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Electrochemically modulated liquid chromatographic separations of inorganic anions

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Abstract

Inorganic anion retention on a porous graphitic carbon (PGC) stationary phase is investigated by electrochemically modulated liquid chromatography (EMLC). Through various combinations of the potential applied (E_{app}) to the PGC packing and/or changes in the composition (sodium salts of tetrafluoroborate, sulfate, and fluoride) and concentration (10, 25, and 50 mM) of an aqueous mobile phase, conditions for the separation of two different inorganic anion mixtures (iodate, bromide, nitrite, and nitrate or iodate, bromate, and chlorate) are developed. Results show that retention was affected by both variables, with the analyte retention factor, k', changing in a few cases by as much as a factor of ca. six. Moreover, plots of $\ln k'$ are linearly dependent on both E_{app} and $\ln [SE]$, where [SE] is the supporting electrolyte concentration. Based on these findings, insights into the retention mechanism are briefly discussed by drawing on the theory for ion exchange chromatography.
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1. Introduction

Several reports have described the use of carbonaceous packings like porous graphitic carbon (PGC) for the separation of inorganic anions [1–9]. One set of strategies takes advantage of the hydrophobic character of PGC to control retention by either the dynamic modification of the stationary phase or the addition of ion-interaction reagents to the mobile phase. In the former, modification of PGC with the weak anion exchanger polyethyleneimine enabled the separation of several inorganic anions [1]. With the latter, tetrabutylammonium hydroxide [2] and alkylamines [3] were added to the mobile phase to affect the separation.

Another pathway to these separations exploited the semi-metal character of PGC. This strategy relied on the formation of a "mirror-charge" at the packing surface, which lead to retention by a charge-induced dipole [4,5]. The separation of the oxo-anions TcO_4^- and ReO_4^- was proposed to arise from this mechanism [6,7]. A recent report has extended this concept by the use of electronic competitors [8]. This study found that adsorptive competition between carboxylic acids and inorganic anions for PGC dictated analyte retention. Inorganic anions were also separated on PGC with dilute aqueous sodium sulfate as the eluent [9], work that also demonstrated a retention mechanism with ion exchange characteristics.

This paper examines the separation of inorganic anions by electrochemically modulated liquid chromatography (EMLC) [10]. In EMLC, a conductive stationary phase, such as PGC, is packed into an LC column that is also configured to function as a three-electrode electrochemical cell. Thus, the packing acts as both a chromatographic stationary phase and a high surface area working electrode. Through changes in applied potential (E_{app}), the donor–acceptor properties (e.g., surface charge density) of the conductive packing can be manipulated, which subsequently alter analyte retention.

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EMLC can therefore be viewed as an approach for fine-tuning separations by controlling the effective composition of the stationary phase.

Utilizing this dimension for affecting retention, reports from several laboratories [11–17], including our own [18–26], have shown that changes in E_{app} can be exploited for the separation a wide range of mixtures. Early reports examined the effect of E_{app} on the separation of monosubstituted benzenes [19], aromatic sulfonates [22], and pyridines and anilines [26]. More recent studies explored the effectiveness of EMLC for manipulation of the retention of corticosteroids [18], benzodiazepines [21], short-chain alkanoic acids [16], and metal ion complexes [17]. An investigation that evaluated the ability to enhance performance by operation at elevated temperatures has also appeared [24], along with efforts to detail the mechanistic basis of EMLC separations [15,22,23,25,26].

The work presented herein explores the effects of E_{app} and different aqueous electrolytes in the mobile phase on the separation of various inorganic anion mixtures (iodate, bromide, nitrite, and nitrate or iodate, bromate, and chlorate) by using an EMLC column packed with PGC. The following sections therefore examine: (1) the ability of E_{app} to manipulate retention for optimization of such separations and (2) the dependence of retention on the identity and concentration of sodium tetrafluoroborate, sodium sulfate, and sodium fluoride as supporting electrolytes. Both sets of findings are then examined to gain insights into the retention mechanism, drawing in particular on the theoretical underpinnings of ion exchange chromatography [27–33].

