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Controlled changes of selectivity in the separation of ions by capillary electrophoresis

W. R. JONES* and P. JANDIK
Ion Analysis Department, Waters Chromatography Division of Millipore, 34 Maple Street, Milford, MA 01757 (U.S.A.)

ABSTRACT

The selectivity of low-molecular-weight inorganic and organic anions is evaluated on a capillary electrophoresis system utilizing a negative power supply and indirect UV detection at 254 nm. The background electrolyte chromate was found to be most useful for highly mobile inorganic anions and short chain carboxylates. Incorporated in this electrolyte is an additive that reverses the direction of electroosmotic flow (EOF) in the capillary, so that the EOF augments the mobility of the analytes. This results in exceedingly short analysis times, under 5 min, with efficiencies aproaching 600 000 theoretical plates. From migration time data, a correlation between ionic equivalent conductance and analyte mobility in the electrolyte is established. This empirical correlation equation aids in the prediction of migration order (selectivity) of a separation.

Other parameters evaluated on the chromate electrolyte are ionic strength, pH and EOF modifier concentration. It was found that pH and the EOF modifier provided significant selectivity control over the analytes while the other electrolyte parameters permitted only subtle changes in selectivity.

INTRODUCTION

Currently the most prevalent methodology employed for the analysis of low-molecular-weight inorganic and organic anions is ion chromatography (IC). This technique, introduced in the seventies [1,2], uses low-capacity anion-exchange columns for separation and conductivity as the "universal" mode of detection for ions. Originally developed to analyze several inorganic anions such as fluoride, chloride and sulfate, IC has expanded to encompass a variety of mono-, di- and trivalent inorganic and organic anions. These expanding requirements necessitated an increase in sophistication of IC hardware and chemistry. Specialty columns combined with either gradient elution or coupled separation systems are the most common approaches to maximize the peak capacity of analysis [3,4]. Increased system complexity stems from the limited selectivity and efficiency of anion-exchange columns. For most isocratic anion-exchange separations short-chain monocarboxylic acids coelute with early eluting anions such as fluoride and chloride, while trivalent anions (*e.g.*, citrate) require gradient elution for a reasonable analysis time.

In contrast to that, capillary electrophoresis (CE) separates ions according to their mobility in the electrolyte rather than by an interaction with a stationary phase and correspondingly the early detected anions are small inorganic mono- and divalent

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anions, while the later migrating anions are organic species with a larger Stokes radii. Separation efficiency in a capillary, unlike in a packed column, depends upon the applied field strength (V cm^{-1}) and not on capillary length [5]. It is optimized through use of small-I.D. capillaries for greater dissipation of Joule heating with high running voltages.

Eqn. 1 describes the Giddings [6–8] relationship between the maximum number of peaks that can be resolved (peak capacity n) and the column efficiency as measured by the theoretical plates (N):

$$n = 1 + 0.25 [N^{1/2} \ln (V_x/V_0)] \quad (1)$$

V_0 and V_x are the initial and final volume of an available retention range on any given chromatographic separation device. Eqn. 1 allows us to compare the peak capacity of a commonly used anion-exchange column with that of a fused-silica capillary. Using Fig. 1 for obtaining V_x/V_0 ratio we observe that both IC and CE separations have peaks beginning and ending in the range of 1.4 to 3.1 min. The Waters IC-Pak A column (upper separation trace) yields $N = 1500$ while the average plate count for CE using Waters AccuSep fused-silica capillary (bottom separation) is $N = 300\ 000$. This results in $n = 9$ for IC and 110 for CE. For randomly distributed single analyte peaks (n_r), theory [8] shows that this value never exceeds 18% of n. This leaves a peak capacity of 2 for anion-exchange and 20 for CE. The theoretically obtained n_r values are in good agreement to the 3 and 30 peaks observed for IC and CE, respectively (see Fig. 1). CE thus shows a ten-fold increase in peak capacity over a conventional anion-exchange column. The highest efficiency achieved in the CE separation in Fig. 1 is 568 350 plates by the W_{TAN} method (tangent method) [9] for peak 1 belonging to thiosulfate. Fig. 2 shows peak 1 in an expanded view of a 15-s range together with the first 9 peaks of the

