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Characterization of ion chromatography columns based on hydrophobicity and hydroxide eluent strength

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ABSTRACT

Only a few systematic studies have been performed on the factors affecting retention and selectivity in modern ion chromatography. In this study retention and selectivity of Dionex AS10, AS11-HC, AS15, AS16, AS18, AS19, AS20 and AS24 anion exchange columns with hydroxide eluent were studied using the Virtual Column Separation Simulator database. The hydrophobicity and hydroxide eluent strength on each of the columns were quantified. The hydrophobicity measured based on retention of the homologous series of alkyl sulfonates ($H_{RSO_3^-}$) do not correlate with the hydrophobicities quoted by the manufacturer (H_{Dionex}). Rather the H_{Dionex} reflect the strength of hydroxide as an eluent on these columns. The relative eluent strength of hydroxide ($K_{OH^-,A}$) on commercial Dionex IC columns were calculated *vs.* four reference ions. The K_{OH^-,Cl^-} range from 0.32 (AS10) to 7.3 (AS16), with a ranked order of AS10 ≪ AS15 ≪ AS19 < AS24 < AS18 < AS11-HC ≈ AS20 < AS16. Column selectivity for the inorganic anions is reflected by the behaviour of the halides but does not correlate with either the hydrophobic retention of the alkyl sulfonates ($H_{RSO_3^-}$) or hydroxide eluent strength ($K_{OH^-,A}$) of the columns. Column selectivity for organic monovalent anions correlates with the $H_{RSO_3^-}$ on the IC columns.

1. Introduction

Ion chromatography (IC) has become one of the most popular methods for determining inorganic anions and cations, and small organic ions in aqueous samples [1,2]. A key to successful IC is the control of selectivity [1]. IC selectivity reflects the exchange ability of analytes ions with eluent ions in the stationary phase [3,4]. In general in HPLC selectivity is determined by both the stationary phase chemistry and the mobile phase chemistry. However in IC, the choice of mobile phase is limited because suppressed conductivity detection restricts the eluent ions to those that can be easily suppressed, *i.e.*, the conjugate base of a weak acid. Moreover, carbonate/bicarbonate and hydroxide have become even more prevalent as mobile phases, due to the convenience of online eluent generation [5]. In contrast, there are numerous stationary phase chemistries available for IC. Chromatographers can be easily overwhelmed by the number of columns available when it comes to method development, and the key differences between the columns and their selectivity are not readily apparent.

There are a number of companies that produce IC columns, including Dionex, Metrohm AG and Alltech Associates Inc. Organic polymer-based columns dominate in IC because of their rigidity and stability in extreme pH conditions. In recent years, there have been a number of articles on the improvement of IC columns. They describe the general trends in IC columns [6,7], the principles determining selectivity [3,8], or the novel stationary phases usually designed for specific applications [9,10].

To date, few systematic studies have been performed on the effect of the stationary phase hydrophobicity on IC separations [6,11,12]. Slingsby et al. compared retention of common anions (F^-, Cl^-, Br^-, NO_3^-, ClO_3^-, I^-, SO_4^{2-} and PO_4^{3-}) on different stationary phases when using hydroxide eluent [12]. They found that retention was much larger on phases possessing trimethylamine and triethylamine ion exchange sites *vs.* alkanolamine sites. This was attributed to the alkanolamine making the ion exchange site more hydrophilic, which in turn made the highly hydrated hydroxide a more effective eluent. Soon after this work, Dionex started quoting "hydrophobicities" for their hydroxide selective columns, which we will refer to as H_{Dionex}. However it is not clear how these values were determined.

Similarly, Bruzzoniti et al. studied retention of diprotic acids on matched agglomerated columns possessing quaternary amine exchange sites with 0, 1 and 2 alkanolamines [13]. Increasing the number of alkanolamine sites on the exchange site resulted in higher affinity for OH^- ions in the eluent. Further, increasing the number of alkanolamines yielded greater relative retention of hydrophilic diacids such as mucic acid (HOOC–$(CHOH)_4$–COOH) *vs.* hydrophobic diacids such as adipic acid (HOOC–$(CH_2)_4$–COOH).

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This work clear demonstrated the importance of the hydrophobicity of the IC column on selectivity.

Pirogov et al. studied the effect of ionene structure ($-[R_2N^+-(CH_2)_n-NR_2^+-(CH_2)_m]-$) on anion retention and selectivity [14]. Ionenes with short aliphatic segments ($n<5$ and $m<5$) showed low retention of I^-, SCN^- and ClO_4^- relative to Cl^-, and so were described as "hydrophilic". In contrast, ionenes with long aliphatic segments ($n>5$ and $m>5$) showed considerable stronger relative retention of I^-, SCN^- and ClO_4^- and were classified as having a higher hydrophobicity.

Thus, the hydrophobicity of the ion exchange site and column influences the retention and selectivity of IC columns. However to date hydrophilic and hydrophobic have only been used to describe IC columns in a qualitative manner. In this work, the retention and selectivity of commercial columns (Table 1) are systematically studied to provide more quantitative measures of the factors affecting retention and selectivity. This study focuses on Dionex Corp. columns due to the availability of a large database of retention data within the Virtual Column Separation Simulator 2. Virtual Column 2 is a computer software developed by Madden et al. [15] and marketed by Dionex. The software contains over 2500 retention data points for 78 anions and 11 anion exchange columns [16]. It predicts retention time of many common anions and cations on a variety of Dionex IC columns to within 1% for most of the analytes [17].

