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Review

Factors controlling ion-exchange selectivity in suppressed ion chromatography

Christopher A. Pohl, John R. Stillian, Peter E. Jackson*

Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94088-3606, USA

Abstract

The control of ion-exchange selectivity is the most important means of moderating separations in suppressed ion chromatography. Selectivity variations are primarily achieved through the use of different stationary phases, hence the construction of the stationary phase plays a key role. The major factors which determine the selectivity of the ion-exchange phase are: the polymer composition of the stationary phase, the type of ion-exchange site and the structure of the ion-exchange site. The eluent can also play a significant role in determining the overall selectivity of an ion-exchange separation. The mobile phase parameters which affect the separation selectivity are: the choice of eluent ion, the concentration (and pH) of the eluent, the presence of non-ionic eluent modifiers and the eluent temperature. © 1997 Elsevier Science B.V.

Keywords: Selectivity; Reviews; Stationary phases, LC; Mobile phase composition; Ion chromatography; Inorganic anions; Inorganic cations

Contents

1. Introduction	30
2. Ion-exchange selectivity	30
2.1. Stationary phase-related factors.....	31
2.1.1. Stationary phase composition	31
2.1.2. Type of ion-exchange site	33
2.1.3. Structure of ion-exchange site	36
2.2. Mobile phase related factors	37
2.2.1. Choice of eluent ion	37
2.2.2. Concentration and pH of the eluent.....	38
2.2.3. Non-ionic eluent modifiers.....	39
2.2.4. Temperature	40
3. Conclusions	41
Acknowledgements	41
References	41

*Corresponding author.

1. Introduction

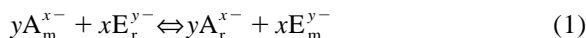
Ion chromatography (IC) is now a well established, regulatory approved technique for the determination of ionic species [1]. While IC was initially seen as a tool for the analysis of inorganic anions and cations, particularly in environmental samples [2–4], the use of different separation and detection methods has greatly expanded the range of solutes and samples to which the technique is now applied. This diversity has led to the point where IC is perhaps now best defined by the solutes to which it is commonly applied, rather than any specific combination of separation and detection modes. Hence, IC can be considered to encompass liquid chromatographic techniques which can be used for the determination of the following solutes: inorganic anions; inorganic cations, including alkali metal, alkaline earth, transition metal and rare earth ions; low-molecular-mass (water-soluble) carboxylic acids and organic phosphonic and sulfonic acids, including detergents; low-molecular-mass organic bases; and ionic organometallic compounds [5–7].

While IC is applicable to a broad range of solutes, the simultaneous analysis of the common inorganic anions (fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate) continues to be the most important routine application of IC, followed by determination of ammonium and the alkali/alkaline earth cations [5–7]. These solutes are generally determined using an ion-exchange separation and suppressed conductivity detection, hence variation of ion-exchange selectivity remains the important means of moderating IC separations. This review will discuss factors controlling ion-exchange selectivity for separations which use suppressed conductivity detection. This detection approach permits the use of higher capacity stationary phases and higher ionic strength eluents, in turn, allowing greater scope for variation in ion-exchange selectivity compared to methods which use non-suppressed conductivity detection.

2. Ion-exchange selectivity

Ion-exchange selectivity ultimately reflects the likelihood of exchange occurring between particular

ions, while the selectivity coefficient describes the equilibrium constant for the ion-exchange process. This process can be illustrated by considering an anion-exchange separation, where y moles of a solute (A^{x-}) is exchanged with x moles (i.e. the stoichiometric amount) of an eluent anion (E^{y-}), as shown in Eq. (1):



where the subscript m denotes the mobile (or solution) phase and r denotes the stationary (or resin) phase. The solution phase also contains a co-cation with the same charge as the functional group on the ion-exchange resin, however this co-cation plays no part in the anion-exchange process and is not generally shown. The selectivity coefficient is the equilibrium constant for the reaction shown in Eq. (1). Under conditions where the activity coefficients approximate unity, it is given by Eq. (2):

$$K_{A,E} = \frac{[A_r^{x-}]^y [E_m^{y-}]^x}{[A_m^{x-}]^y [E_r^{y-}]^x} \quad (2)$$

where the brackets indicate molar concentrations in the respective phases. The selectivity coefficient provides information on the degree of interaction between the charged solutes and the ion-exchange resin. If $K_{A,E} = 1$, then the ion-exchange resin shows no preference for anion A^{x-} over E^{y-} . If K is greater than unity, A^{x-} interacts more strongly with the resin than does E^{y-} and the resin phase will contain a higher concentration of ion A^{x-} than the solution phase. The reverse applies for values of K less than one.

The interaction between charged solutes and the ion-exchange resin depends upon a number of properties of the solute, the resin and the solution phase. These properties include: (a) the charge on the solute ion, (b) the solvated size of the solute ion, (c) the polarizability of the solute ion, (d) the degree of cross-linking of the resin, (e) the ion-exchange capacity of the resin, (f) the functional group on the ion-exchanger, and (g) the nature and concentration of the eluent ion [5]. These properties can be used to predict the relative affinities of an ion-exchanger for different ions, although in reality these affinities show considerable variation with the type of ion-exchanger and the conditions under which it is used.

In this review, the factors which affect the selectivity of ion-exchange separations will be discussed, with a specific focus on separations which use suppressed conductivity detection. These factors can be broadly divided into two categories; factors related to the stationary phase and those related to the mobile phase.