2. Experimental

2.1. Chemicals and reagents

The analytes, i.e., the potassium salts of iodate, bromate, chlorate, bromide, and nitrate and the sodium salt of nitrite were purchased from Aldrich Chemical (Milwaukee, WI). All were used at a concentration of 20 mM after dissolution in Milli-Q purified water (Millipore, Bedford, MA). Most of these analytes were chosen due to their compatibility with UV absorbance detection [34]. Chlorate ion, however, was detected because of a change in the refractive index of the mobile phase, which gave rise to a very weak pseudo peak in the absorbance signal.

The mobile phase consisted of varied concentrations of either sodium fluoride, sodium sulfate, or sodium tetrafluoroborate (Aldrich), which were dissolved in Milli-Q purified water. The mobile phases were passed through a 0.5-μm filter (GE Osmonics, Minnetonka, MN) prior to use. The PGC particles, 7-μm diameter (Hypercarb), were obtained from Thermo Hypersil (Bellfonte, PA). Characterizations of the as-received PGC by X-ray photoelectron spectroscopy agreed with previous results [22], which showed a very low surface oxygen content (0.14 at.%) that was largely distributed among phenol, carbonyl, carboxylic acid, lactone, and quinone groups [35].

2.2. Instrumentation

The design and construction of the EMLC column has been described in detail elsewhere [20]. In brief, the PGC stationary phase is packed inside a Nafion™ (Perma Pure Inc., Toms River, NJ) cation-exchange membrane in tubular form that has been inserted into a porous stainless steel column (Mott Corp., Farmington, CT). The Nafion™ tubing (2.8-mm internal diameter) functions as: (1) a container for the PGC stationary phase, (2) an electronic insulator between working and auxiliary electrode, and (3) a salt bridge for ion transport. The porous stainless steel housing (11 cm length) also serves as a high surface area auxiliary electrode. An Ag/AgCl (saturated NaCl) electrode acts as the reference electrode and was placed in an electrolyte-filled reservoir surrounding the auxiliary electrode; all values of E_{app} are reported with respect to this electrode.

The column was attached to an Agilent Technologies (Palo Alto, CA) model 1050 HPLC equipped with an autosampler, quaternary pump, and a diode array detector. The samples were injected at a volume of 1.0 μL. The elution profiles were monitored at 200 nm. The value of E_{app} was controlled by an Amel high power potentiostat (Milan, Italy) to ± 1 mV. All data were collected at $24 \pm 1\,°C$. A water blank was employed to determine the void time in calculations of the retention factor (k'). The resolution (R_s) was estimated based on the 5 sigma method resident in the Chemstation software. By way of a working definition, a separation of neighboring components that has an R_s value of 1.5 or greater is termed "baseline resolution", whereas "effective resolution" is used to describe values of R_s in the range of 1.0–1.5 [36].

3. Results and discussion

3.1. Retention as a function of E_{app}

The change in retention as a function of E_{app} for a large number of aromatic sulfonates at carbon packings follows predictions based on electrostatic forces [20]. In line with these earlier studies, the retention of the inorganic anions is also dependent on E_{app}. Fig. 1 presents an example of these findings, using a mixture of iodate, bromide, nitrite, and nitrate, four different values of E_{app} (0, +200, +400, and +600 mV), and 25 mM aqueous sodium fluoride as the supporting electrolyte. As is evident, increases in E_{app} result in longer retention times, which is consistent with the increase in the positive surface charge density on the PGC packing. Elution requires ∼2.5 min at the lowest value of E_{app} (0 mV), and ∼4.7 min at the highest value of E_{app} (+600 mV). The elution bands are also characterized by a notable level of tailing, which is occasionally observed with PGC as a stationary phase [3].
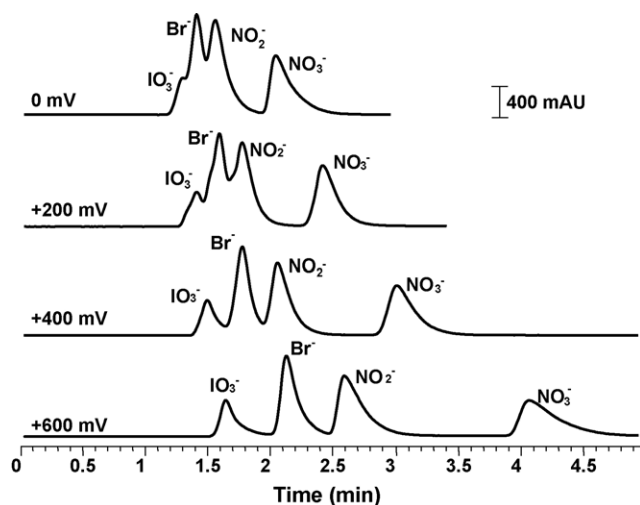
Fig. 1. Chromatograms for a mixture of iodate, bromide, nitrite, and nitrate as a function of E_{app} using a PGC stationary phase. The mobile phase was composed of 25 mM aqueous NaF at a flow rate of 0.5 mL/min.

