>2</sup> have described selectivity in the ion-exchange process which relies on thermodynamic properties of ions in water as well as properties of water itself. They describe the selectivity order for various anions in terms of the relative basicity of these anions, the degree of hydration of the ions, and the hydration of a trimethylammonium resin. Reichenberg<sup>3</sup> has shown that the elution order of halides and  $\text{ClO}_4^-$  may be explained in terms of hydration enthalpies. Pearson<sup>5</sup> has discussed his concept of hard and soft acids and bases in several papers. These papers lend considerable insight into the behavior of harder, less polarizable ions such as  $\text{NO}_3^-$  relative to that of somewhat softer, more polarizable ions, such as  $\text{ClO}_3^-$ . Walton<sup>4</sup> has assembled a group of papers which deals with the application of ion-exchange selectivity to the chromatographic process.

There is no known literature discussing chromatographic selectivity differences for anions with different quaternary ammonium anion-exchange sites using small, hydrophilic eluent anions. Barron and Fritz<sup>6</sup> have discussed chromatographic selectivity using various quaternary ammonium-functionalized resins relative to eluent ions used in non-suppressed ion chromatography. These eluent anions *e.g.*, benzoate, phthalate and succinate, are larger, in two cases, aromatic, and generally less hydrated than those studied here.

Other authors have discussed the role of matrix effects in selectivity<sup>7</sup>, selectivity of resins for organic ions<sup>8</sup>, exchange equilibria<sup>9</sup>, and schemes for predicting ion-exchange selectivity in resins relative to linear polyelectrolyte analogues<sup>10</sup>.

In 1973, Small and Stevens<sup>11</sup> developed and subsequently patented the process for producing ion-exchange materials which, unlike conventional ion-exchange resins, were actually agglomerations of small anion-exchange latexes and larger cation-exchange resin. This type of ion-exchange material is held together by electrostatic forces between the two types of particles. Due to the high charge on both the latexes and resin, this type of packing was found to be very stable. This development produced pellicular anion-exchange packings with higher efficiencies than conventional, micro-

porous, styrene-based anion-exchange resins. The higher efficiencies result from faster kinetics and greater permeability of the pellicular layer.

In this type of packing, the only anion-exchange sites are those in the pellicular layer. Therefore, when substituting in the concentration terms for the resin phase (*e.g.*,  $[A_r]$  and  $[B_r]$ ) in eqn. 1, one must use the concentration in the active pellicular layer rather than the bulk composition. This distinction becomes important in calculating distribution ratios in the packing.

In developing useful selectivities for ion chromatography, the main consideration is the selectivity for the chosen eluent ion relative to each analyte ion. Often in designing special-selectivity columns, certain convenient eluents systems, (*e.g.*,  $\text{OH}^-$ ), are essentially pre-determined by cost, availability etc. before the latex-phase is designed. This constraint serves to guide column development. Creating the ion-exchange selectivity required for major applications cannot be separated from the chromatographic need for high efficiency and the practical need for a relatively short analysis time.

The selectivity of a particular packing is the end result of varying several parameters. These include the chemical nature of the monomers in both the substrate resin and the latex, the ratios of the functionalized monomers to crosslinking monomers and the chemical nature of the ion-exchange functionalities.

In this paper, we discuss the effect of varying the quaternary anion-exchange site on a styrene-based polymer latex, keeping the percentage of crosslinking and backbone polymeric structure constant. Our approach is to study the elution behavior of several different types of analytes in four different eluent systems in an attempt to describe the major factors involved in determining anion-exchange selectivity as related to the nature of the anion-exchange site.

## EXPERIMENTAL

### *Apparatus*

The 4000i gradient-ion chromatograph (Dionex, Sunnyvale, CA, U.S.A.), equipped with a conductivity detector and a Dionex micromembrane suppressor (AMMS), was used for all work. A Dionex AI400 data system was used for data collection and reduction. A helium headspace was maintained on the eluents by means of a Dionex eluent degas module.

### *Reagents*

The sodium hydroxide (50%) was of analytical grade (J. T. Baker, Phillipsburg, NJ, U.S.A.). The hydrochloric acid and sulfuric acid were of J. T. Baker Intra-analyzed grade.