2.1. Stationary phase-related factors

Traditional stationary phase development in HPLC has largely been directed toward improving column efficiency and eliminating any non-ideal behavior, i.e. interaction with residual surface silanol groups [8]. Changes in selectivity are typically achieved through varying the nature of the mobile phase rather than the stationary phase. Alternatively, selectivity variations in suppressed IC have been primarily achieved through the use of different stationary phases. The majority of the stationary phases used in suppressed IC are agglomerated ion-exchange resins [5–7]. These agglomerated, or pellicular, materials consist of a monolayer of charged latex particles which are electrostatically attached to a surface functionalized, internal core particle. This inner particle is totally covered by the fully functionalized latex, consequently the properties of the outer latex determine the ion-exchange selectivity of the composite material. These pellicular ion-exchange resins have higher efficiencies than conventional microporous ion-exchangers as a result of faster kinetics and greater permeability of the pellicular layer [9]. Three major factors determine the ion-exchange selectivity of the stationary phases used in suppressed IC: (1) the composition of the stationary phase resin, (2) the type of ion-exchange site and (3) the structure of the ion-exchange site.

2.1.1. Stationary phase composition

The ion-exchange stationary phases used for suppressed IC are composed from three different types of monomers. A functional (or base) monomer is used to create the ion-exchange site, a cross-linking monomer controls water content, while a non-functional monomer is sometimes used to adjust charge density or control secondary selectivity interactions. The most commonly utilized base materials are polystyrene (PS), which is primarily used to produce

cation-exchange resins; and vinylbenzyl chloride (VBC) or glycidylmethacrylate (GMA), which are used for the production of anion-exchange resins. While polystyrene can also be used to produce anion-exchange resins, direct amination of the polymer is difficult and involves the use chloromethyl methyl ether, which is extremely toxic [10]. Additionally, other non-aromatic monomers can be used besides glycidylmethacrylate, although GMA is a frequently used example of this type of material [11].

The choice of cross-linking agent depends upon the nature of the base monomer. Divinylbenzene (DVB) is used almost exclusively as the cross-linking monomer for aromatic base materials, such as PS or VBC. The degree of cross-linking of the PS–DVB (or VBC–DVB) resins typically used in suppressed IC is in the order of 0.2–5%. As the most useful selectivities tend to be achieved with high water content (low cross-linked) resins, aromatic materials with a higher degree of cross-linking are rarely used. Considerably more flexibility exists for the choice of cross-linking agent when using non-aromatic resins, as a wider variety of materials is available. Ethyleneglycol dimethacrylate is a common example of a cross-linking monomer which is used in the production of methacrylate-based resins. The degree of cross-linking of methacrylate-based resins is typically in the order of 8–40%, as they require a higher degree of cross-linking to achieve the same water content as aromatic resins.

The functionalization of these polymeric materials is carried out by three major reactions, which are shown in Fig. 1. Cation-exchange functionality is most commonly added to PS–DVB resins by reaction with sulfuric acid, as shown in Fig. 1.

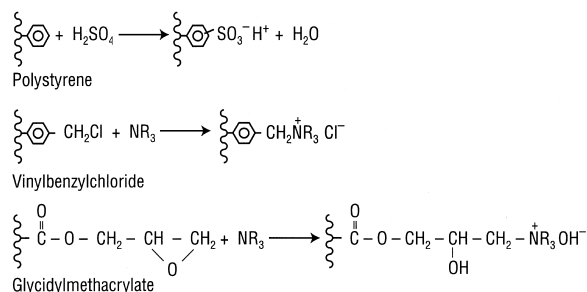


Fig. 1. Most common reactions schemes used for functionalization of the base polymer.

Alternatively, either chlorosulfonic acid or sulfur trioxide can be used in place of sulfuric acid. Monosulfonation of the aromatic ring occurs, with the functional groups being located in the *ortho*, *meta* or *para* positions. The ion-exchange capacity of sulfonated resins can be regulated by controlling the sulfuric acid concentration and also the reaction time and temperature [5]. However, in the case of the pellicular resins used in suppressed IC, the outer latex particles are generally fully functionalized and the ion-exchange capacity of the resin is manipulated by changing the latex particle diameter. It is possible to derive a relationship between the capacity ratio of the two particles and their diameter by using a model which approximates the coating as a shell around a core resin particle. Assuming that the core particle is much larger in diameter than the latex particle (which is always the case), a simple relationship can be developed, as shown in Eq. (3):

$$\frac{C_1}{C_2} = \frac{V_{S1}E_1(1-H_1)}{V_{S2}E_2(1-H_1)} \approx \frac{D_{L1}E_1(1-H_1)}{D_{L2}E_2(1-H_1)} \quad (3)$$

where C is the capacity of the coated particle, V_S is the volume of the latex shell, E is the effective equivalent weight of polymer, H is the water fraction of the particle and D_L is the diameter of the latex particle. This equation predicts that the capacity ratio of two coated particles is directly proportional to the diameter ratio of the latex coating particles, assuming the same core particle diameter. Consequently, if factors such as the effective equivalent weight of polymer and water content of the particle are considered, it is possible to predict the column capacity as a function of the diameter of the latex coated on the resin surface.