In addition to affecting retention, the change in E_{app} also improves the resolution of the separation. At 0 mV, the first three analytes (iodate, bromide, and nitrite) are poorly resolved from one another ($R_s < 1.0$), with only nitrate effectively resolved ($R_s = 1.2$). Increasing E_{app} to more positive values gradually improves the resolution of the separation. All four anions are effectively resolved ($R_s \geq 1.0$) at +400 mV and elute in less than 3.5 min. Near baseline resolution is realized at +600 mV with the smallest resolution between bromide and nitrite ($R_s = 1.1$) at an elution time of ∼4.7 min. Higher values of E_{app} were not examined to avoid triggering the rapid oxidation of the PGC surface [22,37].

We also examined the separation of a mixture composed of the oxo-anions iodate, bromate, and chlorate. These results are shown in Fig. 2 and were obtained under the same set of conditions used for Fig. 1. Again, retention undergoes an increase as E_{app} becomes more positive. At 0 mV, iodate
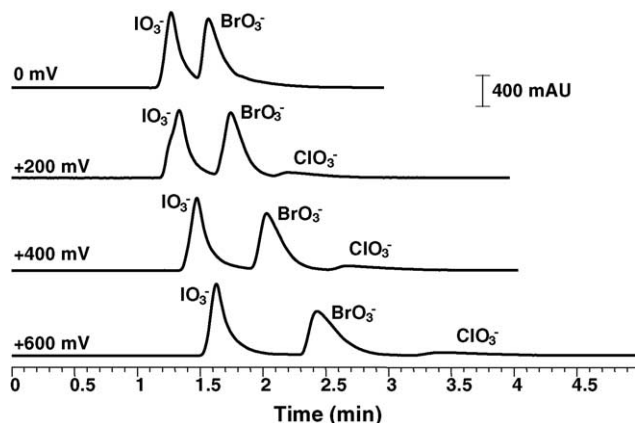

Fig. 2. Chromatograms for a mixture of iodate, bromate, and chlorate as a function of E_{app} using a PGC stationary phase. The mobile phase was composed of 25 mM aqueous NaF at a flow rate of 0.5 mL/min. At 0 mV, ClO_3^- elutes in the tail of the BrO_3^- band.
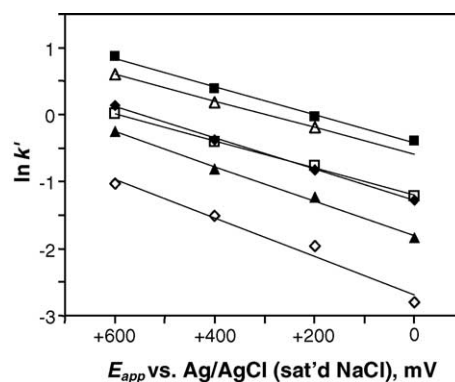

Fig. 3. Dependence of $\ln k'$ vs. E_{app} for iodate (◇), bromate (□), chlorate (△), bromide (▲), nitrite (◆), and nitrate (■). Error bars are smaller than the size of the data points. Data from Figs. 1 and 2.

and bromate are nearly resolved ($R_s = 0.8$), but chlorate is virtually undetectable in the tail of the bromate elution band. As before, the movement of E_{app} to more positive values gradually increases the retention and resolution of the three components in the mixture. Baseline resolution is realized for iodate and bromate ($R_s = 1.9$), with near baseline resolution for bromate and chlorate ($R_s = 1.3$) at +600 mV.