2. Background

In ion chromatography, the distribution constant of a sample ion and the eluent ion represents a competition between these two ions for exchange sites on the solid ion exchangers [18]. The exchange of two monovalent ions, A^- and E^-, competing for reaction with the resin is represented by Eq. (1):

$$A_m^- + E_r^- \rightleftharpoons A_r^- + E_m^- \quad (1)$$

$$K_{A,E} = \frac{[A^-]_r}{[A^-]_m}\frac{[E^-]_m}{[E^-]_r} \quad (2)$$

where the brackets indicate the ion concentration in mmol/ml for the mobile phase (m) and in mmol/g for the resin phase (r). The equilibrium constant in Eq. (2) is called the selectivity coefficient $K_{A,E}$. A large value for $K_{A,E}$ means that the resin has a higher affinity for the A (analyte) ion than for the E (eluent) ion.

Assuming trace conditions (analyte occupies <1% of the column capacity) the retention factor of a monovalent analyte A is

$$k_A = \frac{K_{A,E}}{[E^-]_m}\frac{Q_{col}}{V_m} \quad (3)$$

where $[E^-]_m$ is the eluent concentration in mmol/ml, Q_{col} is the capacity of the column in mequiv., and V_m is the dead volume of the column in ml. The logarithmic form of this equation is the Linear Solvent Strength Model governing retention for a monovalent ion with a monovalent eluent [19–21]:

$$\log k_A = \log K_{A,E} + \log(Q_{col}) + \log\left(\frac{1}{V_M}\right) - \log\left[E_m^{y-}\right] \quad (4)$$

Thus many factors affect retention in IC.

Two expressions derived from Eqs. (3) and (4) will be used to characterize the retention and selectivity of IC columns. Firstly, the reciprocal of Eq. (2) (*i.e.*, $K_{E,A}$) is a measure of the eluent strength of E^-. Rearrangement of Eq. (3) yields:

$$K_{E,A} = \frac{Q_{col}}{V_m[E^-]_m}\frac{1}{k_A} \quad (5)$$

In the studies that follow, $K_{OH^-,A}$ will be determined for the common anions Cl^-, NO_2^-, NO_3^- and Br^- to characterize the eluent strength of hydroxide on ion exchange columns of differing hydrophobicity.

Secondly, the Linear Solvent Strength Model (Eq. (4)) can be simplified using the relative retention α (selectivity) of a monovalent ion *vs.* a reference ion such as Cl^-:

$$\log\alpha = \log\frac{k_A}{k_{Cl}} = \log K_{A,E} - \log K_{Cl,E} \quad (6)$$

That is, use of relative retention factors out terms related to the capacity and size of the column and the nature of the eluent. This allows one to focus solely on selectivity, as was done by Bruzzoniti et al. in their study IC of diacids [13]. Relative retention of monovalent anions on commercial IC columns will be compared herein to provide insight into the selectivity of these columns.

3. Experimental

3.1. Apparatus

The full commercial version of Virtual Column Separation Simulator 2 (Dionex, Sunnyvale, CA, USA) was used to obtain retention data on Dionex AS10, AS11-HC, AS15, AS16, AS18, AS19 and AS20. Details of the Virtual Column simulator are available in reference [15], and a demonstration version for education purposes [17] is freely available at http://www.virtualcolumn.com. Additional data on the IonPac AS24 was graciously provided by John Madden of Dionex Corp.

In brief, the simulator fits an embedded database of retention data for a specific column and eluent to the Linear Solvent Strength Model-Empirical Approach (LSSM-EA) defined by

$$\log k_A = C_1 - C_2\log[E_m^{y-}] \quad (7)$$

where C_1 and C_2 are constants experimentally determined for a specific ion on a specific column with a specific eluent. The data used herein was for hydroxide (either NaOH or KOH) as eluent. The flow rate was set at 1.0 mL/min. The column temperature was set at 30 °C except for the AS10 and AS24, for which the retention data was only available at 25 °C and 15 °C.

Additional IC separations of alkyl sulfonates were performed using an ICS-2000 chromatography system (Dionex) consisting of an ICS-2000 pump, an ICS-2000 column heater, an EGC II eluent generator (NaOH), an Anion Atlas Electrolytic Suppressor (AAES) in recycle mode and an DS6 heated conductivity detector. Data acquisition and control were performed using Chromeleon version 6.8 SP3 software (Dionex).

3.2. Materials

Table 1 lists the structural and technical characteristics of the columns studied. Their hydrophobicities (H_{Dionex}), as reported by the manufacturer varied from ultra low to medium high. There are three different backbone structures, MicroBead, grafted and hyperbranched [22].

Table 2 lists the analytes studied including 43 monovalent and divalent anions. Chemicals were of reagent grade or better and purchased from Sigma–Aldrich (Oakville, ON, Canada). The sodium salts of methanesulfonate, ethanesulfonate, propanesulfonate, 1-butanesulfonate, 1-pentanesulfonate and hexanesulfonate were used. All solutions were prepared in deionised 18 MΩ water (Nanopure Water System, Barnstead, Chicago, IL, USA) that had been filtered through 0.22 μm Magna nylon membrane filter papers (GE Osmonic, Trevose, PA, USA) under vacuum. All solutions were filtered again through 0.22 μm filters under vacuum after they were prepared.

