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Manipulation of separation selectivity of inorganic anions in electrostatic ion chromatography by the use of mixed cationic–zwitterionic micelles as the column coating solution

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Abstract

This paper describes an electrostatic ion chromatographic system in which the separation selectivity for inorganic anions, especially for sulfate and phosphate, could be manipulated by altering the molar ratio of the zwitterionic and cationic surfactants in the column coating solution used to prepare the stationary phase. The zwitterionic surfactant used for this study was 3-(*N,N*-dimethyltetradecylammonio)propanesulfonate (Zwittergent-3-14) and the cationic surfactant was tetradecyltrimethylammonium (TTA). Using a reversed-phase C₁₈ column (250×4.6 mm I.D.) coated with 10/10 (mM/mM) of TTA/Zwittergent-3-14 mixed micelles as the stationary phase and either NaHCO₃ or Na₂CO₃ aqueous solution as the eluent, together with suppressed conductivity detection, baseline separation of seven model inorganic anions was obtained. The elution order for those anions was found to be F⁻ < HPO₄²⁻ < Cl⁻ < SO₄²⁻ < NO₂⁻ < Br⁻ < NO₃⁻. Under the same conditions but using 1/10 (mM/mM) of TTA/Zwittergent-3-14 mixed micelles as the column coating solution, the elution order for these model ions was F⁻ < HPO₄²⁻ < SO₄²⁻ < Cl⁻ < NO₂⁻ < Br⁻ < NO₃⁻. The early elution of phosphate and sulfate is a unique attribute of this system. Detection limits for F⁻, HPO₄²⁻, Cl⁻, SO₄²⁻, NO₂⁻, Br⁻ and NO₃⁻ (*S/N*=3, sample injection volume 100 μl) were 0.11, 0.12, 0.12, 0.18, 0.49, 0.49, 0.52 μM, respectively. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the separation of inorganic anions using ion-

exchange chromatography [1], the divalent and multivalent analytes are usually eluted later than the monovalent species (except in the case of the samples containing very polarizable anions, such as SCN⁻ and ClO₄⁻) and typically give broad peaks. This leads to relatively poor detection limits for these species and also long analysis times. Increasing the

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concentration of the competing ion in the eluent [2,3] accelerates the elution of these ions, but also leads to increased background conductance and baseline noise, so that detection limits are often not improved.

Over recent years the authors have developed a new type of ion chromatography (IC) system which shows unique selectivity for inorganic anions [4–6]. This method, termed electrostatic ion chromatography (EIC), involves the use of stationary phases comprising a layer of a zwitterionic surfactant (in which both positively and negatively charged functional groups are in close proximity) adsorbed onto an octadecylsilica reversed-phase material. When a sulfobetaine-type zwitterionic surfactant was used to create the stationary phase and either pure water or an electrolyte solution was used as the mobile phase, the EIC system showed good resolution of monovalent anions. On the other hand, this system showed a poor ability to retain and separate the divalent and multivalent anions. Because of this, EIC has been demonstrated to be a highly useful approach to the determination of monovalent anions in the presence of divalent and/or multivalent anions [7,8]. However, EIC has not been found to be well suited to the determination of the multivalent anions themselves.

This paper utilises a new type of stationary phase which shows affinities for multivalent anions, obtained by coating the ODS stationary phase with a solution of mixed zwitterionic cationic micelles. In a preliminary study [9] we observed that by introducing a small amount of cationic surfactant to a column coating solution containing a zwitterionic surfactant, the retention of divalent anions was increased. A molar ratio of 1:10 between the cationic and zwitterionic surfactants was used, with tetraborate as the eluent. The aim of the present work has been to investigate the use of much larger molar ratios between the two surfactants, employed with stronger eluting ions (carbonate and bicarbonate), in order to ascertain whether the separation selectivity can be controlled by manipulating the molar ratio of the zwitterionic and cationic surfactants in the column coating solution. In other words, this study examines whether the same reversed-phase ODS column could be used to create a range of stationary phases of differing selectivity for the separation of anions.

2. Experimental

2.1. Apparatus

A Dionex DX500 IC system (Sunnyvale, CA, USA) was used for this study. This system comprised a GP40 pump, an AS50 autosampler with a 100- μ l injection loop, and an AD20 UV visible detector and an ED40 conductivity detector connected in tandem. The column was housed in a Waters (Milford, MA, USA) column heater operated at 30°C. A Dionex anion self-regenerating suppressor (Model ASRS) was inserted between the UV visible detector and the conductivity detector to reduce the conductance of the eluent. PeakNet 5.1 (Dionex) software was used for data collection.