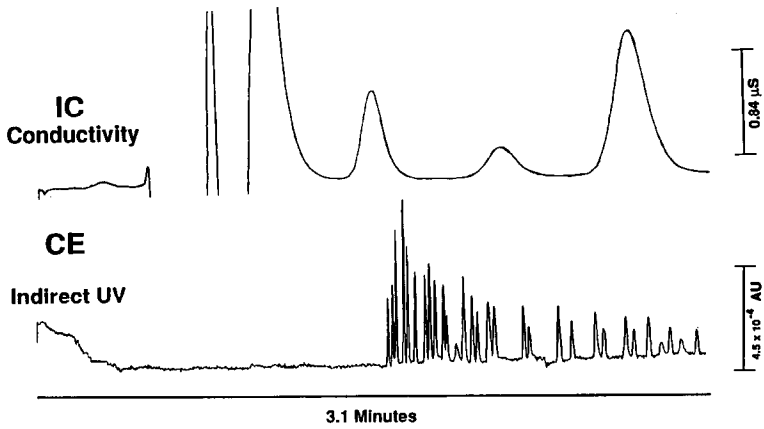

Fig. 1. Comparison of first 3.1 min of an IC separation *vs.* a CE separation. IC chromatogram (top) separates only 3 anions, fluoride, carbonate and chloride (last three peaks) using a Waters IC-Pak A, borate–gluconate eluent at 1.2 ml/min and Waters 431 conductivity detection. A detailed description of this separation system is given in refs. 3, 4 and 10. The negative and positive peaks found prior to the three anions are the water dip and excluded cations, respectively. The electropherogram (bottom) separates 30 anions using Waters AccuSep fused-silica capillary, chromate high-mobility electrolyte at 30 kV and indirect UV detection at 254 nm.

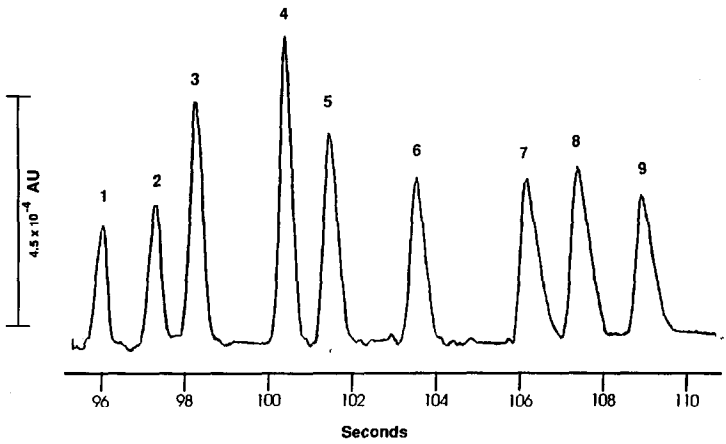

Fig. 2. Close view of the first 9 peaks of the 30-anion electropherogram shown in Fig. 1. High separation efficiency enables baseline resolution of all anions shown in this 15-s electropherographic segment.

30-anion electropherogram. Note that the peaks are baseline resolved with sufficient space for 3 additional peaks of comparable height to be placed in the gaps. CE appears to offer an unprecedented level of analysis power unapproachable by today's IC.

EXPERIMENTAL

Instrumentation

The CE system employed was the Quanta 4000 (Water Chromatography Division of Millipore, Milford, MA, U.S.A.) with a negative power supply and an Hg lamp for 254-nm detection. Waters AccuSep polyimide-coated fused-silica capillaries are used throughout this work. The capillary dimensions were 60 cm total length with 52 cm distance from point of injection to the detector cell. Both 50 and 75 μm I.D. capillaries were used. Data acquisition was carried out with a Waters 840 data station and a System Interface Module (SIM) interface. Detector time constant was set at 0.1 s and data acquisition rate was 20 points/s. Collection of electropherographic data was initiated by a signal cable connection between the Quanta 4000 and the SIM.