Table 1
Summary of columns studied.

Columns	Capacity, mequiv.	Dionex "Hydrophobicity"	Backbone	Hydroxide eluent strength			
				$K_{OH^-,Cl}$	K_{OH^-,NO_2}	$K_{OH^-,Br}$	K_{OH^-,NO_3}
AS10	0.170	Low	MicroBead	0.32	0.23	0.08	0.06
AS11-HC	0.290	Med-low	MicroBead	6.4	4.7	2.2	2.1
AS15	0.225	Med-high	Grafted	1.1	0.77	0.33	0.27
AS16	0.170	Ultra low	MicroBead	7.3	6.1	3.6	3.6
AS18	0.285	Low	MicroBead	5.8	3.8	2.1	1.6
AS19	0.240	Low	Hyper-branched	3.5	2.5	1.8	1.5
AS20	0.310	Ultra low	Hyper-branched	6.8	4.7	3.4	2.8
AS24	0.140	Ultra low	Hyper-branched	4.6	2.7	1.7	1.3

4. Results and discussion

The retention properties of ion chromatography columns are a function of their ion exchange capacity (Eq. (4)) and the hydrophobicity of the ion exchange site [12,13] and resin backbone [2,8]. Hydrophobicities (H_{Dionex}) are quoted for many commercial columns (Table 1), but it is unclear how these values are determined. The selectivity of IC columns is investigated below to quantify the hydrophobicity of commercial IC columns.

Table 2
Analytes studied.

All anions (43)	Monovalent organic anions (23)	Monovalent inorganic anions (15)	Divalent anions (5)
Acetate		√	
Acrylate	√		
Azide		√	
Benzoate	√		
Bromate		√	
Bromide		√	
Bromoacetate	√		
Butanesulfonate	√		
Carbonate			√
Chlorate		√	
Chloride		√	
Chlorite		√	
Chloroacetate	√		
Chromate			√
Dichloroacetate	√		
Difluoroacetate	√		
Ethanesulfonate	√		
Fluoride		√	
Fluoroacetate			
Formate	√	√	
Glycolate	√		
Hexanesulfonate	√		
Iodate		√	
Iodide		√	
Lactate	√		
Methacrylate	√		
Methanesulfonate	√		
n-Butyrate	√		
Nitrate		√	
Nitrite		√	
N-valerate	√		
Octanesulfonate	√		
Pentanesulfonate	√		
Perchlorate		√	
Propanesulfonate	√		
Propionate	√		
Pyruvate	√		
Quinate	√		
Selenate			√
Sorbate	√		
Sulfate			√
Sulfite			√
Thiocyanate		√	

4.1. Hydrophobicity based on homologous series of alkyl sulfonates ($H_{RSO_3^-}$)

Retention in RPLC can be fundamentally investigated using a homologous series of molecules possessing the same functional group and increasing alkyl chains [23]. Plots of log k *vs.* carbon number should be linear, with the slope reflecting the incremental increase in the free energy of transfer for each additional methylene (*i.e.*, the hydrophobicity $H_{RSO_3^-}$). Discontinuities in such plots are often observed for shorter homologs (<3–5 carbons) [23]. Alkyl sulfonates are studied herein rather than carboxylates, as retention data for longer homologs is available. Fig. 1 shows the log k of alkyl sulfonates plotted *vs.* the number of carbon in the homolog. Consistent with reversed phase studies [23], methanesulfonate and ethanesulfonate show anomalous behaviour and so are omitted from further analysis.

Table 3 lists the slope and correlation coefficient for log k for propanesulfonate, butanesulfonate, pentanesulfonate and hexanesulfonate *vs.* carbon number. AS15 has the greatest slope, consistent with it having the greatest labelled hydrophobicity (H_{Dionex} = med-high) of the columns in Table 3. AS11-HC has the next highest slope, and is referred to as "med-low hydrophobicity" (H_{Dionex}). However, the AS18 shows a similar slope to the AS11-HC despite being designated a "low hydrophobicity" (H_{Dionex}) column. Similar discrepancies exist between the slope and the labelled H_{Dionex} of the remainder of the columns. Thus the experimental hydrophobicity ($H_{RSO_3^-}$) determined based on

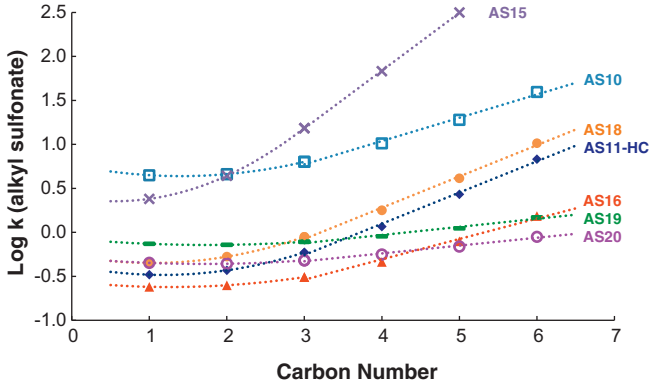

Fig. 1. Log k (alkyl sulfonate) on AS10, AS11-HC, AS15, AS18, AS19 and AS20 columns *vs.* carbon numbers of analytes. Carbon # 1–6 represents methanesulfonate, ethanesulfonate, propanesulfonate, 1-butanesulfonate, 1-pentanesulfonate and hexanesulfonate. All data of AS11-HC, AS16, AS18, AS19 and AS20 was obtained from Virtual Column using 20 mM hydroxide as eluent. Retention data for AS10 and AS15 were obtained by using ICS-2000 system with a 20 μL injection loop, 0.5–3.0 mM of analyte ion solutions were injected in triplicate. Eluent (60 mM NaOH) was generated online using an EGC II generator. The column hydrophobicitiy was provided by the manufacturer.