2.2. Reagents

Tetradecyltrimethylammonium chloride (TTACl) was used as a typical cationic surfactant and 3-(*N,N*-dimethyltetradecylammonio)propanesulfonate (Zwittergent-3-14) was chosen as a typical zwitterionic surfactant. These two surfactants were obtained from Fluka (Buchs, Switzerland) and their purity was higher than 98%. The TTACl was converted to the hydroxide form by first loading it onto a C_{18} stationary phase and then conditioning the column with 0.1 mM NaOH solution for 2 h at a flow-rate of 1.0 ml/min. After this step, 50 ml of acetonitrile–water (50:50) solution was pumped through the column at a flow-rate of 1.0 ml/min, the effluent collected and held at 50°C in an oven for ~8 h in order to remove acetonitrile. The resultant TBAOH solution was stored in a refrigerator.

Inorganic salts used for preparing the samples and the mobile phases were of analytical-reagent grade and were obtained from Wako (Osaka, Japan). Water used throughout this study was prepared in the laboratory using a Millipore (Bedford, MA, USA) Milli-Q water purification system. The reversed-phase C_{18} columns were L-columns (250×4.6 mm I.D.; 5- μ m particle size, 120-Å pore size, 17% C/Si, 340 m²/g) and were obtained from Chemicals Evaluation and Research Institute (Tokyo, Japan).

2.3. Column preparation

The separation columns were prepared in the same manner as described in our previous study [9], namely by coating the reversed-phase column with 50 ml of the desired surfactant solution pumped through the column at a flow-rate of 1.0 ml/min. In order to maintain a constant amount of the surfactant on the stationary phase during subsequent usage and to ensure stable retention times for the analyte ions, the eluents used throughout this study contained 1.0% (v/v) of the same surfactant solution used for the coating step. Surfactant-modified columns were regenerated before re-coating by flushing with acetonitrile–water (50:50).

3. Results and discussion

3.1. Coating the column with a solution of cationic micelles

Cationic surfactants having quaternary ammonium functional groups have been used frequently to convert reversed-phase stationary phases into “permanently” or dynamically-coated materials which are suitable for the separation of anions. In the “permanent” coating method the surfactant is absent from any subsequent mobile phase and typical surfactants used for this task are hexadecyltrimethyl-

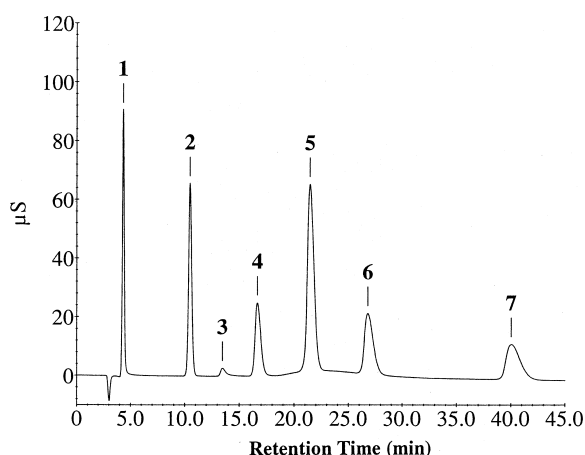


Fig. 1. Chromatogram of a mixture of F^- , HPO_4^{2-} , Cl^- , SO_4^{2-} , NO_2^- , Br^- and NO_3^- (0.1 mM each, except for HPO_4^{2-} which was present at 0.02 mM) obtained using a C_{18} column coated with TTA micelles and 25 mM Na_2CO_3 as the eluent. Detection: suppressed conductivity; sample injection volume: 100 μ l. Peaks: 1= F^- , 2= Cl^- , 3= HPO_4^{2-} , 4= NO_2^- , 5= SO_4^{2-} , 6= Br^- , and 7= NO_3^- .

ammonium (HTA), dodecyltrimethylammonium (DTA), cetylpyridinium (CP) and tetradecyltrimethylammonium (TTA) [2]. TTA was chosen as a representative cationic surfactant in the present study because its alkyl-chain was identical to that of Zwittergent-3-14. A C_{18} column pre-coated to saturation with TTA micelles was used to study the characteristics of the anion-exchange IC system, with

Table 1

Slopes of plots of $\log k'$ versus \log [eluent] for stationary phases coated with different surfactants

Analyte	TTA ^a , eluent: $NaHCO_3$ 10–50 mM	TTA, eluent: Na_2CO_3 10–30 mM	Z3-14 ^b , eluent: $NaHCO_3$ 1–20 mM	Z3-14, eluent: Na_2CO_3 1–20 mM	Z3-14/TTA (10 mM/1 mM), eluent: $NaHCO_3$ 10–50 mM	Z3-14/TTA (8 mM/2 mM), eluent: $NaHCO_3$ 6–23 mM	Z3-14/MTA (10 mM/10 mM), eluent: Na_2CO_3 20–70 mM
F^-	-0.56	-0.38	-	-	0.11	-0.46	-0.24
Cl^-	-0.60	-0.49	-	-	0.06	-0.49	-0.16
NO_2^-	-0.61	-0.46	0.11	0.29	0.03	-0.56	-0.19
Br^-	-0.55	-0.51	0.20	0.36	-0.13	-0.67	-0.14
NO_3^-	-0.61	-0.39	0.27	0.37	-0.89	-0.56	-0.18
HPO_4^{2-}	-0.98	-	-	-	0.24	-1.11	-0.84
SO_4^{2-}	-1.08	-1.15	-	-	0.23	-1.22	-0.82
I^-	-	-	0.50	0.51	-	-	-

^a TTA, tetradecyltrimethylammonium (TTA).

