Mechanistic studies on the separation of cations in zwitterionic ion chromatography

Helmy A. Cook, Greg W. Dicinoski, Paul R. Haddad*

Australian Centre for Research on Separation Science (ACROSS), Department of Chemistry, University of Tasmania, Private Bag 75, Hobart, Tasmania 7001, Australia

Abstract

Electrostatic ion chromatography, also known as zwitterionic ion chromatography, has been predominantly used for the analysis of anions. Consequently, separation mechanisms proposed for this technique have been based on anion retention data obtained using a sulfobetaine-type surfactant-coated column. A comprehensive cation retention data set has been obtained on a C_{18} column coated with the zwitterionic surfactant N-tetradecylphosphocholine (which has the negatively and positively charged functional groups reversed in comparison to the sulfobetaine surfactants), with mobile phases being varied systematically in the concentration and species of both the mobile-phase anion and cation. A retention mechanism based on both an ion exclusion effect and a direct (chaotropic) interaction with the inner negative charge on the zwitterion is proposed for the retention of cations. Despite the relatively low chaotropic nature of cations compared with anions, the retention data shows that cations are retained in this system predominantly due to a chaotropic interaction with the inner charge, analogous to anions in a system where the C_{18} column is coated with a sulfobetaine-type surfactant. The retention of an analyte cation, and the effect of the mobile-phase anion and cation, can be predicted by the relative positions of these species on the Hofmeister (chaotropic) series.
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1. Introduction

Electrostatic ion chromatography (EIC) involves separations performed on a stationary phase in which positively charged (anion-exchange) and negatively charged (cation-exchange) functionalities are present in close proximity to each other. Although this stationary phase is bifunctional, EIC has been used predominantly for the separation of anions [1–3]. The stationary phase is created by either chemical modification of the surface of a suitable substrate [4] or by adsorption of a zwitterionic surfactant onto a hydrophobic chromatographic support material [5], with the latter being the most common approach. The surfactant used for coating has generally been of the sulfobetaine-type [e.g., 3-(N,N-dimethylmyristyl-ammonio)propanesulfonate (C14SB)] which has an inner positively charged functional group (quaternary ammonium group) and an outer negatively charged functional group (sulfonate group) separated

*Corresponding author. Tel.: +61-3-6226-2179; fax: +61-3-6226-2858.

E-mail address: paul.haddad@utas.edu.au (P.R. Haddad).

by three methylene groups. The resultant chromatographic system has an ability to separate anions with a unique selectivity, whilst cations can only be separated into groups of analytes with the same charge [6]. Separation of anions can be achieved using a pure water mobile phase [5], but complex chromatograms result, thereby reducing the analytical utility of this approach [6]. However, addition of a small amount of electrolyte to the mobile phase [2], or an excess of an electrolyte added to the sample [7], overcomes this problem and allows EIC to be applied to the analysis of high ionic strength samples [3]. EIC has great analytical potential but its development and application has been hindered due to a difficulty in manipulating the selectivity as well as a seemingly complex mechanism of separation.

Proposed mechanisms of separation in EIC have been derived from studies of the retention behaviour of anions on sulfobetaine-type stationary phases [8–11]. These mechanisms involve concepts such as the simultaneous electrostatic attraction and repulsion of analytes from the opposite charges of the zwitterion, the formation of ''ion-pairs'' between oppositely charged ions in solution [6], and the formation of a zwitterionic electrical double layer arising from the accumulation of oppositely charged mobile phase ions around the charges on the zwitterion [12]. Okada and Patil [10] investigated mechanisms based on the Poisson–Boltzmann theory, concluding that small, well-hydrated ions interact with the surface via a partition mechanism and large, poorly hydrated ions interact via an ion-pair mechanism. The most recently proposed mechanism [8] depends on two simultaneous effects, one of ion-exclusion and one of chaotropic interaction. The ion-exclusion effect arises from a repulsion of analyte anions by the outer negative sulfonate charge. This repulsion effect can be either increased or decreased depending on the interaction and shielding of the charges on the zwitterion by the mobile-phase anion and cation. Retention is determined by the ability of an analyte to directly (chaotropically) interact with the inner positive quaternary ammonium group, and to compete with the corresponding mobile-phase anion for that interaction. This proposed mechanism is not based on electrostatic interactions as the name electrostatic ion chromatography implies, thus the name zwitterionic ion chromatography (ZIC) was suggested as being more appropriate [8].