Table 3
Linear regression parameters (slopes and R^2 values) of log k (1-propanesulfonate, 1-butanesulfonate, 1-pentanesulfonate and hexanesulfonate) *vs.* Carbon # of the analytes.

Columns	Dionex "Hydrophobicity"	Slopes	R^2
AS10	Low	0.27	0.992
AS11-HC	Med-low	0.36	0.995
AS15	Med-high	0.66	1.000
AS16	Ultra low	0.23	0.988
AS18	Low	0.36	0.996
AS19	Low	0.093	0.978
AS20	Ultra low	0.090	0.988

the homologous series of alkyl sulfonates do not match the manufacturer's values. This discrepancy is consistent with others observations. Retention studies of aromatic anions ranked the hydrophobicity of IC columns as AS20 < AS16 < AS11-HC or AS16 < AS11-HC < AS20 or AS16 < AS20 < AS11-HC depending on the specific analyte studied [24]. Thus, the character of IC columns cannot be characterized based on a classic definition of hydrophobicity.

4.2. Hydroxide eluent strength

Hydroxide is the preferred eluent in IC due to its: superior detection limits and linearity with suppressed conductivity detection; and enhanced ease of use and reliability with on-line eluent generation. However hydroxide is inherently a weak eluent. The effective eluent strength of hydroxide can be increased by increasing the hydrophilic nature of the ion exchange site. For instance for columns of the same ion exchange capacity using the same 100 mM NaOH eluent, the retention factor for chloride decreased from 4.4 to 1.1 to 0.24 (or 18 times decrease) upon changing the ion exchange site from trimethyl amine ($-N(CH_3)_3^+$) to dimethylethanolamine to monomethyl-diethanolamine, and the same trend was observed for other analytes, *e.g.* Br^- (21 times decrease) and NO_3^- (20 times decrease) [12]. Comparable behaviour was observed by Bruzzoniti et al. [13].

The strength of hydroxide on a given ion exchanger can be characterized using the equilibrium constant for the exchange of hydroxide with a reference analyte ion ($K_{OH^-,A}$, Eq. (5)). Table 4 presents the $K_{OH^-,A}$ values for matched agglomerated columns of Slingsby and Pohl [12] which had comparable capacity but differing hydrophilicity of the ion exchange sites. The values of $K_{OH^-,A}$ are small, consistent with OH^- being inherently a weak eluent. For a given column, $K_{OH^-,A}$ becomes smaller as the retention of the reference ion A increases. Most importantly, for a given reference ion, the eluent strength of OH^- () increases as the ion exchange site becomes more hydrophilic. $K_{OH^-,A}$ values calculated from the data of Bruzzoniti et al. [13] show the same trends, but the magnitude of the $K_{OH^-,A}$ are about five-fold greater than those in Table 4. As information regarding the crosslinking of the latex and other factors that affect selectivity are not provided in [13], the cause of this discrepancy is unknown.

Fig. 2 compares $K_{OH^-,A}$ for commercial IC columns. Chloride, nitrite, bromide and nitrate are used as the reference ions, as they are common target analytes for IC and moderately retained (thus their retention data is available for all columns), and their retention behaviour obeys the linear solvent strength model (*i.e.*, slope C_2 in Eq. (7) is ~1.0). Fluoride is too weakly retained on some columns to provide reliable retention factors. Phosphate and sulfate are multiply charged ions. Hence their relative retention depends on both the capacity and selectivity of the column [19], and so is not suitable as reference ions.

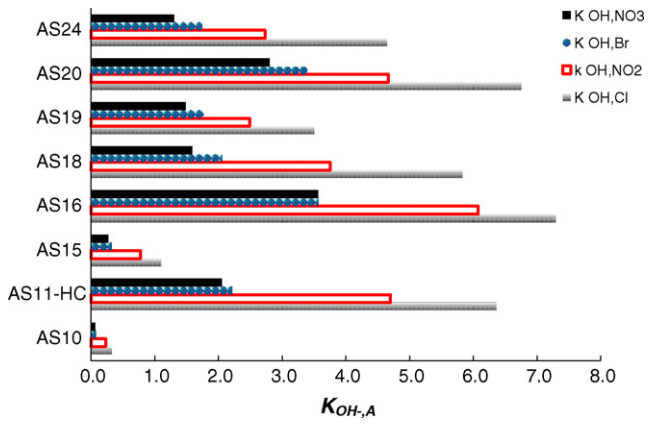

Fig. 2. Hydroxide eluent strength ($K_{OH^-,A}$) on Dionex AS10, AS11-HC, AS15, AS16, AS18, AS19, AS20 and AS24 columns. All data obtained from Virtual Column using 20 mM hydroxide as eluent at 30 °C except for AS10 and AS24. AS10 data was calculated by extrapolating retention data of 60–100 mM at 25 °C from Virtual Column. AS24 data was calculated by extrapolating retention data of 25–55 mM at 15 °C from John Madden (Dionex) by personal communication.