^b Z3-14, 3-(*N,N*-dimethyltetradecylammonio)propanesulfonate.

aqueous NaHCO_3 and Na_2CO_3 solutions as the eluents, and suppressed conductivity detection. Fig. 1 shows the separation of 0.1 mM each of F^- , Cl^- , NO_2^- , Br^- , NO_3^- , SO_4^{2-} and 0.02 mM HPO_4^{2-} (the counterion was Na^+) using 25.0 mM Na_2CO_3 as the eluent. All analytes were separated and F^- was resolved completely from the water-dip. The elution order for these analyte ions was $\text{F}^- < \text{Cl}^- < \text{NO}_2^- < \text{Br}^- < \text{HPO}_4^{2-} < \text{NO}_3^- < \text{SO}_4^{2-}$ for the NaHCO_3 eluent and $\text{F}^- < \text{Cl}^- < \text{HPO}_4^{2-} < \text{NO}_2^- < \text{SO}_4^{2-} < \text{Br}^- < \text{NO}_3^-$ for the Na_2CO_3 eluent, with these retention orders being typical of that shown for anion-exchange stationary phases having chemically-bound functional groups. Very polarizable analytes (e.g. I^- and SCN^-) were not eluted from the TTA-coated column even when the effluent was monitored for more than 20 h.

The concentrations of NaHCO_3 and Na_2CO_3 in the eluents were varied and the retention data used to make plots of $\log k'$ versus $\log [E]$ (where E denotes the eluting ion). Straight lines were observed for all of the analyte anions and the slopes of these plots are listed in Table 1. Negative slopes in the range -0.56 to -1.08 (for NaHCO_3 eluents) and -0.38 to -1.15 (for Na_2CO_3 eluents) were observed, with these values being typical for fixed-site ion-exchangers. These results indicated that the retention of the analytes on the TTA-coated stationary phase occurred predominantly by a conventional anion-exchange mechanism.

3.2. Coating the column with a solution of zwitterionic micelles

The use of C_{18} columns coated with sulfobetaine-type zwitterionic surfactant has been used by the present authors for IC of anions [4–6]. These sulfobetaine zwitterionic surfactants contain a quaternary ammonium group (positively charged group) and a sulfonate group (the negatively charged group) fixed in close proximity to each other. Columns obtained by coating with this type of zwitterionic surfactants showed good retention of monovalent anions (except for F^-), but very little or no retention of the divalent and multivalent anions. Other monovalent analyte ions were baseline separated and were eluted with reasonable retention times. Plots of $\log k'$ versus $\log [E]$ for the EIC system were obtained and

were again linear, but with positive slopes being observed for all analytes (Table 1), indicating that a mechanism other than ion-exchange was operative. It should be noted that a UV detector was used for these plots, so only the UV-absorbing analytes were plotted.

3.3. Coating the column with a solution of mixed zwitterionic–cationic micelles

Three Zwittergent-3-14/TTA mixed micellar solutions were prepared with different molar ratios of these two surfactant species and were used as the column coating solutions. The molar ratios of Zwittergent-3-14/TTA in these mixed micellar solutions were 10:1, 8:2, and 10:10 (mM/mM), respectively, and in each case the same C_{18} column was used and was coated to saturation with the mixed micelles. Separation of the same mixture of anions used in Fig. 1 was undertaken and showed that with the Zwittergent-3-14/TTA ratio of 10:10, the divalent analytes (SO_4^{2-} and HPO_4^{2-}) were well retained (a typical chromatogram obtained with a Na_2CO_3 eluent is shown in Fig. 2). When the molar ratio of Zwittergent-3-14/TTA in the column coating solutions was increased to 10:1 and 8:2, the divalent anions were eluted even earlier than chloride.