The addition of anion-exchange functionality to vinylbenzyl chloride resin involves a substitution reaction with an amine to produce the quaternary aminated resin, as shown in Fig. 1. A similar approach is used for the functionalization of glycidylmethacrylate, to again produce a quaternary aminated resin, as also shown in Fig. 1. However, the glycidylmethacrylate material differs from VBC-based resins in two ways; firstly, the hydroxyl group is *beta* to the nitrogen. Secondly, the hydroxide product of this reaction can catalyze further polymerization of the epoxy groups to produce a sec-

ondary cross-linking mechanism. Both of these factors can result in selectivity differences for some anions. The effects of stationary phase composition on selectivity can be demonstrated by comparing the performance of three different anion-exchange materials; two VBC polymers with 5 and 1% cross-linking, and a glycidylmethacrylate polymer with 8% cross-linking. The same functional group (trimethylamine) was used for all three resins.

Details of the three materials are given in Table 1, which shows that the mole percent cross-linking was the same (5.9%) for both latex 1 and 3, and only 1.2% for latex 2. This material had a lower percent cross-linking, consequently a much higher water content (91%), when compared to latex 1. Methacrylate-based resins characteristically require a higher degree of cross-linking to achieve the same water content as aromatic resins. Consequently, the water content of latex 3 was similar to latex 2, even though the percent cross-linking was much higher. The capacity ratio values shown for latex 2 and 3 are normalized against those of latex 1. It can be seen that the agreement obtained between the experimental and calculated values, as predicted by Eq. (3), was not as good for latex 2 as was the case for latex 3. Typically, better agreement is obtained with higher cross-linked materials when producing colloidal polymers, because the fraction of soluble polymer which competes for the latex uptake is lower. As the percentage of cross-linking decreases, the fraction of soluble polymer increases, resulting in lower

Table 1

Details of the three anion-exchange materials produced to demonstrate the effects of stationary phase composition on selectivity

Parameter	Latex 1	Latex 2	Latex 3
Functional (base) monomer	VBC	VBC	GM
Functional amine	TMA	TMA	TMA
Cross-linking monomer	DVB	DVB	EDM
Mass % cross-link	5.0%	1.0%	8.0%
Mole % cross-link	5.9%	1.2%	5.9%
Raw latex diameter	40 nm	39 nm	57 nm
Aminated latex diameter	71 nm	98 nm	125 nm
Mass % water	75%	91%	87%
Theoretical capacity ratio	1	0.45	0.91
Experimental capacity ratio	1	0.24	0.70

VBC, vinylbenzylchloride; GM, glycidylmethacrylate; TMA, trimethylamine; DVB, divinylbenzene; EDM, ethyleneglycoldimethacrylate.

latex recoveries and less agreement between the actual and predicted capacity ratio values.

The chromatograms of a mixture of seven common anions obtained under identical mobile-phase conditions with these three stationary phase materials are shown in Fig. 2a–c. The selectivity of latex 1 differs from the other two in that bromide and nitrate, peaks 4 and 5 in Fig. 2a, are baseline resolved with this type of material, but the resolution of bromide and nitrate is incomplete on the higher water content resins. Attempts to compensate for capacity differences, i.e. changing the eluent strength, will still not allow complete resolution of bromide and nitrate in very high water content materials which have trimethylamine functional groups. Hence, to a first approximation, the 1% VBC latex is equivalent to the 5% glycidylmethacrylate latex, because they have equivalent water contents. However, if a more sensitive test probe is used, selectivity differences are evident between these two materials. Fig. 3 shows the chromatograms of a mixture of iodide, tetrafluoroborate and thiocyanate obtained on latex 2 (Fig. 3a) and latex 3 (Fig. 3b) under identical mobile phase conditions. In this case, iodide and tetrafluoroborate co-elute on the VBC resin (Fig. 3a), while both solutes have significantly more retention and are baseline resolved using the glycidylmethacrylate polymer (Fig. 3b). Typically, large polarizable anions show considerable selectivity variations upon these high water content polymers.

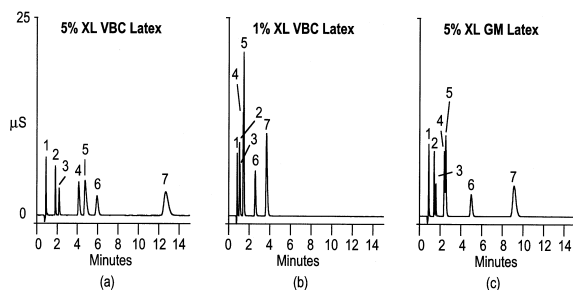


Fig. 2. Effects of stationary phase composition on anion-exchange selectivity. Conditions: stationary phases containing 5% cross-link VBC latex (a), 1% cross-link VBC latex (b) and 5% cross-link GM latex (c) as indicated; eluent, 3 mM sodium carbonate; flow-rate, 2.0 ml/min; detection, suppressed conductivity. Solutes: (1) fluoride, (2) chloride, (3) nitrite, (4) bromide, (5) nitrate, (6) phosphate, (7) sulfate.

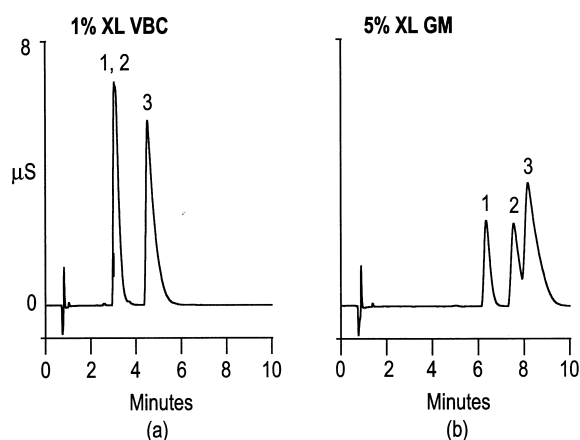


Fig. 3. Effects of stationary phase composition on the separation selectivity of polarizable anions. Conditions: stationary phases containing 1% cross-link VBC latex (a) and 5% cross-link GM latex (b) as indicated. Other conditions as for Fig. 2, except solutes: (1) iodide, (2) tetrafluoroborate, (3) thiocyanate.