The relative eluent strength of hydroxide ($K_{OH^-,A}$) on commercial Dionex IC columns is

$$Cl^- \quad AS10 \ll AS15 \ll AS19 < AS24 < AS18 < AS11\text{-}HC \approx AS20 < AS16 \tag{8a}$$

$$NO_2^- \quad AS10 \ll AS15 \ll AS19 \approx AS24 < AS18 < AS20 \approx AS11\text{-}HC < AS16 \tag{8b}$$

$$Br^- \quad AS10 \ll AS15 \ll AS24 \approx AS19 < AS18 \approx AS11\text{-}HC < AS20 \approx AS16 \tag{8c}$$

$$NO_3^- \quad AS10 \ll AS15 \ll AS24 \approx AS19 \approx AS18 < AS11\text{-}HC < AS20 < AS16 \tag{8d}$$

In general the relative eluent strength of hydroxide on a given column is independent of the reference ion used. Similar (within 6%) $K_{OH^-,A}$ and trends were observed when 40 mM hydroxide eluent was used. This is as would be expected (Section 2).

The hydroxide eluent strength observed in Fig. 1 are broadly consistent with the hydrophobicities quoted by the manufacturer (Table 1). Newer "ultra low hydrophobicity" (H_{Dionex}) columns (AS16, AS20 and AS24) show greater hydroxide eluent strength than "low hydrophobicity" (H_{Dionex}) columns such as the AS18 and AS19; which in turn show greater hydroxide eluent strength than the "medium high hydrophobicity" (H_{Dionex}) AS15 column. However the AS10 is a distinct outlier showing the weakest hydroxide strength of all of the columns studied despite being labelled a "low hydrophobicity" (H_{Dionex}) column. However Weiss has stated that "*the ion exchange functional groups of the AS10 are very hydrophobic*." [2,8], which is consistent with Fig. 1. The $K_{OH^-,A}$ values on the AS10 (Table 1) are comparable to those of the monoethanolamine column studied in [12] (Table 4). Hence hydroxide eluent strength ($K_{OH^-,A}$) provides a quantitative measure of the "hydrophilicity" of the ion exchange site.

Table 4
Effect of the nature of the quaternary amine ion exchange site on the eluent strength of hydroxide ($K_{OH^-,A}$, Eq. (5)).[a]

Columns	Hydroxide eluent strength ($K_{OH^-,A}$)				
	F^-	Cl^-	Br^-	NO_3^-	ClO_3^-
$-N(CH_2CH_3)_3^+$	0.7	0.04	0.008	0.004	0.006
$-N(CH_3)_3^+$	0.7	0.05	0.012	0.010	0.010
$-N(CH_3)_2(CH_2CHOH)^+$	1.6	0.20	0.049	0.044	0.045
$-N(CH_3)(CH_2CHOH)_2^+$	3.7	0.93	0.24	0. 20	0.22

[a] Data from Table IV of Ref. [12]. Q_{col} = 0.0151 mequiv./col; [OH^-] = 0.100 mmol/ml; V_m estimated as 0.68 ml based on dead volume of a similar column agglomerated column reported in [13], correcting for the column length of 150 mm.

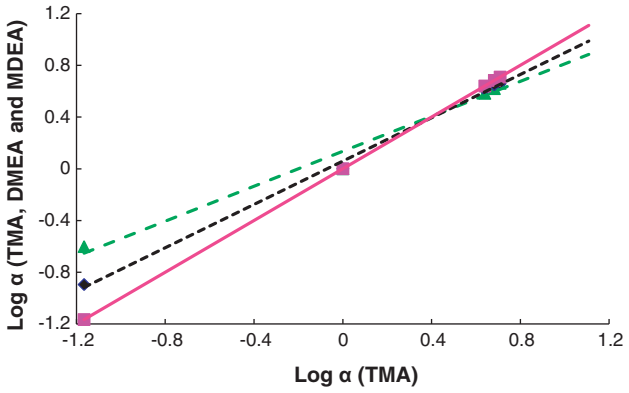

Fig. 3. Logα (anions/Cl^-) of columns with trimethylamine (TMA ■), dimethylethanolamine (DMEA ◆), monomethyl-diethanolamine (MDEA ▲) exchange sites *vs.* that observed for the trimethylamine column for the monovalent ions (F^-, Cl^-, Br^-, NO_3^- and ClO_3^-). (Based on data from Ref. [12]).

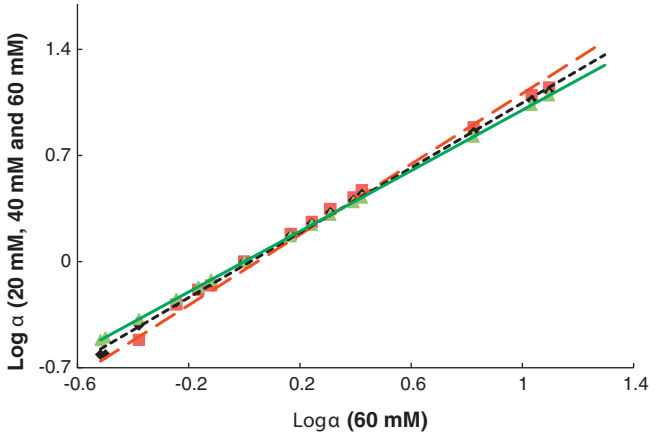

Fig. 4. Logα (anions/Cl^-) when using hydroxide eluent of 20 mM (▲), 40 mM (◆) and 60 mM (■) *vs.* the values when using hydroxide eluent of 20 mM. All data obtained from Virtual Column using AS20 column for separation. 15 monovalent inorganic analyte anions including IO_3^-, F^-, acetate, formate, ClO_2^-, BrO_3^-, Cl^-, NO_2^-, ClO_3^-, Br^-, NO_3^-, N_3^-, I^-, SCN^- and ClO_4^-.