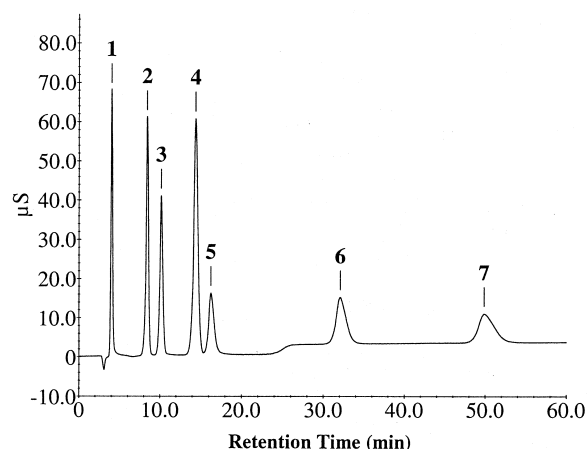


Fig. 2. Chromatogram of mixture of F^- , HPO_4^{2-} , Cl^- , SO_4^{2-} , NO_2^- , Br^- and NO_3^- (0.1 mM each) obtained using a C_{18} column coated with Zwittergent-3-14/TTA (10 mM/10 mM) mixed micelles and 20.0 mM Na_2CO_3 as the eluent. Other conditions were as described in Fig. 1. Peaks: 1= F^- , 2= HPO_4^{2-} , 3= Cl^- , 4= SO_4^{2-} , 5= NO_2^- , 6= Br^- , and 7= NO_3^- .

Polarizable anions (not included in Fig. 2) could be eluted at long retention time.

To evaluate the separation mechanism involved in this system, plots of $\log k'$ versus $\log [E]$ were constructed and the slopes of the resultant plots are listed in Table 1. When mixed micelles having a molar ratio of 10:1 of Zwittergent-3-14/TTA were used as the column coating solution, the slopes for F^- , Cl^- , NO_2^- , SO_4^{2-} and HPO_4^{2-} were positive, indicating that the electrostatic IC mechanism [4–6] was the chief contributor to the separation of these ions. For Br^- and NO_3^- , the slopes were negative, indicating that an anion-exchange mechanism contributed substantially to the separation of these species. For the molar ratios of 8:2 and 10:10, the slopes for all of the model analyte anions were negative. Analysis of the slopes for SO_4^{2-} and HPO_4^{2-} leads to the conclusion that these divalent anions were separated predominantly by an anion-exchange mechanism. In addition, the smaller slopes for the monovalent anions compared to those obtained using TTA alone suggest that these ions were separated by a dual mechanism comprising both the electrostatic attraction/repulsion interactions of EIC and anion exchange.

3.4. Analytical data

The column prepared using the 10:10 Zwittergent-3-14/TTA as the coating solution was used to evaluate the analytical performance data of the system. Baseline separation of F^- from the water-dip was facilitated if the coating solution contained >20% (on a molar basis) of the cationic surfactant. The eluent used was 20.0 mM Na_2CO_3 and suppressed conductivity was employed for detection of the analyte ions. The detection limits for F^- , HPO_4^{2-} , Cl^- , SO_4^{2-} , NO_2^- , Br^- and NO_3^- ($S/N=3$, sample injection volume of 100 μ l) were 0.11, 0.12, 0.12, 0.18, 0.49, 0.49, 0.52 μ M, respectively. The linear calibration range ($r^2>0.998$) for all of the model analyte ions extended up to at least 8.0 mM. Recoveries of the model analyte anions added to a tap water sample at the 10–50- μ M level were >99.2% for all of the analytes. The relative standard deviation (RSD) of retention time and peak heights and peak areas for the standard sample containing 0.1 mM each of the model analyte ions was also

evaluated by analysis of this sample 15 times under the same conditions and RSD values for all analytes were less than 0.45%.

As a practical application, the system was used to analyze inorganic anions in tap water in which the levels of F^- , SO_4^{2-} , and Cl^- were found to be 0.09, 0.11, and 0.28 mM, respectively. The same tap water sample was also analyzed using a conventional anion-exchange IC system and the concentrations for F^- , SO_4^{2-} , and Cl^- were found to be 0.09, 0.10, and 0.29 mM, respectively.

4. Conclusions

Stationary phases formed from an adsorbed coating of zwitterionic–cationic mixed micelles (at a molar ratio of ≥ 0.2) could be used for the separation of anions by a mixture of anion-exchange (provided by the cationic surfactant) and electrostatic attraction/repulsion (provided by the zwitterionic surfactant). Divalent analyte anions were eluted rapidly and by simply varying the molar ratio of the two surfactants in the column coating solution their elution order could be manipulated easily. Increasing the mole fraction of the cationic surfactant in the coating solution required the use of more concentrated eluents and also resulted in longer retention times, with both factors leading to increased detection limits. Thus, the ability to manipulate separation selectivity is achieved at the cost of reduced sensitivity. The ODS column used to support the surfactant stationary phase in this study is not suitable for long-term use with the alkaline eluents employed and more pH-resistant columns (such as polymeric or graphitised carbon) would be necessary for routine application of the methods described. Finally, the mixed zwitterionic–cationic micelles used as the stationary phase in this paper might provide valuable insight for the development of chemically bonded ion-exchange resins of unique separation selectivity.

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