2.1.2. Type of ion-exchange site

Ion-exchange materials are classified according to the type of ion-exchange site, or functional group, bound to the resin surface. Cation-exchange resins are broadly divided into strong acid and weak acid types, while anion-exchangers can be divided into strong base and weak base exchangers. The strong acid (e.g. sulfonic acid) and strong base (e.g. quaternary amine) functionalized exchangers retain their capacity over a wide pH range. Alternatively, weak acid (e.g. carboxylic or phosphonic acids) and weak base (e.g. tertiary or secondary amines) functionalized materials only retain their capacity over a limited pH range. Table 2 shows examples of the types of functional groups (and other details) on a number of commercially available ion-exchange columns which are used in suppressed IC [11]. As Table 2 shows, the anion-exchangers typically used in suppressed IC are quaternary aminated resins. Selectivity variations are introduced into these materials by varying the structure, rather than the type, of ion-exchange site. Alternatively, the use of different types of functional groups is often employed to obtain differences in selectivity for cation-exchange materials.

The effects of the type of ion-exchange site on selectivity can be demonstrated by comparing the performance of three cation-exchangers which have

Table 3

Details of the three cation-exchange materials produced to demonstrate the effects of the type of ion-exchange site on selectivity

Parameter	Graft 1	Graft 2	Graft 3
Functional (base) monomer	KSS ^a	VPA ^b	S-MA ^c
Column capacity (μequiv.)	75	350	2500
Approximate pK _a	0.7	2.4 and 7.7	3.8 and 5.6

KSS, potassium styrene sulfonate; VPA, vinylphosphonic acid; S-MA, styrene-maleic anhydride.

in order to achieve sufficient ion-exchange capacity. As can be seen in Table 3, the graft efficiency goes down as the acidity of the functional group increases, due to electrostatic repulsion. Hence, the styrene sulfonate material has the lowest capacity, while the styrene-maleic anhydride, where no charge repulsion occurs as both monomers are neutral, gives a much higher ion-exchange capacity.

The retention data obtained for six common cations on the three grafted materials using methanesulfonic acid eluents of varying ionic strength is shown in Table 4. While only the monovalent cations elute from all three columns with an eluent of 5 mM methanesulfonic acid, some significant selectivity differences are evident. The ammonium peak elutes near sodium with the carboxylated material, while it elutes closer to potassium with the sulfonated material. In the case of the

phosphonated resin, the ammonium peak actually elutes after potassium at this eluent concentration. Under these conditions, the effective capacity for the monovalent cations is approximately equivalent for all three materials, despite large differences in the resins' nominal capacity. This indicates that the functional groups on both weak acid resins are protonated to a significant degree at the low eluent pH; with the carboxylate group being more affected than the phosphonate group, because of its higher pK_a value.

When the eluent strength is increased to 10 mM methanesulfonic acid, the divalent cations elute from the carboxylated resin, although the monovalent cations are no longer completely resolved, while the resolution is poor on the phosphonated resin. With an eluent of 25 mM methanesulfonic acid, the divalent cations are eluted from the phosphonated resin, although the monovalent cations are now totally unresolved. It is only possible to elute the divalents from the sulfonated resin with an eluent of 100 mM methanesulfonate, although the monovalent cations are unresolved at this ionic strength. While the retention of calcium and magnesium on sulfonated cation-exchangers can be reduced by adding a divalent eluting species such as diaminopropionic acid to the mobile phase, the simultaneous separation of alkali and alkaline earth metals is now typically carried out using carboxylate (or mixed carboxylate/phosphonate) functionalized stationary phases [12].

Table 4

Retention data obtained for six common cations on the three grafted cation-exchangers using methanesulfonic acid eluents of varying ionic strength

Eluent	Column	<i>t_R</i> (min)					
		Lithium	Sodium	Ammonium	Potassium	Magnesium	Calcium
5 mM Methanesulfonate	KSS-Graft 1	11.7	13.8	19.8	23.1	DNE	DNE
	VPA-Graft 2	4.4	4.4	5.7	5.2	DNE	DNE
	S-MA-Graft 3	5.0	6.3	7.2	9.8	DNE	DNE
10 mM Methanesulfonate	KSS-Graft 1	5.5	6.4	8.2	9.3	DNE	DNE
	VPA-Graft 2	3.0	3.0	3.6	3.4	DNE	DNE
	S-MA-Graft 3	2.8	3.3	3.5	4.2	6.5	7.6
25 mM Methanesulfonate	KSS-Graft 1	3.1	3.6	4.4	5.0	DNE	DNE
	VPA-Graft 2	2.5	2.5	2.7	2.7	9.7	13.2
	S-MA-Graft 3	2.2	2.5	2.5	2.7	2.7	2.7
100 mM Methanesulfonate	KSS-Graft 1	2.2	2.2	2.4	2.4	13.2	22.8
	VPA-Graft 2	2.2	2.2	2.2	2.2	2.7	2.9
	S-MA-Graft 3	2.0	2.0	2.0	2.0	2.0	2.4

DNE, did not elute.