Substrate resin used in this study was polymerized from styrene and divinylbenzene monomers (Dow Chemical, Midland, MI, U.S.A.) and sulfonated to 5  $\mu\text{equiv./g}$  using sulfuric acid. The latexes were synthesized from divinylbenzene and vinylbenzyl chloride (Dow Chemical). Trimethylamine (TMA), triethylamine (TEA), methyldiethanolamine (MDEA), and dimethylethanolamine (DMEA) were of reagent grade (Aldrich, Milwaukee, WI, U.S.A.).

The column capacity was determined for each packing by use of a breakthrough experiment. After the materials were packed into a polymeric tube, 150  $\times$  4 mm I.D.,

the anion-exchange sites were converted to the  $\text{OH}^-$  form. Each column was washed with deionized water until the effluent was neutral, and then it was connected to the conductivity detector. A solution of 0.0005 *M* hydrochloric acid was pumped through the columns at 1 ml/min until breakthrough occurred.

## RESULTS

The basic structure of the packings under discussion in this paper is that of an anion-exchange latex, agglomerated to cation-exchange-functionalized substrate resin. This type of structure creates an anion-exchange pellicular layer within which the ion-exchange separation takes place and an oppositely charged under-layer which excludes anions through Donnan forces. Table I summarizes the characteristics of the latexes synthesized for this study.

TABLE I  
CHARACTERISTICS OF THE LATEXES

Column	Amine	% Cross-linking	Size (nm)		Column capacity ( $\mu\text{equiv./column}$ )
			Raw	Functionalized	
1	MDEA	4	38.0	59.0	24.5*
2	DMEA	4	38.0	64.5	15.1
3	TMA	4	38.0	66.5	16.7
4	TEA	4	38.0	67.7	16.3

\* For 5  $\mu\text{m}$  substrate resin.

Fig. 1a, b and c are photographs taken with a scanning electron microscope. Fig. 1a shows unagglomerated 5- $\mu\text{m}$  sulfonated styrene-divinylbenzene substrate resin at 4500  $\times$  magnification. In Fig. 1b, substrate agglomerated with 0.2  $\mu\text{m}$  latex is shown at 9000  $\times$  magnification. When the magnification is increased to 15 000  $\times$ , a close-up of the anion-exchange latex itself is obtained, as shown in Fig. 1c. The latexes in these photographs are larger than the 60-nm latexes actually used in this study, as the larger latexes produce clearer photographs.

### Substrate

The size of the substrate resin was varied in this study, and column capacity and efficiency were evaluated. These data are summarized in Table II. The resin was synthesized with 2% divinylbenzene, a difunctional monomer which provides the crosslinking. The two packings in Table II contain the same latex on different substrates. As can be seen from the efficiency data, the smaller-diameter substrate yields a higher efficiency, assuming that the packing technique used for each material was equally optimized. In general, this latter point is of great importance and considerable skill was required to optimize column packing.

TABLE II  
COMPARISON OF COLUMN CAPACITIES AND EFFICIENCIES WITH SUBSTRATE SIZE

Chromatographic conditions: eluent, 5 mM sodium carbonate, 1 ml/min; suppression with anion micromembrane suppressor, regenerant 20 mM sulfuric acid, 10 ml/min; detection, conductivity; column dimensions, 250 mm  $\times$  4 mm I.D.

Substrate size ( $\mu\text{m}$ )	Latex	$N^*$	Column capacity ( $\mu\text{equiv./column}$ )
5	MDEA	8200	24.5
15	MDEA	2290	10.0

\* Efficiency was calculated by  $N = 5.54 (t_R/w_{1/2})^2$  where  $t_R$  is the retention time for sulfate and  $w_{1/2}$  is the width at half height for sulfate.