Preparation of chromate-based background electrolytes

The chromate electrolytes were prepared from a concentrate containing 100 m*M* Na_2CrO_4 (Mallinckrodt analytical-reagent grade) and 0.69 m*M* H_2SO_4 (J. T. Baker, Ultrex grade, Phillipsburg, NJ, U.S.A.). The dilute sulfuric acid is added to the chromate concentrate to preadjust the electrolyte pH to 8.0 when preparing the carrier electrolyte of 5 m*M* chromate with 0.5 m*M* electroosmotic flow (EOF) modifier. Milli-Q reagent-grade water (Millipore, Bedford, MA, U.S.A.) was used for rinsing and dilution of concentrates. EOF modifier for the reversal of the direction of electroosmotic flow was obtained as a 20 m*M* concentrate from Waters (NICE-Pak OFM Anion-BT[a]). A 100 m*M* NaOH solution was used to adjust the pH of the chromate electrolyte for the pH study.

[a] Patent applied for.

Standard solutions

All standard mixtures were prepared by a dilution of 1000-ppm stock solutions containing a single anion. The stock solutions were prepared fresh every six months and were stored in 200-ml polycarbonate tissue culture flasks (Corning Glass Works, Corning, NY, U.S.A.). All 20-ppm or lower concentration mixed anion standards were prepared freshly for each of the experiments. Milli-Q water and polymethylpentene containers (Nalgene, Rochester, NY, U.S.A.) were used throughout.

System operation

The CE system incorporates two modes of sample entry into the capillary —hydrostatic and by electromigration. All injections for the electrolyte studies were performed in the hydrostatic mode where the capillary was immersed in the sample at a height 10 cm above the running electrolyte level for 30 s. Upon lowering the sample to the 0 cm level the capillary was removed from the sample and the loaded capillary was immersed in the running electrolyte with the voltage ramping up to 20 kV. Electromigration is used only for the electropherogram in Figs. 1–3. Here the cathode and capillary were immersed in the sample at the 0 cm level with an applied voltage of 1 kV for 15 s prior to running the analysis. A 2-min capillary purge is performed prior to all injections. This operation removes the remaining constituents (*i.e.*, water peak) of the last sample from the capillary. The purge is accomplished by a 12 to 15 p.s.i. vacuum applied to the receiving electrolyte vial. Each sample in the carousel has its own electrolyte vial.

RESULTS AND DISCUSSION

Peak capacity

The electropherogram from Figs. 1 and 2 is shown in Fig. 3 as an 89-s segment encompassing the first and last peaks for proper identification. This separation utilizes the same chromate (high mobility) electrolyte described earlier by the authors [10]. However, the previous separation utilized 20 kV and a 75 μm I.D. capillary. The use of a 50 μm I.D. capillary with 30 kV running voltage has improved the plate count in this investigation by a factor of 2. The trade-off for higher efficiency is lower sensitivity. This is due to smaller injection volumes for the same loading time and shorter optical path length of the detector cell which is formed by the capillary. The authors, however, have successfully employed electromigration as a mode of sample enrichment giving detection limits below the ppb (10^9) threshold [11].

Analyte mobility and ionic equivalent conductance

The migration times (T_m) from the electropherogram in Fig. 3 are plotted against the ionic equivalent conductance values obtained from the literature [12,13]. Fig. 4A shows the individual points scattered along the line obtained by a second-order polynomial curve fit with a correlation coefficient $R^2 = 0.967$. A trend does exist but prediction of the actual migration sequence by placing the ionic equivalent conductance values in descending order only approximates the region in which the anions are likely to be found. Fig. 4B shows only the migration times (T_m) of more hydrophilic monovalent anions plotted against their ionic equivalent conductance. Here the curve fit is improved to $R^2 = 0.993$. Plotting and curve fitting the divalent anions as