2.1.3. Structure of ion-exchange site

The final factor which controls the ion-exchange selectivity of the stationary phase is the structure of the ion-exchange site. There are very few options available to vary the structure of cation-exchange sites, hence selectivity variations tend to be introduced into these resins by changing the type of ion-exchange site, as discussed above. However, in the case of quaternary anion-exchangers, there are literally hundreds of possible structures and many studies have been conducted in this area (e.g. [9,13,14]). The size of the ion-exchange site is an important parameter, primarily for large polyvalent ions, due to the steric effects involved in bringing the solute and site into close proximity; however, the shape of the ion-exchange site, the functional groups and the distribution of the functional groups all have an effect.

The influence of the structure of the ion-exchange site on selectivity can be demonstrated by comparing the performance of four anion-exchange materials with very closely related quaternary amines attached to the same polymer substrate. The functional groups used were trimethylamine, dimethylethylamine, dimethylallylamine and dimethylaminopropyne. The structure of the ion-exchange sites are shown in Fig. 5, while the details of the four ion-exchange materials are given in Table 5. The amount of cross-linking was constant for all four materials, hence the water content was essentially the same, within the range of experimental error expected for this measurement. This behaviour is typical, as water content is more a function of cross-linking and is less related to the structure of the site in the case of hydrophobic functional groups. The chromatograms of a mixture of seven common anions obtained under identical mobile phase conditions with these four anion-exchange materials are shown in Fig. 6a–d. Significant selectivity trends are evident with the four materials. A comparison of Fig. 6a and 6b shows that changing one methyl group to an ethyl group causes both bromide and nitrate to be more retained and move further apart, to the point where they now bracket the phosphate peak, which remains essentially unchanged. In the case of the allyl amine, shown in Fig. 6c, bromide and nitrate are further resolved and now both elute later than phosphate, which again is essentially unchanged. Finally, changing the sub-

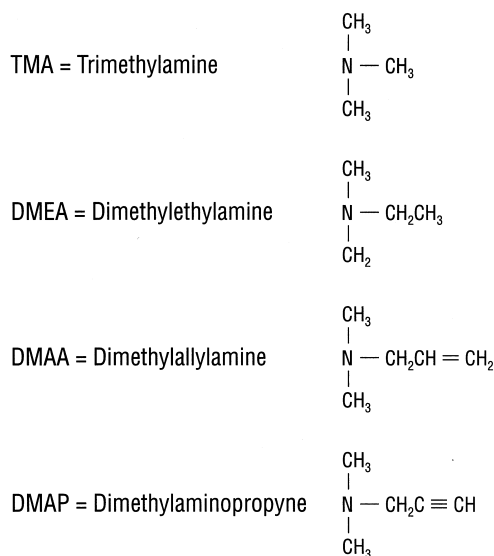


Fig. 5. Anion-exchange functional groups on the materials produced to demonstrate the effects of the structure of the ion-exchange site on selectivity.

stituent to a propyne reverses the trend and bromide and nitrate now elute earlier, as shown in Fig. 6d. This indicates that the hydrogens on the alkyl substituent play a significant role in the interaction between the ion-exchange site and polarizable anions, such as bromide and nitrate.

In general, the retention of hydrophilic, polyvalent anions (e.g. sulfate) decreases as the size of the functional group increases (regardless of the hydrophobicity of the amine), simply because of a decrease in the coulombic interaction between the solute and the larger, hence lower charge density, functional group. Hydrophilic monovalent anions (e.g. chloride) are less affected by the size of the functional group and retention increases slightly as the size of the functional group increases. The separation of more polarizable anions, such as bromide, nitrate or iodide, is highly dependent upon the hydration of the ion-exchange site. Typically, retention increases as the ion-exchange site becomes more hydrophobic and decreases as it becomes more hydrophilic; however, if the eluting species is more polarizable than the solute anions (e.g. *p*-cyanophenol), the opposite effect is observed.

Table 5

Details of the four anion-exchange materials produced to demonstrate the effects of the structure of the ion-exchange site on selectivity

Parameter	Latex 1	Latex 2	Latex 3	Latex 4
Functional (base) monomer	VBC ^a	VBC ^a	VBC ^a	VBC ^a
Functional amine	TMA ^b	DMEA ^c	DMAA ^d	DMAP ^e
Cross-linking monomer	DVB ^f	DVB ^f	DVB ^f	DVB ^f
Mass % cross-link	5	5	5	5
Raw latex diameter (nm)	40	40	40	40
Aminated latex diameter (nm)	71	73	77	75
Mass % water	75	76	79	77

VBC, vinylbenzylchloride; TMA, trimethylamine; DMEA, dimethylethylamine; DMAA, dimethylallylamine; DMAP, dimethylaminopyrene; DVB, divinylbenzene.

2.2. Mobile phase related factors

Ion chromatography differs from traditional reversed-phase liquid chromatography in that generally only limited variations in selectivity are obtained by changing the mobile phase. Selectivity variations in suppressed IC are more commonly introduced through the use of different stationary phases. This situation exists for two main reasons; firstly, the elution order in ion-exchange chromatography is largely dictated by the interaction between the charged solute and the ion-exchange resin. Secondly, only a restricted number of eluents are compatible with suppressed conductivity detection; therefore, the most common approach is to use an eluent which has

appropriate ‘suppression characteristics’ with a number of different column types. While this strategy generally permits the widest range of selectivity changes possible in suppressed IC, variation of the mobile phase can play an important role in controlling ion-exchange selectivity. There are four major, mobile phase-related factors which affect separation selectivity in suppressed IC: (1) the choice of eluent ion, (2) the concentration (and pH) of the eluent, (3) the use of non-ionic eluent modifiers and (4) temperature.