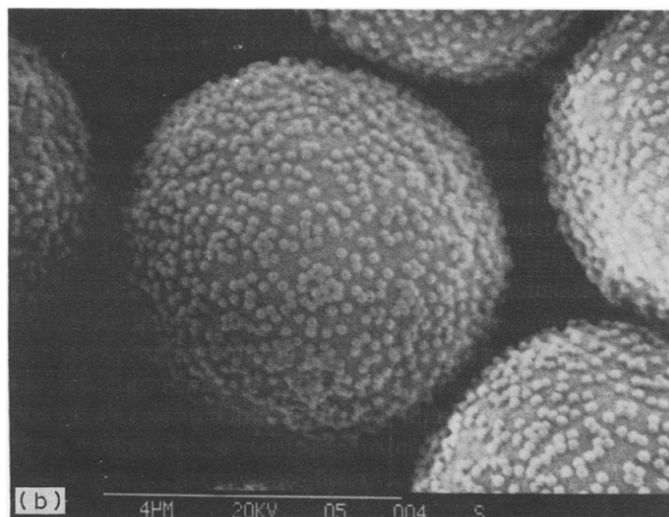
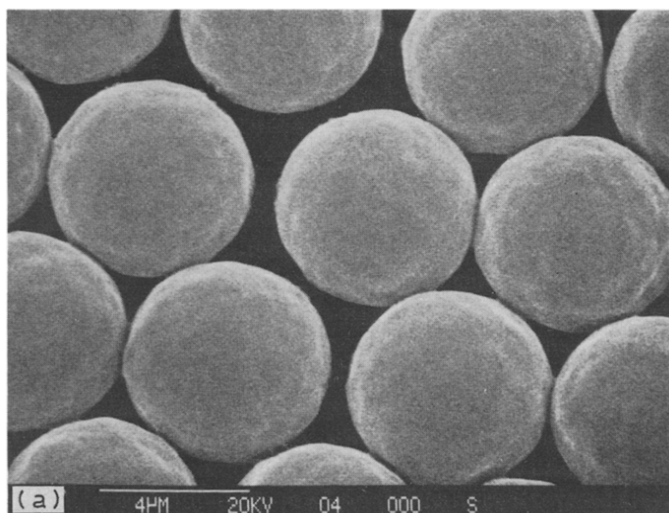


Fig. 1.

(Continued on p. 246)

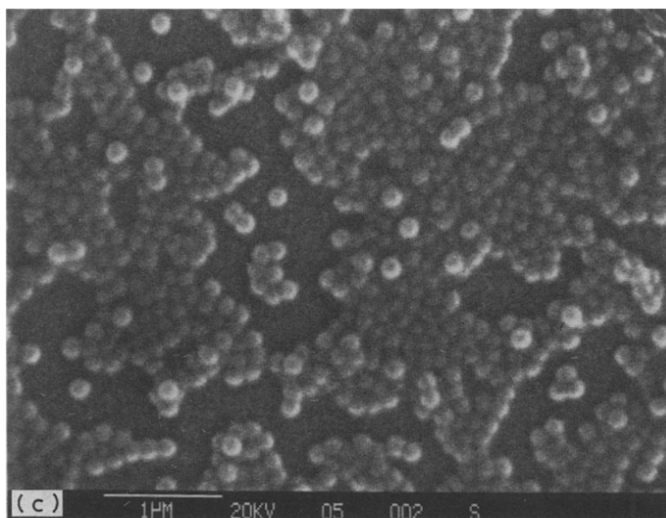


Fig. 1. (a) Scanning electron microscopy (SEM) photograph of 5- $\mu\text{m}$  substrate resin before latex agglomeration; magnification is 4500  $\times$ . (b) SEM photograph of 5- $\mu\text{m}$  substrate resin agglomerated with 0.2  $\mu\text{m}$  anion-exchange latex; magnification is 9000  $\times$ . Note that this material contains larger latex than that under discussion in this paper. (c) SEM photograph of 0.2  $\mu\text{m}$  anion-exchange latex particles; magnification is 15 000  $\times$ .

### *Latex*

The amines used in the quaternization of the latexes and other important characteristics of these latexes are summarized in Table I. The tertiary amines used to quaternize the vinylbenzylchloride-based resin, MDEA, DMEA, TMA and TEA, represent a range of hydrophilicity. Triethylamine is also larger than TMA. This difference provides a variation in charge density.

The percentage of crosslinking and the size before and after functionalization are shown in Table I. As can be seen from these data, functionalization increases the diameter of the 4% crosslinked latexes by about 60%. The volume of a latex in the column, the pellicular layer, in these columns is about 57  $\mu\text{l}$ . This calculation is based on the assumption of hexagonal, closed packing of substrate particles and complete coverage of the 5- $\mu\text{m}$  substrate with 60-nm latex particles. A calculation of about 28 000 latex particles per 5- $\mu\text{m}$  substrate resin particle is obtained. The SEM photographs indicate that coverage of 5- $\mu\text{m}$  substrate by the larger latex used for Fig. 1a–c is not 100% although coverage is reproducible.