Investigations into ZIC have increasingly extended to the analysis of cations [13]. As mentioned earlier, it was found that the sulfobetaine-type system used for the analysis of anions was not very effective in the separation of cations, as they could only be separated into charge groups [6,12]. Hu and Haddad [12] suggested that this problem may be overcome by using stationary phases in which the positions, spacing or acid–base strength of the charged functional groups on the zwitterion were varied. Altering the acid–base strength of the functional groups [14] or utilising a mixture of anionic and zwitterionic surfactants on the stationary phase [15] allowed the separation of cations, but this outcome was attributed to the additional ion-exchange interactions introduced into the separation. In an alternative approach, Hu and co-workers [9,13,16] investigated the use of a phosphocholine-type surfactant [*N*-tetradecylphosphocholine (C14PC)] to create the stationary phase. This surfactant is analogous to the C14SB used for the analysis of anions, but the charge positions are reversed to give the surfactant a negative inner charge (phosphonate group) and a positive outer charge (quaternary ammonium). This study found that while the C14SB showed a higher selectivity for anions, the C14PC displayed a high selectivity for cations. It was also found that addition of electrolyte to the mobile phase diminished the selectivity of the C14PC for anions, analogous to the effect seen on selectivity of cations for the C14SB [17].

A comprehensive set of retention data presented previously for the anion system [18] revealed characteristics of ZIC not observed previously and which were of importance to the understanding of the separation mechanism. A similar investigation of the retention of cations on the C14PC phase is now necessary to determine whether this ZIC system behaves in the same manner as the C14SB system. Anions dominate cations in terms of Hofmeister (chaotropic) effects [18] so it was not known whether the cation system would minor the trends of the anion system in which direct chaotropic interactions play a major role.

The aim of this paper has been to produce a systematic retention data set to use in conjunction with surface potential data from the literature to reveal the nature of analyte interactions with the inner negative charge and the formation and modulation of the surface potential, and to use this in-

formation to develop a separation mechanism for ZIC of cations on a C14PC stationary phase

2. Experimental section

2.1. Apparatus

A Dionex (Sunnyvale, CA, USA) DX 500 IC system was used throughout this study, consisting of a GP4O pump, an AS50 auto-sampler with a 100 μl injection loop, an AD20 UV–Vis absorbance detector, an ED40 electrochemical detector and a Waters (Milford, MA, USA) column heater. PeakNet 5.1 (Dionex) Software was used to record the chromatograms. The column used throughout this study (L-column, 250×4.6 mm I.D., Chemical Inspection and Testing Institute, Tokyo, Japan) was packed with ODS material which was coated with N-tetradecylphosphocholine. The procedure for coating the column with a zwitterionic surfactant has been described elsewhere by Hu et al. [19].

A Varian (Palo Alto, CA, USA) Spectra AA-800 system was used for peak identity confirmation of K, Li [atomic emission spectrometry (AES) mode] and Ag [atomic absorption spectrometry (AAS) mode] due to the many system peaks observed when indirect UV and conductivity detection was employed. The peak identity of NH_4^+ was confirmed by the post-column addition of Nessler's Reagent [an alkaline solution of potassium tetraiodomercurate(II)], producing a yellow/orange precipitate where NH_4^+ was present. Tl^+ peaks were identified by the post-column addition of NaI, whereby a yellow precipitate [TlI(s)] indicated the presence of Tl^+.

2.2. Reagents

N-Tetradecylphosphocholine (Anatrace, Maumee, OH, USA) was used for column coating. Inorganic salts used to prepare samples and the mobile phase were of analytical grade or >98% purity and were obtained from Aldrich [$AgNO_3$, $Ce_2(SO_4)_3$, $Ce(ClO_4)_3$, $Cu(ClO_4)_2$, $Cu(NO_3)_2$, $Co(ClO_4)_2$, KI, $ZnCl_2$], BDH (KNO_3, $TlNO_3$, $HgCl_2$), Ajax [$CaCl_2$, $Co(NO_3)_2$, NaOH], Sigma ($CoSO_4$) and Univar (NH_4NO_3, $NaNO_3$) and were used as received. Nessler's reagent was prepared according to literature methods [20]. Water used throughout this study was prepared in the laboratory using a Millipore (Bedford, MA, USA) Milli-Q water purification system, and was filtered through a 0.22-μm membrane filter prior to use.