4.3. Selectivity

A secondary effect of increasing the hydrophilicity of the ion exchange site is to alter the relative retention of analyte ions. Increased hydrophilicity of the ion exchange site would increase the relative retention of highly hydrated anions such as F^- and decrease the relative retention of less hydrated ions. This is illustrated in Fig. 3 which compares the relative retention (k_A/k_{Cl}) of monovalent ions on columns with trimethylamine ($-N(CH_3)_3^+$), dimethylethanolamine, monomethyl-diethanolamine exchange sites *vs.* that observed for the trimethylamine column [12]. In Fig. 3, the squares are the comparison of the trimethylamine column *vs.* itself, and so naturally has a slope of 1.00 and a R^2 of 1.000. Increasing the hydrophilicity of the ion exchange site to dimethylethanolamine (diamonds) results in a decrease in the slope to 0.84 ± 0.06 ($R^2 = 0.998$), *i.e.*, increasing the hydrophilicity of the ion exchange site enables the highly hydrated F^- to be more retained and ClO_3^- less retained relative to Cl^-. Increasing the hydrophilicity further by using monomethyl-diethanolamine exchange sites (triangles) reduces the slope to 0.68 ± 0.06 ($R^2 = 0.980$). Similar trends are observed for the data from Bruzzoniti et al. [13]. In both cases, increasing the hydrophilicity of the ion exchange sites has the desirable effects of increasing retention of F^- (thereby moving it away from the water dip) and decreasing the retention of polarizable monovalent ions such as ClO_3^-.

The following sections validate and explore the use of relative retention plots such as Fig. 3 to quantify the selectivity of current IC columns. This approach is analogous to the Hydrophobic Subtraction Model used to characterize reversed phase columns [25–28].

4.3.1. Effect of eluent concentration on relative retention

The linear solvent strength model [19–21] predicts that eluent concentration does not affect the relative retention of monovalent anions (Eq. (6)). To test this prediction Virtual Column 2 was used to explore the effect of hydroxide concentration on relative retention on a Dionex AS20 column. Fig. 4 shows the effect of eluent concentrations on column selectivity for monovalent inorganic anions. Eluent concentration would affect relative retention of multivalent *vs.* monovalent ions [21], and so are excluded from Fig. 4. As discussed above the relative retention (α) of each analyte ion is the ratio of retention factor of the analyte (k_A) to that of a standard ion (Cl^- in our study). In Fig. 4 the relative retention for 20 mM hydroxide is used as the *x*-axis. For all eluent strengths the selectivity plot shows good linearity ($R^2 > 0.99$) for the AS20 column shown in Fig. 4, and for all other columns studied. As discussed in Section 2, using relative retention should eliminate the influence of variations in column volume and capacity and the eluent concentration [11]. In Fig. 4, increasing the eluent concentration from 20 to 40 to 60 mM hydroxide results in slopes of 1.00, 1.07 ± 0.01 and 1.16 ± 0.03. This is comparable to the shift in dynamic selectivity coefficient observed on a Dionex AS15 column using 10–40 mM KOH eluent [29]. Thus while there is some residual effect of eluent concentration on the relative retention, the effect of eluent is minimal compared to those caused by changing columns (below). Therefore, for the rest of the study, only 20 mM hydroxide was used as mobile phase for comparison purposes and no further study of the effect of mobile phase was performed.

4.3.2. Comparison of the AS19 and AS11-HC with the AS20 column

The Dionex AS19 and AS20 [22] are both high capacity columns with "low hydrophobicity" (H_{Dionex}) for the analysis of trace amounts of oxyhalides. Both columns consist of a hyper-branched anion exchange condensate polymer electrostatically attached to 7.5 μm beads with 55% cross-linking [26]. The capacity of the