2.2.1. Choice of eluent ion

The ion-exchange selectivity coefficient determines the extent to which a solute is able to displace an eluent ion from the stationary phase, as shown in Eq. (2). Clearly, retention and selectivity will vary as the extent of the interaction between the eluent ion and the stationary phase changes. The main factors which effect this interaction, and ultimately the separation selectivity, include the hydration enthalpy and hydration entropy, polarizability, valency, size and structure of the eluent (and solute) ions. The choice of the eluent ion in suppressed IC is obviously restricted to those species which are ‘suppressed’ after being passed through an appropriate suppressor. For the determination of anionic solutes, the eluent anion must be readily protonated to give a weakly conducting acid, this anion must be able to elute the solutes from the stationary phase within a reasonable timeframe while the eluent co-cation must be able to displace H⁺ from the suppressor [5]. The situation is essentially the opposite for the determination of cationic solutes; the eluent cation must be

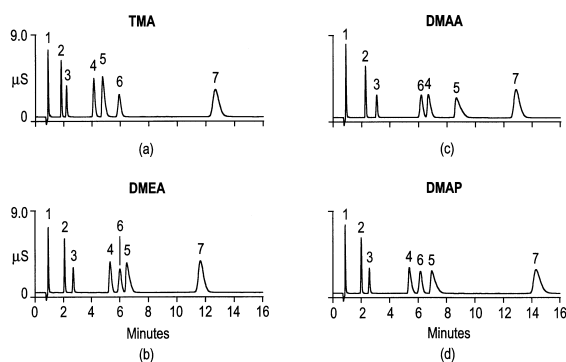


Fig. 6. Effects of the structure of the ion-exchange site on anion-exchange selectivity. Conditions: stationary phases containing VBC latex functionalized with TMA (a), DMEA (b), DMAA (c) and DMAP (d) as indicated; other conditions as for Fig. 2.

readily hydroxylated to give a weakly conducting base, this cation must also be able to elute the solutes from the stationary phase within a reasonable time-frame while the eluent co-anion must be able to displace OH^- from the suppressor.

The eluent anions which satisfy these requirements for anion separations include hydroxide, borate, bicarbonate, carbonate, phenates and some zwitterions, while sodium is an appropriate eluent cation [7]. Mixtures of carbonate and bicarbonate are most widely used in suppressed IC, as the resulting mobile phase is buffered, the elution strength can be varied easily by altering the ratio between the two anions and both species are readily protonated to form weakly conducting carbonic acid [5]. The most widely used eluents for cationic solutes are strong acids, such as nitric, sulfuric or methanesulfonic acids, as the hydronium ion is an effective eluting cation, water is the weak base formed by neutralization with hydroxide in the suppressor and nitrate, sulfate and methanesulfonate all readily displace hydroxide from the suppressor. Changing the eluent ion is mostly used as a means to vary selectivity for anion separations, whereas the hydronium ion is used almost exclusively as the eluting cation for separations which use suppressed conductivity detection.

Fig. 7 shows the effect of adding *p*-cyanophenol

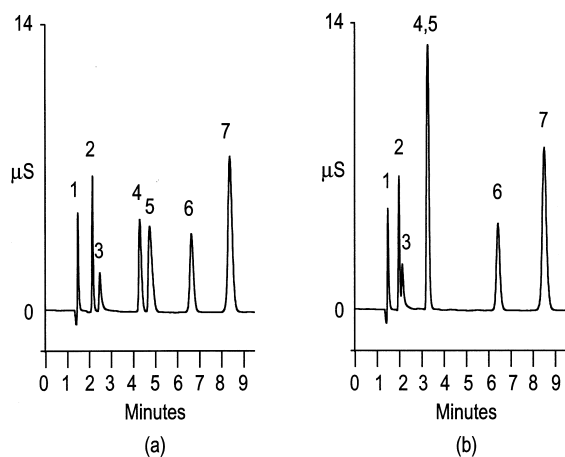


Fig. 7. Effect of the addition of *p*-cyanophenol on anion-exchange selectivity. Conditions: column, Dionex PAX-100; eluents, 3 mM sodium carbonate–4 mM sodium bicarbonate containing no *p*-cyanophenol (a) and 1.0 mM *p*-cyanophenol (b); other conditions as for Fig. 2.

to a carbonate/bicarbonate mobile phase when using a Dionex PAX-100 column for the separation of seven common anions. The addition of *p*-cyanophenol (a weak eluting, hydrophobic ion) has little effect on the retention of the hydrophilic anions, fluoride, chloride, phosphate and sulfate. Alternatively, the presence of *p*-cyanophenol has a significant effect on the retention of nitrite, bromide and nitrate. The addition of a hydrophobic eluting ion to the mobile phase results in more effective displacement of these anions, with the nitrate ion being most affected by the addition of *p*-cyanophenol. Nitrate displays increased retention on VBC–DVB-based resins and this behaviour has been attributed to specific interaction between the π -electron clouds of nitrate and the aromatic rings of the polymer backbone [9]. The aromatic *p*-cyanophenol can interact with the π -orbitals to a greater extent than nitrate, consequently the retention of nitrate is decreased by a larger extent than observed for either nitrite or bromide.