Fig. 3 summaries the retention data in Figs. 1 and 2 through plots of $\ln k'$ versus E_{app}. As observed for several sample types in EMLC [20], each plot has a linear dependence. These dependencies can be qualitatively understood by applying the ion distribution law [26], which details the influence of a potential difference on the equilibrium concentration of ions within the region between the potential difference [26,38].

The results in Fig. 3 also reveal that the EMLC-based retention sensitivity, S, which is defined as the slope of the plot, for the six analytes is comparable. This conclusion is supported by the data presented in Table 1, which includes the R^2 value of each plot. The table shows an average slope of for all the analytes of 2.32, with a relative standard deviation 16%. This agreement lends support to the argument that the dependence of inorganic anion retention with respect E_{app} is controlled primarily by the change in the stationary phase surface charge density. In other words, ions with the same charge should be affected in the same manner via the ion distribution law [26]. The slight variations in the sensitivities for ions of the same charge are attributed to differences in

Table 1
Sensitivities[a] (S) of retention for a series of inorganic anions to changes in E_{app} [b]

Analyte	$S (\times 10^3)$	R^2
NO_2^-	2.34 (0.05)[c]	0.996
ClO_3^-	1.98 (0.04)	0.997
IO_3^-	2.89 (0.12)	0.961
NO_3^-	2.10 (0.05)	0.994
BrO_3^-	2.03 (0.03)	0.997
Br^-	2.59 (0.06)	0.992

[a] The sensitivity is defined as the slope of a plot of $\ln k'$ vs. $\ln$ [SE].
[b] Data from Figs. 1 and 2.
[c] Standard error from the linear regression listed in parentheses.

their specific (i.e., chemical) interactions with PGC (see last section). Experiments using 50 mM NaF as the eluent (data not presented) also showed a linear dependence, though with much shorter retention times. The next section examines the importance of the supporting electrolyte in more detail.

3.2. Retention as a function of electrolyte identity and concentration

Three different salts were examined as mobile phase additives: sodium tetrafluoroborate, sodium sulfate, and sodium fluoride. These salts served as the supporting electrolyte in the mobile phase for control of E_{app} and were tested for their ability to function as an electronic competitor for retention manipulation. Each electrolyte was used at a concentration of 10, 25, and 50 mM. Fig. 4 shows the chromatograms for the separation of iodate, bromide, nitrite, and nitrate as a function of the identity and concentration of the different supporting electrolytes. These data were collected with E_{app} set at +600 mV, as guided by the data in Fig. 1. These results yield three immediate observations. First, fluoride is the most effective of the three anionic eluents in resolving the mixture. Second, tetrafluoroborate is a slightly stronger elut-
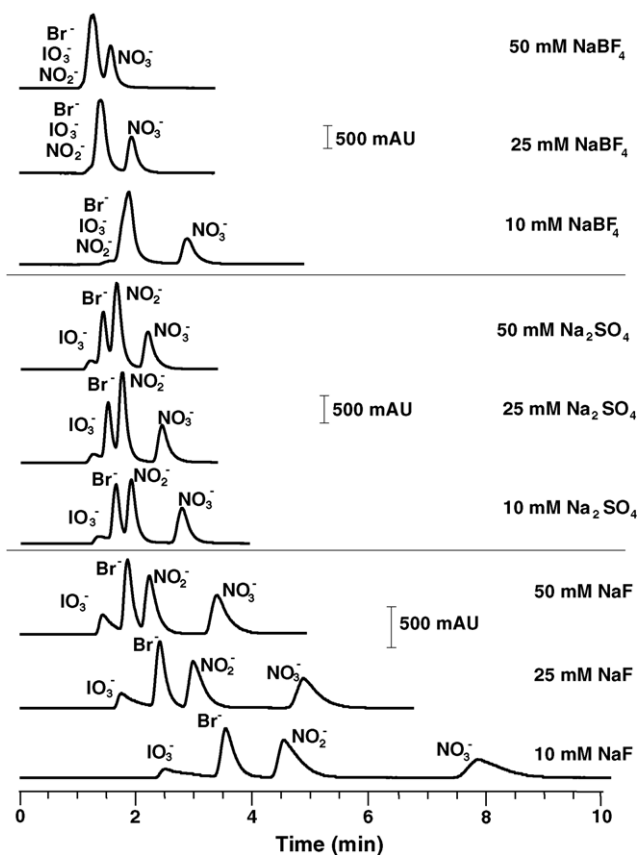