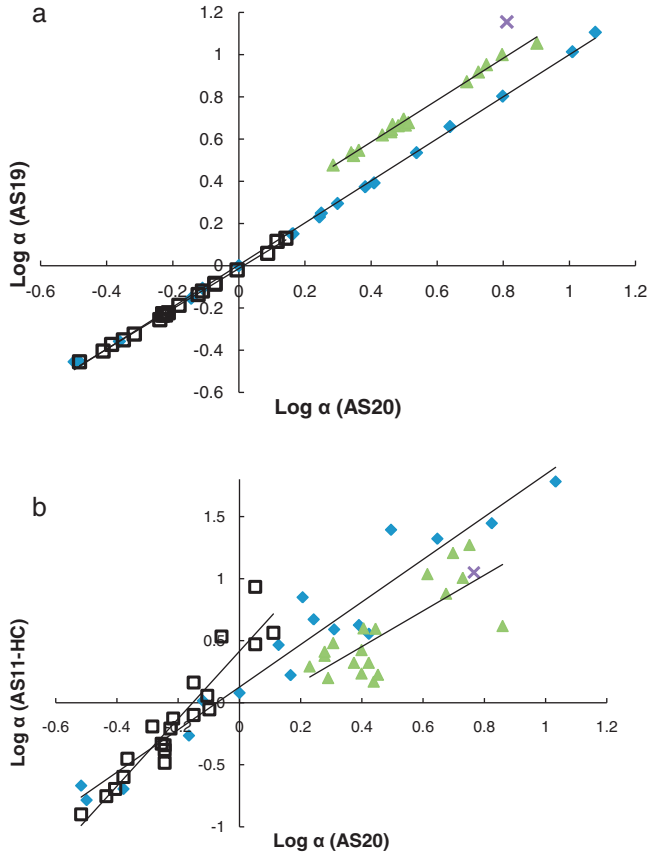

Fig. 5. (a) Log $\alpha_{A,Cl}$ on AS19 column *vs.* values on AS20 column. All data obtained from Virtual Column using 20 mM hydroxide as eluent at 30 °C. Analytes are: 18 monovalent inorganic anions (◆) including F^-, IO_3^-, acetate, ClO_2^-, BrO_3^-, Cl^-, NO_2^-, trifluoroacetate, dibromoacetate, ClO_3^-, Br^-, NO_3^-, N_3^-, I^-, trichloroacetate, tetrafluoroborate, SCN^- and ClO_4^-; 21 monovalent organic anions (□) including quinate, lactate, glycolate, propionate, n-butyrate, n-valerate, ethanesulfonate, methanesulfonate, formate, methacrylate, acrylate, pyruvate, propanesulfonate, chloroacetate, butanesulfonate, bromoacetate, difluoroacetate, pentanesulfonate, sorbate, hexanesulfonate and dichloroacetate; 17 divalent anions (▲) including carbonate, monofluorophosphate, selenite, sulfate, malonate, malate, maleate, selenate, tartrate, glutarate, oxalate, succinate, phthalate, tungstate, thiosulfate, chromate and fumarate; and 1 polyvalent ion (✖), phosphate. (b) Log $\alpha_{A,Cl}$ on AS11-HC columns *vs.* values on AS20 column. All data obtained from Virtual Column using 20 mM hydroxide as eluent at 23 °C. Analytes are: 17 monovalent inorganic anions (◆) including F^-, IO_3^-, acetate, ClO_2^-, BrO_3^-, Cl^-, trifluoroacetate, NO_2^-, dibromoacetate, ClO_3^-, Br^-, NO_3^-, N_3^-, trichloroacetate, tetrafluoroborate, I^- and SCN^-; 21 monovalent organic anions (□) including quinate, lactate, glycolate, propionate, n-butyrate, n-valerate, ethanesulfonate, acrylate, methanesulfonate, pyruvate, formate, methacrylate, propanesulfonate, chloroacetate, butanesulfonate, bromoacetate, difluoroacetate, pentanesulfonate, sorbate, hexanesulfonate and dichloroacetate; 19 divalent anions (▲) including carbonate, monofluorophosphate, sulfite, selenite, benzoate, sulfate, malonate, malate, maleate, selenate, tartrate, glutarate, oxalate, succinate, phthalate, tungstate, thiosulfate, chromate and fumarate; and 1 polyvalent ion (✖), phosphate.

resin depends on the number of alternating treatments of epoxy monomer and amines used.

Fig. 5(a) is a plot of log $\alpha_{A,Cl}$ for the AS19 *vs.* log $\alpha_{A,Cl}$ for the AS20. The selectivity for both the monovalent organic ions (open squares) and monovalent inorganic ions (diamonds) are highly correlated on these two columns (R^2 = 0.999 and 0.997). This similarity is consistent with recent selectivity comparisons based on the constant C_1 in Eq. (7) [30] (which would be a function of both capacity and selectivity). The selectivity of the divalent ions (triangles) are also highly correlated between the two columns (R^2 = 0.993), but offset from the monovalent ions presumably due to the differences in the column capacities. Nonetheless the three lines are almost parallel: the slope of the monovalent organic, monovalent inorganic,

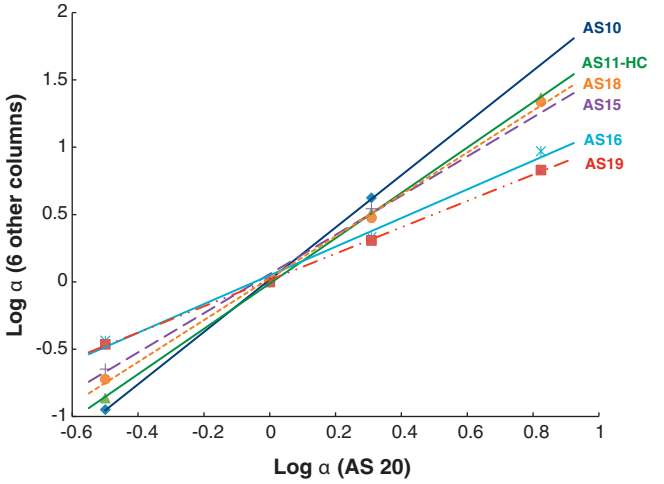

Fig. 6. Relative retention of F^-, Cl^-, Br^- and I^- on AS10, AS11-HC, AS15, AS18, and AS19 columns *vs.* values on AS20 column. All data obtained from Virtual Column using 20 mM hydroxide as eluent.

and the divalent ions are 0.95 ± 0.01, 0.996 ± 0.009, and 1.00 ± 0.02, respectively. The phosphate ion (pK_{a3} = 12.4) was plotted separately because in 20 mM eluent (pH 12.3) it exists as approximately an equimolar mixture HPO_4^{2-} and PO_4^{3-}.