2.2.2. Concentration and pH of the eluent

The concentration of the eluent ion exerts a major effect on retention by influencing the ion-exchange equilibrium, shown in Eq. (1). The higher the eluent ion concentration, the more effectively the eluent displaces the solute ions from the stationary phase and the shorter the elution time. Most importantly, from a selectivity viewpoint, the rate at which retention can be varied by changing the eluent concentration depends on the charges carried by both the solute and the eluent ions. In ion-exchange chromatography, a plot of the log of analyte capacity factor (k') versus log eluent concentration [E], results in a straight line with a negative slope equal to the ratio of the valency of the analyte ion and the eluent ion [15]. Fig. 8 demonstrates the effect of varying the concentration of a monovalent eluent ion on the retention of monovalent (–1) and divalent (–2) solutes. An increase in the concentration of the monovalent eluent ion decreases the retention of the divalent analyte twice as rapidly as that of the monovalent analyte, which can lead to changes in peak elution order.

The mobile phase pH influences retention and selectivity by affecting the form of the ion-exchange functional group; and also the forms of both the

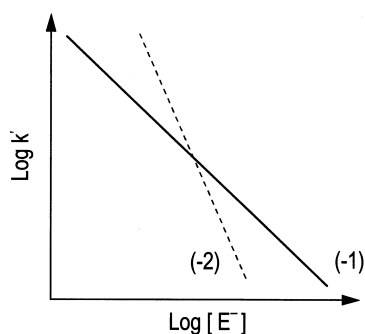


Fig. 8. Plot of log analyte capacity factor (K'_A) versus log eluent concentration [E]. The eluting species is a monovalent ion and the solutes are monovalent (-1) and divalent (-2) ions.

eluent and solute ions. These effects are most important in the separation of anions, particularly in non-suppressed IC, where they play a large part in governing solute retention. If the eluent ion is a weak acid (or its salt), changing the mobile phase pH will affect the dissociation of the acid, hence its net charge and ability to elute anionic solutes. The same effects are observed for the separation of cations using weak base eluents. In a similar manner, solute which are weak acids or bases will show pH effects, since their charge will also be governed by the eluent pH. Increased solute charge results in increased retention because the electroselectivity effect of the solute ion is enhanced with higher charge. Examples of important solutes which display these pH effects include the carboxylate anions, fluoride, phosphate, silicate, cyanide, borate and most amines. Hence, control of eluent pH is an important consideration when these ions are present in mixtures with other solutes which show no pH effects, i.e. strong acid anions and strong base cations.

Fig. 9 shows the effect of varying the composition of a carbonate/bicarbonate mobile phase on the separation of common anions. As the eluent ionic strength increases, the overall retention decreases, as shown in Fig. 9a–c. However, the rate of decrease is more rapid for the divalent anions, consequently the nitrate/phosphate and nitrate/sulfate selectivity changes significantly as the eluent ionic strength increases. This strategy of varying the eluent concentration to alter the separation selectivity between mono- and divalent anions is commonly employed in IC, particularly when using hydroxide mobile phases

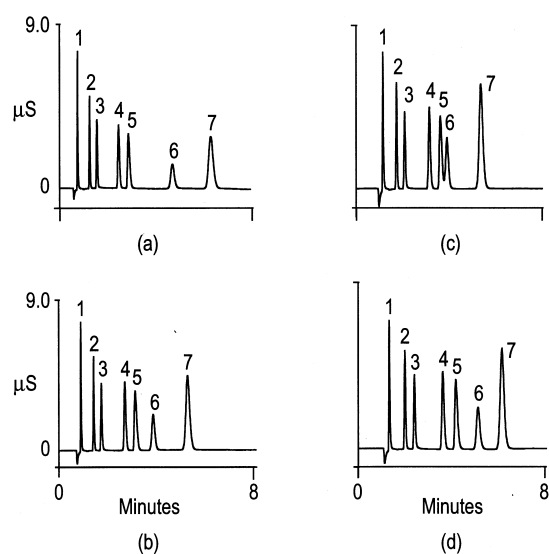


Fig. 9. Effect of carbonate–bicarbonate eluent composition on anion-exchange selectivity. Conditions: column, Dionex AS4A-SC; eluents, (a) 1.8 mM sodium carbonate–1.7 mM sodium bicarbonate, (b) 2.7 mM sodium carbonate–2.6 mM sodium bicarbonate, (c) 3.6 mM sodium carbonate–3.4 mM sodium bicarbonate, and (d) 4.0 mM sodium carbonate–1.5 mM sodium bicarbonate; other conditions as for Fig. 2.

[16,17]. Fig. 9d again shows the same effect for nitrate and sulfate; as the ionic strength increases, the selectivity of this peak pair changes due to the increased rate of change for sulfate. However, changing the carbonate/bicarbonate ratio results in increasing the eluent (and stationary phase) pH, causing the charge (hence retention) of the phosphate peak to increase. This results in a selectivity change for the nitrate/phosphate peak pair, as shown by comparison of Fig. 9c and 9d. When using even higher pH mobile phases, such as hydroxide, phosphate and sulfate, will actually reverse elution order as the degree of charge on the phosphate anion increases [16].

2.2.3. Non-ionic eluent modifiers

Non-ionic eluent modifiers, such as methanol, butanol, glycerol or acetonitrile, can be added to the mobile phase as a means of varying selectivity in suppressed IC. These modifiers can exert a variety of effects, such as changing the ion-exchange affinity of hydrophobic ions, altering the degree of ionization (pK_a values) of any solutes which are weak acids or

weak bases and influencing the solvation of both the functional groups and solute ions. The major properties of the modifier which can influence selectivity in IC include the type of modifier, the shape of the modifier and its concentration. Care must always be taken when using organic modifiers in IC to ensure that both the column and suppressor device are compatible with the type and concentration of modifier being used. Many columns and suppressor devices are not fully compatible with all solvents, over all concentration ranges.