Eluents and analytes were selected to give information on the nature of the retention mechanisms operating in the latexes. These topics are discussed in the following sections.

### *Analyte selection*

A standard mixture of analytes was needed which would provide information on basic features of the retention mechanisms. The standard mixture contained  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_3^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{SO}_4^{2-}$ .  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  were used to evaluate monovalent–divalent selectivity and  $\text{Br}^-$ – $\text{NO}_3^-$ – $\text{ClO}_3^-$  were used to study parameters

TABLE III

## RETENTION DATA\* WITH 5 mM SODIUM CARBONATE AS ELUENT

Chromatographic conditions as described in Table II; column designations as in Table I.

Column	Analyte						
	$F^-$	$Cl^-$	$Br^-$	$NO_3^-$	$ClO_3^-$	$SO_4^{2-}$	$PO_4^{3-}$
1	0.09	0.54	2.2	2.6	2.6	5.2	3.3
2	0.18	1.0	3.7	4.4	4.2	5.3	6.4
3	0.16	1.2	4.5	5.4	5.3	3.3	7.6
4	0.13	1.9	9.6	16.8	9.6	3.7	5.6

\*  $k'$  Corrected for column capacity, normalized to column 2.

that effect monovalent selectivity for analytes with different polarizabilities, degrees of hydration and other features which will be described later. Tables III–VI list  $k'$  (normalized for column capacities) for these analytes on each of the packings for various eluent systems.

TABLE IV

## RETENTION DATA\* WITH 100 mM SODIUM HYDROXIDE AS ELUENT

Chromatographic conditions as described in Table II, except for eluent; column designations as in Table I.

Column	Analyte						
	$F^-$	$Cl^-$	$Br^-$	$NO_3^-$	$ClO_3^-$	$SO_4^{2-}$	$PO_4^{3-}$
1	0.06	0.24	0.92	1.1	1.0	0.20	0.31
2	0.14	1.1	4.5	5.0	4.9	3.0	6.7
3	0.30	4.4	19.2	22.5	21.2	51.4	>100
4	0.30	5.8	26.1	55.8	35.7	24.9	>100

\*  $k'$  Corrected for column capacity, normalized to column 2.

TABLE V

RETENTION DATA\* WITH 20 mM SODIUM HYDROXIDE–5 mM *p*-CYANOPHENOL AS ELUENT

Chromatographic conditions as described in Table II, except for eluent; column designations as in Table I.

Column	Analyte						
	$F^-$	$Cl^-$	$Br^-$	$NO_3^-$	$ClO_3^-$	$SO_4^{2-}$	$PO_4^{3-}$
1	0.13	0.38	0.86	0.74	0.40	1.3	6.5
2	0.30	0.92	2.4	2.1	2.1	6.5	38.2
3	0.34	1.4	3.4	3.3	3.3	15.0	112
4	0.24	0.77	2.4	2.8	2.6	13.8	>150

\*  $k'$  Corrected for column capacity, normalized to column 2.

TABLE VI

RETENTION DATA\* WITH 100 mM SODIUM HYDROXIDE-5% METHANOL AS ELUENT

Chromatographic conditions as described in Table II, except for eluent; column designation as in Table I.

Column	Analyte						
	$F^-$	$Cl^-$	$Br^-$	$NO_3^-$	$ClO_3^-$	$SO_4^{2-}$	$PO_4^{3-}$
1	0.06	0.23	0.99	1.1	1.2	0.25	0.86
2	0.14	1.2	4.7	5.3	5.2	3.5	7.6
3	0.34	4.6	19.2	23.6	21.4	58.2	n.d.
4	0.34	5.9	33.9	55.7	54.6	27.1	n.d.

\*  $k'$  Corrected for column capacity, normalized to column 2.*Eluent compositions*

Four eluent compositions were used in the evaluations: 100 mM sodium hydroxide, 20 mM sodium hydroxide with 5 mM *p*-cyanophenol, 100 mM sodium hydroxide with 5% methanol, and 5 mM sodium carbonate. The  $k'$  data from Table IV can be used to show the enhanced  $OH^-$  selectivity of the alkanolammonium latexes relative to the alkylammonium latexes. The  $k'$  values with 100 mM sodium hydroxide as eluent increase in the order of MDEA < DMEA < TMA < TEA, with exceptions, because the alkanolammonium sites are more  $OH^-$  selective than the alkylammonium sites. As the fixed sites become more selective for the eluting ion,  $k'$  values decrease. This topic is discussed at greater length below.