In contrast, Fig. 5(b) compares the relative retention on the AS11-HC *vs.* AS20 column. The AS11-HC is a MicroBead (latex) agglomerated column reported to have a "medium-low hydrophobicity" (H_{Dionex}) (Table 1). The scatter within Fig. 5(b) indicates that the interactions between analytes and the AS11-HC column are very different from those with the AS20. The slope of the selectivity plot is 2.4 ± 0.2 for the monovalent organic (open squares) anions and 1.7 ± 0.1 for the monovalent inorganic (diamonds) anions. This selectivity difference is consistent with principle component analysis based on C_1 in Eq. (7) [30]. Multivalent anions also show different behaviour on the AS11-HC, but are beyond the scope of the current discussion. Thus, Fig. 5 shows that comparing relative retention between columns allows the selectivity characteristics of the columns to be explored.

4.3.3. *Relative retention on commercial IC columns*

Fig. 3 shows that the hydrophilicity of the ion exchange site greatly affects selectivity in IC [12]. An increase in the relative hydrophilicity of the ion exchange site results in a decreased slope in a selectivity plot such as Fig. 3.

Fig. 6 shows the relative retention of halide ions on various commercial columns plotted against their relative retention on the AS20 column (R^2 > 0.99). The AS20 was used as the reference column as Virtual Column 2 contained the greatest number of analytes for this column. The relative slopes of the selectivity plots in Fig. 6:

$$\text{AS10} \gg \text{AS11-HC} \approx \text{AS18} \approx \text{AS15} \gg \text{AS16} > \text{AS20} \approx \text{AS19} \quad (9)$$

Expanding the selectivity plot to include all 15 monovalent inorganic anions (Table 2) results in linear plots ($R^2 \geq 0.90$). The trends for this expanded analyte set are the same as that for the halides. Table 5 summarizes the slopes and correlation coefficients for these plots. For divalent anions, the trend in the slopes of the selectivity plots (Table 5) is

$$\text{AS11-HC} \approx \text{AS10} > \text{AS15} \approx \text{AS18} > \text{AS20} \approx \text{AS16} \approx \text{AS19} \quad (10)$$

This trend is broadly similar to that observed for the monovalent inorganic anions (Eq. (9)), but with some columns switching order.

Neither the monovalent or divalent inorganic anion selectivity trends correlate with the hydroxide eluent strength (Eq. (8)) or the reversed phase behaviour of the columns (Table 3). This indicates

Table 5
Linear regression parameters (slopes and R^2 values) of the selectivity plots ($\log\alpha$ of anions/Cl^- *vs.* values using AS20 as a point of reference) of the columns studied.

Columns	Halides (4)		Monovalent inorganic anions (15)		Divalent inorganic anions (5)		Monovalent organic anions (23)	
	Slopes	R^2	Slopes	R^2	Slopes	R^2	Slopes	R^2
AS10	1.94	1.00	1.9	0.95	1.81	1.00	1.9	0.92
AS11-HC	1.68	1.00	1.6	0.98	1.83	1.00	2.4	0.87
AS15	1.5	0.99	1.5	0.90	1.48	0.99	2.6 ± 1.3	0.33
AS16	1.1	0.99	1.1	0.98	1.03	0.99	2.3	0.97
AS18	1.56	1.00	1.5	0.97	1.46	1.00	2.3	0.83
AS19	0.98	1.00	0.99	1.00	1.03	1.00	0.96	0.99

that factors other than hydrophilicity, however it is defined, influence retention of inorganic anions. However it is interesting that the key factors affecting IC column selectivity for the inorganic anions is reflected by the halide behaviour.

Selectivity plots prepared for 23 monovalent organic anions showed lower correlation than observed for the inorganic anions (Table 5). The general trend is the slope of the selectivity plots for the organic monovalent anions was:

$$(\text{AS15}) \approx \text{AS11-HC} \approx \text{AS18} \approx \text{AS16} > \text{AS10} > \text{AS20} \approx \text{AS19} \quad (11)$$

The AS15 column is indicated in brackets to the large uncertainty in the slope for this column. Overall the selectivity of the IC columns for the organic monovalent anions mirrors the reversed phase behaviour of the columns (Table 3). Thus, unlike the inorganic anions, hydrophobicity of the IC column does influence the column selectivity for organic anions.

5. Conclusions

Previous fundamental studies had indicated the importance of the hydrophilicity of the ion exchange site on IC retention and selectivity. However, the hydrophobicities commonly quoted for IC columns actually reflect the hydroxide eluent strength of the column. Herein both hydroxide eluent strength ($K_{OH,A}$) and hydrophobicity ($H_{RSO_3^-}$) for a number of commercial IC columns are quantified. Column selectivity for inorganic anions does not correlate with either of these parameters, indicating that other factors govern the column selectivity for these ions. Column selectivity for organic monovalent anions correlates with the hydrophobicity of the columns.

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