Fig. 4. Chromatograms for a mixture of iodate, bromide, nitrite, and nitrate as a function of eluent identity and concentration using a PGC stationary phase at E_{app} of +600 mV. The mobile phase was composed of aqueous sodium tetrafluoroborate, sodium sulfate, or sodium fluoride at either 10, 25, or 50 mM. The flow rate was 0.5 mL/min.

ing anion than sulfate, with fluoride being much weaker than either tetrafluoroborate or sulfate. Third, analyte retention in all three electrolytes increases with decreasing concentration.

With respect to resolution, Fig. 4 shows that three (iodate, bromide, and nitrite ions) of the four analytes co-elute with sodium tetrafluoroborate; only nitrate is effectively resolved ($R_s = 1.0$). With sodium sulfate, the separation approaches, but does not quite reach baseline resolution for the four analytes. The mixture is effectively resolved when carrying out the separation with fluoride as the eluent ($R_s \geq 1.0$ for all concentrations). Unfortunately, tailing is particularly evident in these separations. We attribute this observation to the weaker elution strength of fluoride relative to the other two anionic eluents. These results also suggest that running separations at lower supporting electrolyte concentrations may further improve sample resolution. However, too low of an electrolyte concentration may compromise the ability to control E_{app}, which may degrade the repeatability of the observed retention times.

3.3. Mechanistic insights

In addition to serving as a basis for the design of protocols for manipulating the separation, the data in the last two sections provide mechanistic insights into the retention of these analytes at PGC. At a conventional anion exchange column [9], the elution order is $IO_3^- < NO_2^- < Br^- < NO_3^-$. The elution order, for example, in Fig. 4 is $IO_3^- < Br^- < NO_2^- < NO_3^-$. Although, not in complete agreement, a comparison of elution orders suggests that the retention of these analytes at PGC has mechanistic similarities to that in ion exchange chromatography.

Takeuchi et al. [9] also recently concluded that the retention of inorganic anions by PGC exhibits ion-exchange characteristics. This assertion was based on an investigation of the dependence of $\ln k'$ on $\ln [SE]$, where $[SE]$ is the concentration of an ionic eluent added to the mobile phase. A plot of $\ln k'$ versus $\ln [SE]$ at a resin-based ion exchange packing generally follows a linear dependence with a slope that often, but not always, correlates with the ratio of the analyte-to-eluent charge [29,34]. A classic example of this dependence was reported by Rocklin et al. [39] Rocklin and co-workers investigated the effect hydroxide ion concentration has on inorganic anion retention at an anion exchange resin, and found slopes for plots of $\ln k'$ versus $\ln [SE]$ for chloride, nitrate, sulfate, and fumarate equal to -1.03, -0.95, -2.10, and -2.03, respectively. Takeuchi et al. [9] determined that the elution of iodate and iodide at PGC versus sulfate concentration resulted in slopes close to the expected value of -0.5, i.e., -0.58 for iodate and -0.50 for iodide.

An analysis of the data in Fig. 4 also shows the existence of a linear relationship between $\ln k'$ and $\ln [SE]$ for each analyte–eluent combination. The results of this analysis are presented in Fig. 5, with each plot having a R^2 value greater than 0.99. These dependencies further confirm the importance of electrostatic interactions to the EMLC-based sepa-
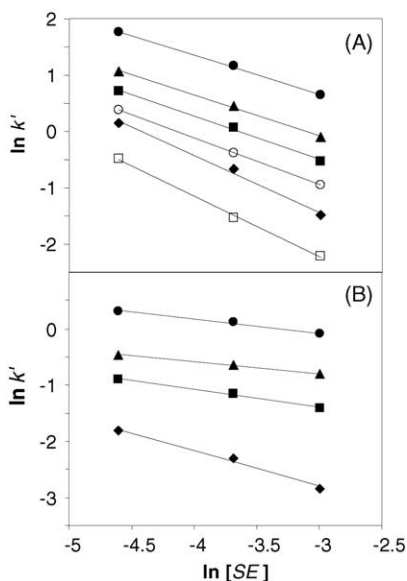
Fig. 5. Dependence of $\ln k'$ vs. $\ln[SE]$. Plot A: iodate (♦), bromide (■), nitrite (▲), and nitrate (●) with NaF; and iodate (□), bromide (□), nitrite (□), and nitrate (○) with NaBF$_4$ (iodate, bromide, and nitrite coelute with NaBF$_4$). Plot B: iodate (♦), bromide (■), nitrite (▲), and nitrate (●) with Na$_2$SO$_4$. All eluent concentrations are molar. Error bars are smaller than the size of the data points. Data from Fig. 4.