The *p*-cyanophenolate ion is a strong eluting ion. This is evident from the lower  $k'$  values for all analytes in Table V relative to Table IV. The *p*-cyanophenolate ion also competes effectively with  $NO_3^-$  and  $ClO_3^-$  for sites in the latexes that have high selectivity for these oxyanions. The  $k'$  values for  $NO_3^-$  and  $ClO_3^-$  are lowered by a greater percentage than those of the other analytes.

The addition of methanol to the 100 mM sodium hydroxide eluent was used to study the possible role of a nonaqueous protic solvent in anion-exchange selectivity.

## DISCUSSION

When selectivity is viewed in terms of the thermodynamic properties of hydration, comparisons are necessarily made between the resin (fixed site) phase and the eluent (solution) phase. For our purposes here, a highly hydrated ion is viewed as having a large negative free energy of hydration from the gaseous state. Reichenberg noted that the use of free energies versus enthalpies has been a matter of discussion.

The free energy that is driving retention can be viewed as the difference in free energies between the resin phase and the solution phase. Entropy-driven processes often occur in the solution phase; that is, processes associated with a disturbance of the structure of water. An example of an enthalpy-driven process is that of the stabilization of charge through interactions with the resin phase.

A highly hydrated ion will prefer to remain in the aqueous solution phase (low  $k'$ ) where molecules of water of hydration are readily available, if some other interaction with the resin phase which has a larger negative free energy associated with it, is not



available. Discussion of selectivity in view of thermodynamics must be within the context of the relationship between the thermodynamic properties of the various analytes in both phases. Hypotheses for retention behavior are included throughout the following text.

Discussion of these data may be divided into several parts. These include the types of quaternary ammonium sites and their features, the types of analytes and their classification, and types of eluents.

#### *Anion-exchange sites*

The anion-exchange functionalities in the four latexes studied are, in the order of decreasing hydrophilicity, MDEA > DMEA > TMA > TEA. With increasing hydroxyl content, the sites become more hydrated as a result of increased hydrogen-bonding. The more hydrated latexes show increased  $\text{OH}^-$  selectivity in several ways. For example, in Table III the retention of  $\text{SO}_4^{2-}$  is stronger on MDEA and DMEA than on TMA and TEA. This could be explained by considering that the  $\text{OH}^-$ -selective phases concentrate  $\text{OH}^-$  from the  $\text{CO}_3^{2-}$  eluent; monovalent  $\text{OH}^-$  is a less effective eluent than divalent  $\text{CO}_3^{2-}$ , especially for divalent analytes. For the  $\text{OH}^-$ -based eluent systems (Table III–VI), the  $k'$  data of all analytes are lower on the alkanolammonium latexes than on the alkylammonium latexes.

Another difference between the latexes is that of size. For example, between TMA and TEA functionalities the TEA sites are larger than the TMA sites, assuming the radius values available for the analogous free molecules serve as valid reference. Because the TEA sites are larger than the TMA sites, the charge density of the former latex is lower, thereby reducing the selectivity for multivalent species, such as  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$ . This is evident from the  $k'$  data, shown in Table III–VI. The  $k'$  values for  $\text{SO}_4^{2-}$  are lower on TEA than on TMA, except with  $\text{CO}_3^{2-}$  as eluent. A highly hydrated eluting ion, such as  $\text{CO}_3^{2-}$  would be expected to be less effective on less hydrated ion exchangers, such as TEA, if other factors, such as  $\text{OH}^-$  selectivity and charge density do not mask the effect.

#### *Analytes*

The multivalent ions,  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$ , most clearly show the effect of  $\text{OH}^-$  selectivity of the anion-exchange sites. As seen in the  $k'$  data (Table III–VI),  $\text{SO}_4^{2-}$  is eluted much earlier from the alkanolammonium latexes than are the monovalent analytes. The enormity of the selectivity change between the MDEA latex and the other three latexes (Table IV) with  $\text{OH}^-$  as eluent indicates the value of the MDEA phase for systems with  $\text{OH}^-$  as eluent.