3. Results and discussions

3.1. Proposed mechanism

With a water mobile phase the opposite charges of adjacent zwitterionic molecules can interact, resulting in a tangled surface morphology. This interaction decreases with the addition of salt to the mobile phase due to shielding of the charges on the zwitterion by electrolyte ions of opposite charge. This unfurls the entangled zwitterion molecules and allows greater accessibility of ions to the charges of the zwitterionic stationary phase.

Fig. 1a illustrates the equilibration of mobile-phase anions and cations with the charges on the C14PC zwitterion. The outer positive charge on the zwitterion (the quaternary ammonium group) acts as
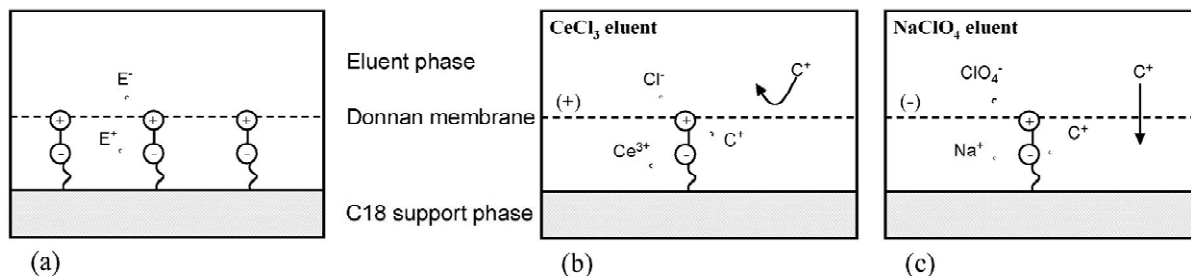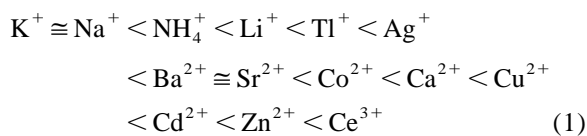

Fig. 1. Schematic representation of the proposed mechanism for the phosphocholine stationary phase cation system. (a) Establishment of the Donnan membrane, (b) use of a $CeCl_3$ mobile phase, (c) use of a $NaClO_4$ mobile phase.

a Donnan membrane. This charge is effective in repelling analyte cations, but the charge is reduced due to the close proximity of the negative phosphonate group. The magnitude and sign of the overall charge on the Donnan membrane depends on the interaction and shielding capability of the mobile-phase anions and cations as they interact with the positive and negative charges on the zwitterion, respectively.

The interaction of cations with the phosphonate group (as observed by increased retention for the C14PC stationary phase using water as mobile phase) was found to increase across the series:

$$K^+ \cong Na^+ < NH_4^+ < Li^+ < Tl^+ < Ag^+$$
$$< Ba^{2+} \cong Sr^{2+} < Co^{2+} < Ca^{2+} < Cu^{2+}$$
$$< Cd^{2+} < Zn^{2+} < Ce^{3+} \qquad (1)$$

Hu et al. [7] studied the retention of H^+ on this stationary phase with a water mobile phase and found that H^+ was highly retained ($> Ca^{2+}$), with retention dependent on the nature of the counterion. Hence, H^+ is seen as a special case, and was not included in the present study. The retention times of anions under the same conditions (reflecting interactions of these anions with the quaternary ammonium group) increase across the series:

$$IO_3^- \approx SO_4^{2-} < Cl^- < NO_2^- < CNO^- < Br^-$$
$$< NO_3^- < ClO_3^- < I^- < ClO_4^- \qquad (2)$$
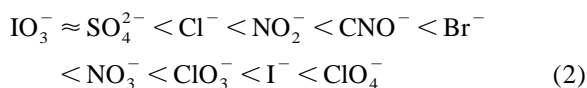
These series follow the general trend of the Hofmeister or chaotropic series [18,21] and reflect the order of increasing polarisability of the analytes. As a consequence, the negative charge on the zwitterion will be shielded to the greatest extent with a Ce^{3+} mobile-phase cation, resulting in a more positive Donnan membrane. The overall Donnan membrane will be most positive when a strongly shielding mobile-phase cation (Ce^{3+}) is combined with a mobile-phase anion (such as C^-) that only weakly shields the outer positive charge of the zwitterion. This is illustrated in Fig. 1b where the mobile phase is $CeCl_3$. The Donnan membrane will be least positive (or even negative) when the mobile-phase anion greatly shields the outer positive charge and the mobile-phase cation only weakly shields the

inner negative group, i.e., with a $NaClO_4$ mobile phase as illustrated in Fig. 1c.