ration of these compounds. Interestingly, the slopes with fluoride and tetrafluoroborate, the two singly charged eluents, are roughly the same (Fig. 5A). Moreover, the slopes for bromide, nitrite, and nitrate with the doubly charged sulfate as the eluent are all notably lower than those the tetrafluoroborate and fluoride eluents, and can also be loosely grouped together (Fig. 5B). Iodate, however, has a much steeper slope than those for bromide, nitrite, and nitrate. Importantly, the slopes in Fig. 5A are generally steeper than those in Fig. 5B, which is qualitatively consistent with the correlations expected for analyte–eluent charge ratios. These results support the claim that the EMLC-based separation of these analytes has ion exchange characteristics.

Two additional observations develop from a more exacting analysis of the data in Fig. 5. This analysis is presented in Table 2 as the slope of the plots, which are listed in increasing analyte elution order for each supporting electrolyte.

Table 2
Slopes from plots of $\ln k'$ vs. $\ln[SE]$ with E_{app} set at +600 mV[a]

Analyte	Supporting electrolyte/eluent		
	NaF	Na$_2$SO$_4$	NaBF$_4$
IO$_3$$^-$	−1.01 (0.02)[b]	−0.63 (0.03)	−1.09[c] (0.03)
Br$^-$	−0.77 (0.01)	−0.31 (0.01)	−1.09[c] (0.03)
NO$_2$$^-$	−0.72 (0.01)	−0.21 (0.01)	−1.09[c] (0.03)
NO$_3$$^-$	−0.69 (0.01)	−0.25 (0.01)	−0.83 (0.01)
Theoretical prediction	−1	−0.5	−1

[a] Data from Fig. 4.

[b] Standard error from the linear regression listed in parentheses.

[c] Since all three analytes coeluted, k' was calculated based on peak height of the combined peak.

First, one of the singly charged analyte–eluent combinations (iodate–fluoride) has a slope that is experimentally identical to the analyte–eluent charge ratio. The other slopes for fluoride as the eluent, the bromide–, nitrite–, and nitrate–fluoride combinations, deviate by as much as −31%. The iodate–, bromide–, and nitrite–tetrafluoroborate combinations also have slopes within +10% of expectations; the deviation for the nitrate–tetrafluoroborate combination, however, is −17%. Interestingly, the data with the doubly charged sulfate as the eluent shows both significant positive (+26% with iodate) and negative (e.g., −58% for nitrite) deviations. Takeuchi et al. [9] also found a positive deviation (+16%) for iodate with sulfate as the eluent.

Second, the magnitude of the deviation in the plots of $\ln k'$ versus $\ln[SE]$ largely correlate with the extent of analyte retention. For example, nitrate is the most strongly retained analyte when fluoride is used as the supporting electrolyte. Nitrate also has the largest departure from the slope based on the analyte–eluent charge ratio. Nitrite follows nitrate in elution order with fluoride as the eluent, and ranks second in terms of the departure from the charge ratio expectation. An examination of the data for bromide and iodate completes the trend. Most of the data with the other two eluents exhibit the same trends. Only the data with nitrate and nitrite as the analytes and sulfate as the eluent falls outside of this correlation, but only by an amount slightly greater than the uncertainty in the data.