The pH dependence of the  $\text{PO}_4^{3-}$  ion is also evident. The  $\text{PO}_4^{3-}$  ion has its third  $\text{p}K$  at 12.67 so that at high eluent pH this ion becomes trivalent. The  $k'$  values for this trivalent ion are shown only as a  $>$  value for the TMA and TEA latexes (Table IV–VI) due to the extremely long retention times. The  $\text{SO}_4^{2-}$ – $\text{PO}_4^{3-}$  elution order for the MDEA latexes with  $\text{CO}_3^{2-}$  (Table III) as eluent suggests that this latex concentrates  $\text{OH}^-$  from the eluent resulting in a higher pH in the latex than in the eluent.

The elution order of  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  and  $\text{ClO}_4^-$  can be explained by differences in enthalpy of hydration from the gaseous state of these ions<sup>3</sup>, although most authors make little or no reference to chromatographic eluents. Table VII shows thermodynamic properties for the anions under discussion. It is worthy to note that if

TABLE VII

THERMODYNAMIC PROPERTIES OF SELECTED MONOVALENT ANIONS<sup>2,11,12</sup>

<i>Ion</i>	$\Delta H^{0*}$ (kcal/mole)	$-\Delta H^{***}$ (kcal/mole)	$-\Delta S^{i***}$ (e.u.)	$-\Delta G^{i§}$ (kcal/mole)
H <sup>+</sup>	0	265	—	—
F <sup>-</sup>	- 78.7	116	30.7	107
Cl <sup>-</sup>	- 40.0	84	17.1	79
Br <sup>-</sup>	- 28.9	76	13.42	72
I <sup>-</sup>	- 13.4	67	8.05	64
NO <sub>3</sub> <sup>-</sup>	- 49.4	74	16.9	69
ClO <sub>3</sub> <sup>-</sup>	- 23.7	69	—	—
ClO <sub>4</sub> <sup>-</sup>	- 31.4	54	13.4	50
CO <sub>3</sub> <sup>2-</sup>	-161.6	127	65.3	108
OH <sup>-</sup>	- 54.9	122	37.6	111

\* Heat of formation of the aquo ion<sup>11,15</sup>.\*\* Enthalpy of hydration of the gaseous ion; generally accepted value for H<sup>+</sup> is 260.7, although ref. 12 uses values as shown. Values at infinite dilution and 25°C<sup>12</sup>; values from ref. 14 vary slightly.\*\*\* Entropy of hydration of the gaseous ion at infinite dilution and 25°C<sup>12</sup>.§ Free energy of hydration of the gaseous ion at infinite dilution and 25°C<sup>12</sup>.

enthalpies of formation of the aquo ion are compared<sup>11</sup>, the elution order cannot be predicted for ClO<sub>4</sub><sup>-</sup> although the halide elution order remains the same. This suggests that the crystal lattice energies included in the enthalpies from the gaseous state are very important in the thermodynamics of ion-exchange for ClO<sub>4</sub><sup>-</sup>.

In our study, which includes aspects of the chromatographic process, *i.e.* relative selectivity between analyte and eluting ion, the F<sup>-</sup> < Cl<sup>-</sup> < Br<sup>-</sup> elution order is maintained on all four of these latexes for all eluent compositions studied. I<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> are not included in our data because of their extremely long retention times but they are in fact eluted in that order after Br<sup>-</sup> as expected from the hydration enthalpies.