A negative Donnan membrane allows analyte cations to enter the stationary phase (Fig. 1c), while a positive Donnan membrane exerts a repelling effect on analyte cations (Fig. 1b). In the latter case, analyte cations may still move into the stationary phase if their interaction with the inner charge is sufficiently energetically favourable to overcome this repulsion barrier. Conversely, even if the Donnan membrane is negative, retention may still be small if the nature of the analyte cation does not allow it to interact effectively with the inner charge. Furthermore, analyte cations must compete with mobile-phase cations for interaction with the inner charge and their affinity for the inner negative charge must be comparable or greater than that of the mobile-phase cation for retention to occur.

In Fig. 1c the mobile-phase cation is Na^+ and according to series (1) all cations except for K^+ can compete with Na^+ for interaction with the inner negative charge. With little or no repulsion from the Donnan membrane occurring due to the shielding effects of the mobile-phase anion, ClO_4, it would be expected that most analyte cations would be retained in this system. It would also be predicted that retention would increase (compared to that in a water mobile phase) with increased mobile phase concentration due to the unfurling of the surface morphology and greater accessibility of the inner charge. In Fig. 1b the analyte cation may overcome the repulsion of the Donnan membrane if the attraction to the inner charge is sufficient, but it must also compete with Ce^{3+} for interaction with the inner charge. Of the cations listed in the series above, there are none that are more chaotropic than Ce^{3+}, hence it would be expected that all analyte cations would show little retention when the mobile-phase cation is Ce^{3+}.

If the analyte cation lies to the left of the mobile-phase cation in series (1), then its retention should be decreased compared with its retention in a water mobile phase. Additionally, the greater the interaction of the mobile-phase anion with the outer positive charge, the greater the ability of the analyte cation to be retained. With the chaotropic series in mind, the effect of various mobile phases on the retention of analytes can be predicted.

3.2. Elution effects of analyte anions

The retention of anions was studied on the phosphocholine stationary phase and it was found that although retention was much less than for cations, the mobile phase still modulated the retention of anions. For example, a $CaCl_2$ mobile phase increased retention of anions, while a $NaClO_4$ mobile phase decreased retention compared to that with a water mobile phase. Selectivity of anions on this stationary phase was determined by chaotropic effects, also suggesting that analyte anions interacted directly with the positive charge on the zwitterion, whether that charge was the inner charge (sulfobetaine-type surfactant) or the outer charge (phosphocholine-type surfactant). The fact that interaction, and hence retention, was greater when the positive charge was the inner charge may be due to the close proximity of the hydrophobic C_{14} chain. As chaotropic interactions occur most readily with large, low-charged ions such as ClO_4^- (K. Irgum, University of Umeå, Umeå, personal communication, May 2000), the larger the quaternary ammonium ion, the greater will be its chaotropic interaction with analyte ions. The inner quaternary ammonium group on the sulfobetaine surfactant has a larger hydrophobic moiety, namely the C_{14} chain, compared to the quaternary ammonium group positioned on the end of the phosphocholine surfactant. Thus, the sulfobetaine quaternary ammonium group would be expected to have a greater water structure breaking capacity and therefore should associate more readily with analyte ions in solution. This has been demonstrated by Barron and Fritz [22] who found that the relative retention of anions increased as the hydrophobic moiety of trialkylammonium resins was systematically increased.