Deviations from charge ratio expectations in plots of $\ln k'$ versus $\ln[SE]$ can in some cases be accounted for by the dependence of the activity coefficients of ions in the mobile phase on eluent concentration [28,39]. An analysis to correct for this effect uses the slope from a plot of $\ln(\gamma_A/\gamma_E^{-z_A/z_E})$ versus $\ln[SE]$, where γ_A and γ_E are the respective activity coefficients for the analyte and eluent, and z_A and z_E are the respective analyte and eluent charges[39]. Nevertheless, the results from corrections to the data in Fig. 5, which used literature activity coefficients [40], only marginally improve the correlations between the expected and observed slopes. For example, the activity coefficient correction calculated for fluoride as the eluent equals −0.07 and that with sulfate as the eluent is −0.10. Thus, the slopes corrected for differences in activity coefficients with fluoride as the eluent continue to show large negative deviations (e.g., −24% for nitrate), whereas both large positive (+44% for iodate) and negative (−30% for nitrate) deviations persist in the data with sulfate as the eluent.

There is, however, an important difference in separations using ion-exchange resins and those based on EMLC that should be considered in this analysis. In ion exchange chromatography, the fixed charge groups on the resin define the surface charge density, which dictates the surface potential, and therefore the potential gradient within the interphase between the resin and bulk solution. Importantly, the fixed charge density limits changes in the activity coefficients of both the eluent and analyte in the stationary phase when the eluent concentration in the mobile phase is low (less

than ~100 mM) [29] with respect to the concentration of fixed charges (~0.006–0.06 meq/g for low-capacity resins and 0.8–2.4 meq/g for high capacity resins) [33] on most ion exchange resins.

The surface charge density of the packing in EMLC develops differently. In EMLC, it is the potential applied to the packing, and not the surface charge density, that is directly controlled by the potentiostat. The charge density on the packing surface and the gradient in the potential in the interphase reflect the response of the interphase to the applied potential. Estimates to be reported elsewhere [25], which extract the surface charge density at PGC as a function of E_{app} between +50 and −150 mV, yield a value of ~1.3 μC/cm^2 when extrapolated to +600 mV. Based on the surface area of PGC (~120 m^2/g) [4] this charge density translates to ~20 μeq/g. Thus, the charge density of the packing in EMLC is comparable to that of low-capacity ion exchange resins [33].

The difference in the two modes of separation, however, becomes apparent when considering that the charge density of the stationary phase in EMLC is affected by the concentration of the supporting electrolyte. That is, when the supporting electrolyte concentration increases, its capacitance increases and the surface charge density of the stationary phase at a given value of E_{app} will, in turn, increase. A direct application of activity coefficient corrections becomes even more complicated if an anion interacts with PGC by both nonspecific (electrostatic) and specific (chemical) interactions. The correlation between the magnitude of the deviation with elution time lends supports to this possibility, noting that specific interactions can alter the charge density of an adsorbate, and therefore the structure of the electrical double layer. In other words, the theoretical framework behind the mechanistic analysis of the plots of ln k' versus E_{app} or ln [SE] in Figs. 3 and 5, respectively, is based solely on electrostatic interactions. However, if specific interactions contribute to retention, then factors, such as the charge and desolvation of an analyte or supporting electrolyte ion when specifically adsorbing on the surface can result in a dramatic change in the structure and electrostatics at the interphase of the packing, further complicating an objective treatment of the activity coefficients of the species in the interphase.

Complex retention mechanisms are not uncommon occurrences in ion exchange chromatography and can be elucidated, for example, by examining the temperature dependence of retention under varying mobile phase compositions [41,42]. By employing temperature as an adjustable parameter, a van't Hoff-type analysis can be utilized to quantify both the enthalpic and entropic contributions to retention, paralleling our recent study on the separation of organic dianions [23]. Work to this end is underway.

4. Conclusion

The manipulation and optimization of inorganic anion retention on PGC through changes in both the mobile phase composition and the E_{app} of the stationary phase is demonstrated. The choice of an electronic competitor and its concentration in the mobile phase has a profound impact on the resolution of the separation, with fluoride proving the most effective eluent of the three electronic competitors tested. Results also showed that these separations could be manipulated by changes in E_{app}. From a mechanistic perspective, plots of ln k' were found to be linearly dependent on both E_{app} and ln [SE]. This behavior can be described in the context of an ion-exchange mechanism between analyte ions in the mobile phase and eluent ions in the interphase formed on the surface of PGC. Deviations from the expectations for the slopes of the ln k' versus ln [SE] plots were attributed to effects specific interactions, in addition to electrostatic interactions, on retention. Efforts to test this conclusion are presently being designed.

Acknowledgements

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