The discussion of the relative retention behaviour of ClO<sub>3</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> deals with attempts to explain variations in relative *k'* values for the four different latexes. The enthalpies of formation of the aquated ions (Table VII) from the gas state suggest that the order of hydration is ClO<sub>3</sub><sup>-</sup> < NO<sub>3</sub><sup>-</sup> ~ Br<sup>-</sup>. Following the hypothesis used for halide elution, these hydration enthalpies would suggest an elution order of Br<sup>-</sup> ~ NO<sub>3</sub><sup>-</sup> < ClO<sub>3</sub><sup>-</sup> with eluent ions that also compete on the basis of hydration enthalpy. (Although we were interested in the relationships between free energies and entropies for these ions, we were unable to find these values from the gaseous state for ClO<sub>3</sub><sup>-</sup> in the literature. However, the values for Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup> are listed in Table VII.) Although it is apparent that the elution order of the halides with CO<sub>3</sub><sup>2-</sup> and OH<sup>-</sup> as eluting ions can be explained by enthalpies of hydration from the gaseous state, it seems that in the case of NO<sub>3</sub><sup>-</sup>-ClO<sub>3</sub><sup>-</sup> with eluent systems of 5 mM sodium carbonate, 100 mM sodium hydroxide and 100 mM sodium hydroxide containing 5% methanol, this notion fails completely. In addition, when *p*-cyanophenate is added to the eluent (Table V), the elution order is reversed for Br<sup>-</sup> and ClO<sub>3</sub><sup>-</sup> between the MDEA and TEA latexes; ClO<sub>3</sub><sup>-</sup> is affected more than Br<sup>-</sup>. The conclusion here is that the retention mechanisms for NO<sub>3</sub><sup>-</sup> and ClO<sub>3</sub><sup>-</sup> are different from those of the halides. Some insight may be

obtained from examining the geometries of these ions and ion-pairing as a major retention mechanism.

Retention data based on the different eluents used in this study suggest that  $\text{ClO}_3^-$  and  $\text{NO}_3^-$  are retained by somewhat different mechanisms. Conventional ion-pair chromatography may give a clue as to these differences. Ion-pair chromatography may be viewed as a dynamic ion-exchange<sup>16</sup> technique which is dependent on the formation of ion-pairs at the low dielectric resin-water interface. This technique then is capable of distinguishing among the retention mechanisms of various ions by identifying those which form more stable ion pairs.

In conventional ion-pair chromatography with quaternary ammonium ion-pairing reagents,  $\text{ClO}_3^-$  is eluted after  $\text{NO}_3^-$ . This suggests that  $\text{ClO}_3^-$  forms more stable ion pairs than  $\text{NO}_3^-$ . Considering that the stereochemical structure of  $\text{ClO}_3^-$  is pyramidal<sup>13</sup> while that of  $\text{NO}_3^-$  is planar and that a less hydrated ion should be able to form an ion pair more efficiently, this ion-pairing hypothesis seems plausible.

Diamond and Whitney<sup>2</sup> have described water-structure-enforced ion pairing, which becomes stronger as ions become larger and less able to become involved in electrostatic, Bjerrum-type ion pairing. According to Diamond and Whitney<sup>2</sup>, the less-hydrated ions disturb the normal structure of water more than more-hydrated ions. The associated thermodynamic terms serve to drive these ions to the resin phase where water is less structured. This type of mechanism would be consistent with the retention behavior of  $\text{ClO}_3^-$  relative to  $\text{Br}^-$  on our latexes shown in Table III-V. However, the large  $k'$  values for  $\text{NO}_3^-$  require further explanation.

On the latexes used in this study, the  $k'$  values for  $\text{NO}_3^-$  increase dramatically as the quaternary ammonium group becomes more hydrophobic and larger (Table III-V). Selectivity in terms of hydration energies would dictate that ions with the highest hydration energies should prefer to remain in the aqueous external phase or eluent rather than give up part of their water of hydration to enter the dehydrated water-structureless environment of the anion exchanger. Nitrate, therefore, is behaving like a softer, less polarizable, less hydrated ion than any of its thermodynamic properties (Table VII) would suggest.

A hypothesis for the retention of  $\text{NO}_3^-$  may be made based on molecular geometry. Looking at the planar structure of  $\text{NO}_3^-$  ion it is evident that three resonance hybrids, viewed in terms of valence bond theory, create an extended  $\pi$ -cloud (with 2  $\pi$ -electrons) similar to that created in the aromatic ring of the benzyl chloride monomer. Overlap of the  $\pi$ -clouds of  $\text{NO}_3^-$  with those of the benzyl monomer coincident with close association with the ion-exchange site should cause significant stabilization energies. If this stabilization drives the retention of  $\text{NO}_3^-$ , then it must have a larger negative free energy associated with it than the energy of hydration, which is fairly large for  $\text{NO}_3^-$  (Table VII).