3.3. Zeta potential data

According to the mechanism proposed, the mobile-phase anion and cation should together modulate the surface charge of the stationary phase depending on their relative affinities for the opposite charges on the zwitterion. This modulation should be evident in experimentally measured zeta potentials. Iso and Okada [23] determined the effect of various electrolytes on the zeta potential of a phosphocholine-type surfactant through measurement of the electrophoretic mobility of the surfactant micelles in a silica capillary using a capillary electrophoresis system. Their method involved introducing a sample of pyrene and acetone into a capillary filled with electrolyte and surfactant micelles. Pyrene is partitioned completely into the micelles and therefore migrates with the micelles, while acetone marks the electro-osmotic flow, allowing measurement of the mobility of the micelles and hence the zeta potential. A solution of $NaClO_4$ (160 mM) resulted in a zeta potential of -13.9 mV, supporting the supposition that the ClO_4 ion shields the quaternary ammonium group to a greater extent than Na^+ shields the inner phosphonate group. A Bu_4NCl solution (80 mM) resulted in a positive zeta potential of 28.4 mV, illustrating the ability of an electrolyte to modulate the zeta potential from negative to positive. In this case, a strong shielding of the negative functionality (phosphonate group) by the Bu_4N^+ ion and weak shielding of the outer positive quaternary ammonium group by the Cl^- mobile phase ion leads to the overall positive zeta potential. These results support the proposed mechanism and are consistent with those obtained on the anion system using C14SB as the zwitterion [8].

3.4. Elution effects of analyte cations

The proposed mechanism was further tested by studying the elution behaviour of a range of monovalent inorganic cations, namely K^+, NH_4^+, Li^+ and Ag^+ under varying concentrations of mobile-phases containing different anionic and cationic species. Divalent cations (Sr^{2+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Zn^{2+}) were studied in preliminary investigations but were found to have extremely high retention factors when the mobile-phase cation was monovalent, while Zn^{2+} was found over time to give irreproducible, broad and shouldered peaks.

The mobile-phase anion and cation species (Na^+, Co^{2+}, Cu^{2+}, Ce^{3+}, SO_4^{2-}, NO_3^- and ClO_4^-) were chosen such that they covered a wide range of chaotropic strengths. The elution effects of three representative analytes (K^+, Li^+ and Ag^+) on a phosphocholine-coated column are shown in Fig. 2, with increasing concentration of four different mobile phase salts [$NaClO_4$, $Co(ClO_4)_2$, $Cu(ClO_4)_2$
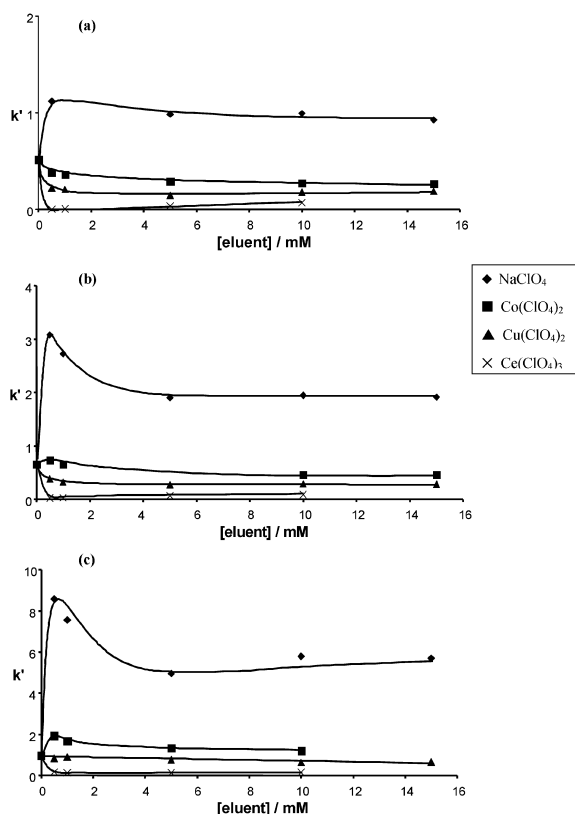
Fig. 2. Effect of the concentration of various perchlorate salts in the mobile phase on the retention of (a) K^+, (b) Li^+ and (c) Ag^+. Conditions: column, ODS modified with C14PC; flow-rate, 1.0 ml/min; detection, indirect conductivity (with AAS used for peak identity confirmation); sample, 100 µl containing 1.0 m*M* of each cation.