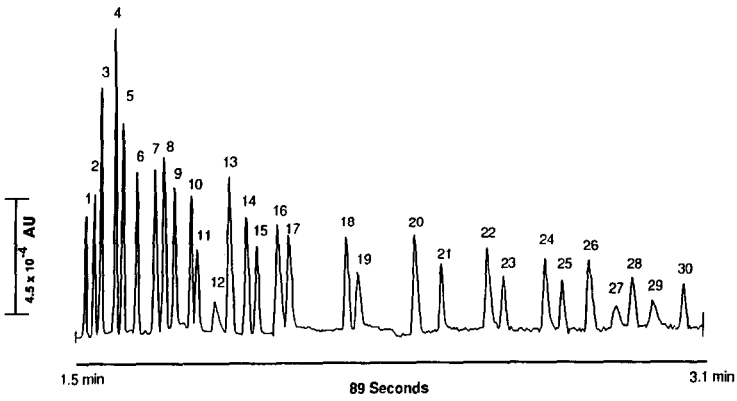

Fig. 3. Peak identity and concentrations (ppm) for 30-anion electropherogram displayed in an 89-s electropherographic segment. Electromigration injection at 1 kV for 15 s. Peaks: 1 = thiosulfate (4); 2 = bromide (4); 3 = chloride (2); 4 = sulfate (4); 5 = nitrite (4); 6 = nitrate (4); 7 = molybdate (10); 8 = azide (4); 9 = tungstate (10); 10 = monofluorophosphate (4); 11 = chlorate (4); 12 = citrate (2); 13 = fluoride (1); 14 = formate (2); 15 = phosphate (4); 16 = phosphite (4); 17 = chlorite (4); 18 = galactarate (5); 19 = carbonate (4); 20 = acetate (4); 21 = ethanesulfonate (4); 22 = propionate (5); 23 = propanesulfonate (4); 24 = butyrate (5); 25 = butanesulfonate (4); 26 = valerate (5); 27 = benzoate (4); 28 = L-glutamate (5); 29 = pentanesulfonate (4); 30 = D-gluconate (5). The electrolyte is a 5 m*M* chromate and 0.5 m*M* EOF modifier adjusted to pH 8.0.

a separate group Fig. 5A, we see that all the divalents are consistently slower than their ionic equivalent conductance values would indicate. The trivalent anion citrate is shifted by approximately an equal amount from the divalents as these are from the monovalent anions. Such dependence upon ionic charge or valence state is very consistent. It indicates that the anions are being slowed down, possibly by wall charge. For this to occur the wall charge must be positive which is apparently the case with the electroosmotic flow modifier in the electrolyte [5]. Reducing the divalent anions ionic equivalent conductance values by 5 S cm^2 equiv.$^{-1}$ and the trivalent anion by 10 S cm^2 equiv.$^{-1}$ helps to eliminate what is assumed to be the wall interaction of the divalent and trivalent anions as shown in Fig. 5B. The correlation coefficient of the second-order polynomial curve fit is now 0.992, an improvement from 0.967. Included in Fig. 5B, but not in the correlation, are the known hydrophobic anions iodide, thiocyanate and perchlorate. These monovalent species have very long retention times on resin based anion exchange columns, far in excess of what their valence charge would indicate. This behavior is usually attributed to the relatively lipophilic character of these anions and to the fact that their retention is mostly due to reversed-phase effects rather than to ion exchange [14]. The lipophilic character of iodide, thiocyanate and perchlorate plays a significant role in CE as well. This is discussed in more detail in one of the following sections of this article. As shown in Fig. 6 for a number of highly mobile anions, the relationship between the ionic equivalent conductance and migration times is essentially linear. The vertical dashed line indicates the projected migration time for hydroxide ions from such linear dependency. At migration times longer than *ca.* 1.8 min the linear relationship no longer applies and is replaced by a second-order exponential curve to approximate the assumed influence of wall