The remaining question, that of why retention of  $\text{NO}_3^-$  is greater on the TEA latex, may perhaps be answered as follows. As there is less water in the vicinity, there is more room for the  $\text{NO}_3^-$  to maneuver into an overlapping position near enough to the ion-exchange site for ion-exchange, and also to the aromatic  $\pi$ -cloud. It also seems that a more dehydrated environment would help to stabilize the  $\pi$ -overlap. Associated, polarized water serves to delocalize some of the charge throughout the water network. In this scheme, the more hydrophobic the ion-exchange site, *i.e.* TEA > TMA > DMEA > MDEA, the greater the probability that orbital overlap would occur. The

$\pi$ -overlap concept also explains the especially strong eluting power of the *p*-cyanophenolate ion for  $\text{NO}_3^-$  (Table V). This point is discussed below. This unusual retention mechanism may explain the unusually low overload capacities of  $\text{NO}_3^-$  relative to other anions on most columns; that is, statistically fewer sites are available which can fulfill both requirements for  $\text{NO}_3^-$  retention.

### Eluents

As Table VII shows,  $\text{CO}_3^{2-}$  and  $\text{OH}^-$  are hydrated similarly in the free energy term from the gaseous ion. Both of these ions are more hydrated than the analyte anions. It seems then that the increased retention of anions on increasingly hydrophobic latexes can be explained not only in terms of increased affinity of the ion-exchange sites for less hydrated anions but also in terms of the diminished eluting power of highly hydrated eluent ions. Carbonate remains a very effective eluting ion, because it is divalent, although as the charge density of the latexes increases (*e.g.*, TEA > TMA), the divalent-ion eluting power is somewhat diminished.

Increased selectivity of the alkanolammonium latexes for  $\text{OH}^-$  may be considered in terms of the extraordinary interaction of  $\text{OH}^-$  with water. This interaction is evidenced by the high electrical conductivity in water relative to other anions. The powerful elution of anions with  $\text{OH}^-$  eluents from these latexes is evident when comparing the  $k'$  data in Table IIIb for the various latexes. Lower  $k'$  values indicate higher selectivity for the eluting ion compared to the analyte ion.

The *p*-cyanophenolate ion, with its aromatic structure can interact with the  $\pi$ -orbitals to a greater extent than  $\text{NO}_3^-$ . The *p*-cyanophenolate ion reduces the retention of  $\text{NO}_3^-$  and  $\text{ClO}_3^-$  to a much greater extent than that of the other analytes (Table V). The enhanced elution of  $\text{ClO}_3^-$  may suggest a stereochemical retention mechanism for  $\text{ClO}_3^-$  similar to but weaker than that for  $\text{NO}_3^-$ , in addition to ion pairing.

The addition of methanol to the 100 mM sodium hydroxide eluent has the effect of increasing the retention of all ions except  $\text{Cl}^-$  and  $\text{NO}_3^-$  in this study (Table VI). If we use hydration theories to help provide a model, it seems that the hydration of the latexes is decreasing relative to the eluent phase. This should have a large effect on retention mechanisms based on ion pairing. This also has the effect of making highly hydrated eluting ions, such as  $\text{OH}^-$ , less effective eluents for reasons already discussed. From these points it seems that the retention of all ions should have been increased. The fact that the retentions of  $\text{Cl}^-$  and  $\text{NO}_3^-$  were not increased suggests a retention mechanism not yet identified. This is a subject for further study.

### CONCLUSION

Ion-exchange packings can be made by agglomeration of anion-exchange latexes and cation-exchange resin. This paper discusses selectivity that can be varied by changing the quaternary ammonium group on the latex, although other parameters not under discussion here, such as crosslinking, also affect selectivity.

Monovalent anions, as analytes or as eluents, can be categorized on the basis of their thermodynamic properties, their geometries and their abilities to interact with the anion-exchanger phase in specific ways, *i.e.* polarizability,  $\pi$ - $\pi$  interactions etc. By probing the anion-exchange of various types of analytes on several different quaternary ammonium latexes with different eluent systems for suppressed ion

chromatography, we have attempted to identify selectivity differences among the various types of anion-exchange sites. Of special note is the high selectivity of the alkanolammonium latices for  $\text{OH}^-$ . There are many areas for continued research, including the role of different types of solvents on ion-exchange and the selection of better probes for the elucidation of retention mechanisms for a wider variety of oxyanions.

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