and $Ce(ClO_4)_3$]. The plots show that as the mobile phase composition was changed from pure water to one with ~1 m*M* electrolyte concentration, an abrupt change in retention was observed. This corresponds to the unfurling of the surface morphology with the addition of a small amount of electrolyte, which provides sufficient shielding of the charges to prevent the interaction of adjacent zwitterionic molecules and their subsequent entanglement. This increased accessibility of the charges either abruptly increases or decreases the retention of analyte ions depending on the relative affinities of the mobile-phase anion, mobile-phase cation and analyte cation for the functional groups on the zwitterion. Further

increases in mobile phase concentration had little effect on the retention. The $NaClO_4$ mobile phase resulted in an increase in retention compared with that of a pure water mobile phase for all three analytes. This was due to the ability of analyte cations to partition through the negative Donnan membrane (see Fig. 1c), and the fact that all three analytes can compete to some extent with the mobile-phase cation, Na^+ for the inner negative charge. Thus, the unfurling of the surface morphology with the addition of $NaClO_4$ resulted in a greater ability of these analytes to interact with the inner charge. The greatest increase in retention with the addition of $NaClO_4$ was seen for Ag^+ due to the fact that its interaction with the inner negative charge was the greatest of the three representative analytes (see interaction series shown in (1). Ag^+ also has the highest selectivity compared to the mobile-phase cation, Na^+.

The $Co(ClO_4)_2$ mobile phase caused decreased retention for K^+ compared to that of a pure water mobile phase, but increased the retention of Li^+ and Ag^+. According to the chaotropic series, it would be expected that the Co^{2+} ion would compete more strongly for the anionic sites on the stationary phase than the three monovalent analytes. The results observed can be explained by assuming that the ClO_4^- mobile-phase anion produced a negative Donnan membrane, resulting in a favourable partitioning of the analyte cations. At low concentrations of the mobile phase, retention of Li^+ and Ag^+ increased due to greater accessibility of the inner negative charge; however, retention decreased at increasingly higher concentrations as the highly chaotropic mobile-phase cation, Co^{2+}, competed effectively for the inner negative charge site. This resulted in a decrease in retention for K^+ and Li^+, but had little effect on the Ag^+ ion. $Ce(ClO_4)_3$ resulted in a decrease in the retention of all analytes due to the strong competition afforded by the highly chaotropic Ce^{3+} ion, which possibly also created a repulsive positively charged Donnan membrane. The same trends were observed for all analytes studied, as well as for SO_4^{2-} mobile phases and were consistent with those seen for the anion system using C14SB [8].

Fig. 3 shows the effect of the nature of the mobile-phase cation species on the retention of analyte cations. It is clearly evident that as the
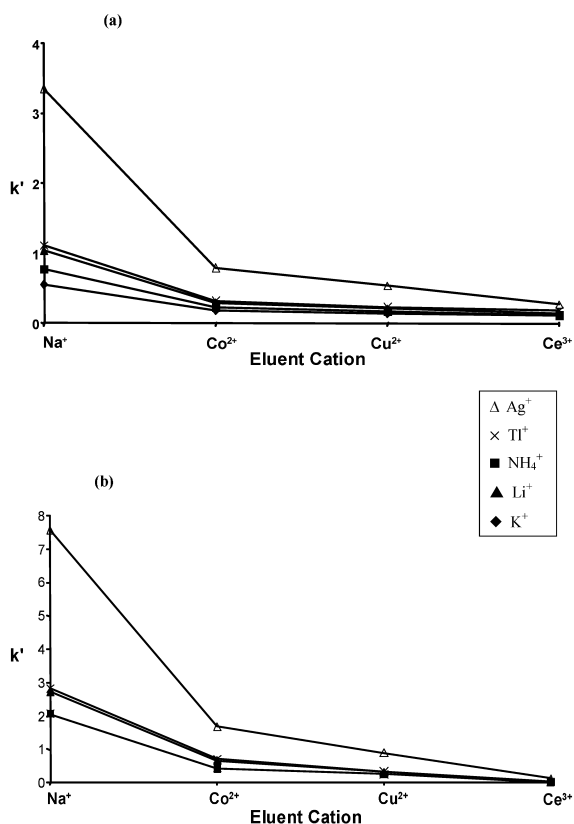
Fig. 3. Effect of the mobile-phase cation species on the retention of various analytes using mobile phases containing 10 mM (with respect to the cation) (a) SO_4^{2-} salts, and (b) ClO_4^- salts. Other conditions are the same as described in Fig. 2.
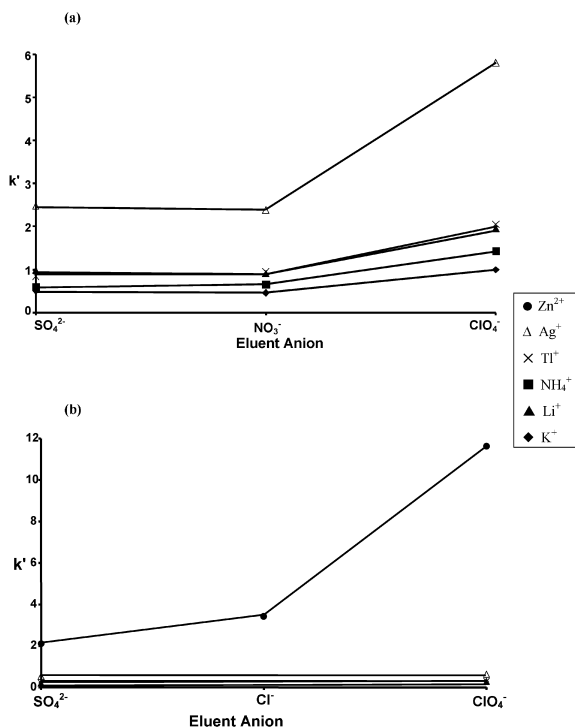