Fig. 10a–c shows the effect of adding acetonitrile to a carbonate/bicarbonate mobile phase when using a Dionex AS4A-SC (solvent compatible) column for the separation of common anions. As the concentration of acetonitrile increases, the retention of the hydrophobic anions (nitrite, bromide and nitrate) decreases. Nitrate is most affected by the addition of acetonitrile; presumably the presence of the modifier prevents the interaction between the π -electron clouds of nitrate and the aromatic rings of the polymer backbone. Hence, the acetonitrile has a similar effect to the addition of *p*-cyanophenol, as discussed previously in Section 2.1.1. At higher modifier concentrations, sulfate and phosphate reverse elution order, as shown in Fig. 10c. This selectivity change is the net result of the influence of the modifier on the degree of ionization (and solvation) of both the eluent and solute anions. Similar effects have also been observed when using carbonate eluents containing aliphatic alcohols [18] and with phthalate eluents containing acetonitrile in non-suppressed IC [19].

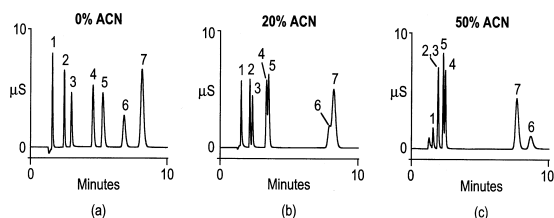


Fig. 10. Effect of the addition of acetonitrile on anion-exchange selectivity. Conditions: column, Dionex AS4A-SC; eluents, 1.8 mM sodium carbonate/1.7 mM sodium bicarbonate containing no acetonitrile (a), 20% acetonitrile (b) and 50% acetonitrile (c); other conditions as for Fig. 2.

2.2.4. Temperature

Temperature has a somewhat less predictable effect on selectivity than the other mobile phase parameters. Temperature can affect retention (hence selectivity) in suppressed IC either by alteration of the stationary phase mass transfer characteristics, or by influencing the degree of ionization of the solute and/or the fixed ion-exchange site. Retention times usually decrease while chromatographic efficiency increases at elevated temperatures, due to improved mass transport. The effects of temperature on ionization typically vary with the type of solute or functional group. Certain solutes (particularly weak acids) or functional groups show changes in their degree of ionization at elevated temperatures, leading to changes in solute retention and selectivity.

Fig. 11 shows the effect of temperature on the retention behaviour of 10 common cations chromatographed on a Dionex CS12A column, which contains both phosphonate and carboxylate functional groups. An 18 mM methanesulfonic acid eluent was used with suppressed conductivity detection for both separations. Chromatographic efficiency increased for all solutes at the higher temperature, while retention times decreased significantly. At higher temperatures, the carboxylic acid groups on the resin

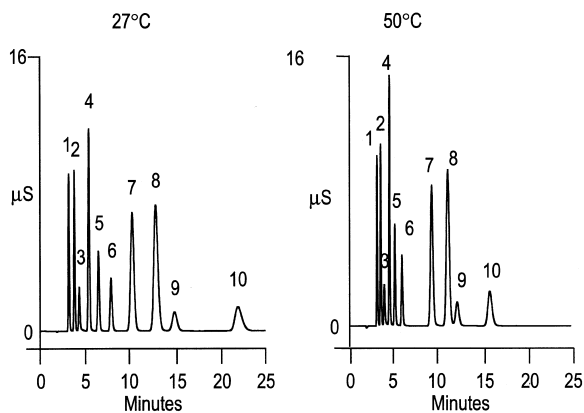


Fig. 11. Effect of temperature on cation-exchange selectivity. Conditions: column, Dionex CS12A; eluent, 18 mM methanesulfonic acid; flow-rate, 1.0 ml/min; detection, suppressed conductivity; temperature, 27 and 50°C as indicated. Solutes: (1) lithium, (2) sodium, (3) ammonium, (4) potassium, (5) rubidium, (6) cesium, (7) magnesium, (8) calcium, (9) strontium, (10) barium.

are less ionized, effectively lowering the column capacity, resulting in shorter retention times. Additionally, the separation selectivity also changes because the retention decrease becomes more pronounced as the ionic radii of the solutes (within a given group) decreases in size. The separation between lithium and cesium decreases, as does the separation between magnesium and barium, hence the 'class' separation between the mono- and divalent cations is more pronounced at higher temperatures. Even more significant selectivity variations are observed with temperature changes on the CS12A column for mixtures of common inorganic cations and amines [20].

3. Conclusions

The ability to control ion-exchange selectivity is the most important means of moderating separations in suppressed ion chromatography. Selectivity variations are primarily introduced through the use of different stationary phases, rather than by varying the mobile phase. The construction of the stationary phase plays a key role and the major factors which determine the selectivity of the ion-exchange phase are: the polymer composition of the stationary phase, the type of ion-exchange site and the structure of the ion-exchange site. Changes to the composition and the structure of the ion-exchange site are mostly used affect the selectivity of anion separations, while variation of the type of ion-exchange site is used to control the selectivity of cation separations. The eluent can also play a significant role in determining the overall selectivity of an ion-exchange separation. The mobile-phase parameters which affect the separation selectivity are: the choice of eluent ion, the concentration (and pH) of the eluent, the use of non-ionic eluent modifiers and the eluent temperature.

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