Fig. 4. Effect of the mobile-phase anion species on the retention of various analytes using mobile phases containing (a) 10 mM (with respect to the anion) Na salts, and (b) 10 mM (with respect to the cation) Cu^{2+} salts. Other conditions are the same as described in Fig. 2.

affinity of the mobile-phase cation for the inner charge increased, the retention of analyte cations decreased. This supports the proposed mechanism in relation to the competition for interaction with the inner charge between the mobile phase and analyte cations. This effect was observed for both a weakly interacting mobile-phase anion (such as SO_4^{2-}, Fig. 3a) or strongly interacting mobile-phase anion (such as ClO_4^-, Fig. 3b).

The effect of the mobile phase counter-anion species on the retention of analyte cations is illustrated in Fig. 4a for which the mobile-phase cation was Na^+, which is weakly interacting. There was a marked increase in retention with increasing chaotropic character of the mobile-phase anion, which was particularly evident on changing from NO_3^- to

ClO_4^-. Thus, the counter anion can affect the retention of analyte cations. This corresponded directly to a decrease in the repulsive nature of the Donnan membrane as the mobile-phase anion increasingly shielded the outer positive charge, allowing the analyte cation greater access to the inner negative charge. This effect can be seen despite the presence of a strongly competing mobile-phase cation (Cu^{2+}), as illustrated in Fig. 4.The high affinity of Cu^{2+} for the inner negative charge of the stationary caused the effect of the mobile-phase anion to be depressed for all analytes except Zn^{2+} for which a significant increase in retention was noted on changing the mobile-phase anion from Cl^- to ClO_4^-. Again, the results for the effects of the mobile-phase anion support the proposed mechanism and are consistent with the reported mechanism operating in the anion system with C14SB as the zwitterion.

4. Conclusions

This study has confirmed that a phosphocholine surfactant stationary phase has greater selectivity for cations over anions, although there is also the potential to separate polarisable anions, depending on the electrolyte added to the mobile phase. The retention data presented here characterise the effects of the mobile-phase anion and cation on the retention of cations on a phosphocholine surfactant-coated column. The data show that cations are retained due to the same chaotropic interactions observed with anions on the sulfobetaine-type surfactant system. The proposed mechanism explains the elution effects based on both ion-exclusion effects and direct chaotropic interactions with the inner charge on the zwitterion. The ion-exclusion component, namely the build up of a Donnan membrane at the outer positive charge that is dependent on the shielding ability of the mobile-phase anion and cation, is supported by the elution trends observed, as well as by zeta potential studies reported in the literature. Shielding and retention at the inner negative charge is determined by the chaotropic series: $K^+ \cong Na^+ < NH_4^+ < Li^+ < Tl^+ < Ag^+ < Ba^{2+} \cong Sr^{2+} < Co^{2+} < Ca^{2+} < Cu^{2+} < Cd^{2+} < Zn^{2+} < Ce^{3+}$, and by the ability of mobile-phase anions to shield the outer positive charge, which follows the chaotropic series for anions $IO_3^- \approx SO_4^{2-} < Cl^- < NO_2^- < CNO^- < Br^- < NO_3^- < ClO_3^- < I^- < ClO_4^-$.

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