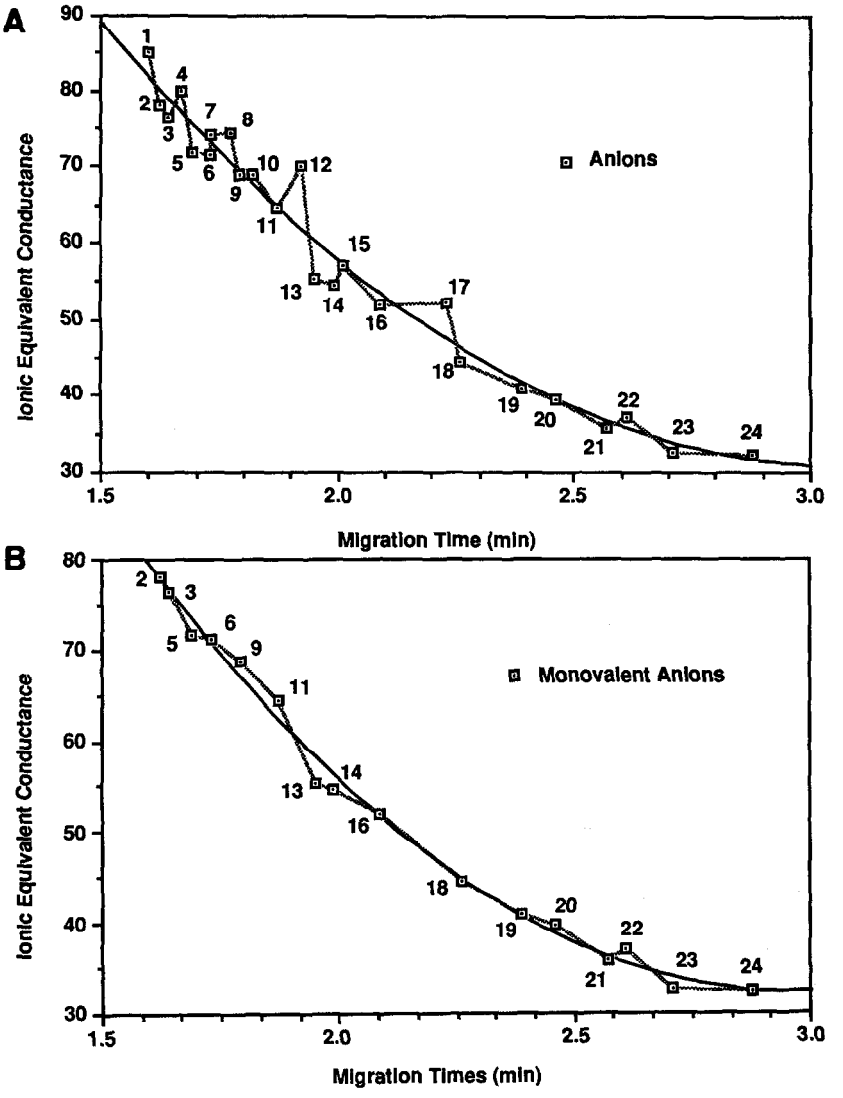

Fig. 4. (A) Migration times of some anions from Fig. 3 plotted against their respective ionic equivalent conductance obtained from the literature [12,13]. The ionic equivalent conductance values for the prevalent ionic form at pH 8 were chosen for this plot (*i.e.*, bicarbonate and not carbonate etc.). $y = 253.91 - 145.48\ x + 23.724\ x^2$; $R^2 = 0.967$. (B) Migration times of the more hydrophilic, monovalent anions separated in Fig. 3 are plotted against ionic equivalent conductance values. Second-order polynomial curve fit is noticeably improved by exclusion of the polyvalent anions. $y = 254.15 - 149.75\ x + 25.270\ x^2$; $R^2 = 0.993$ *versus* 0.967 in (A). 1 = Thiosulfate; 2 = bromide; 3 = chloride; 4 = sulfate; 5 = nitrite; 6 = nitrate; 7 = oxalate; 8 = molybdate; 9 = azide; 10 = tungstate; 11 = chlorate; 12 = citrate; 13 = fluoride; 14 = formate; 15 = phosphate; 16 = chlorite; 17 = phthalate; 18 = carbonate; 19 = acetate; 20 = ethanesulfonate; 21 = propionate; 22 = propanesulfonate; 23 = butyrate; 24 = benzoate.

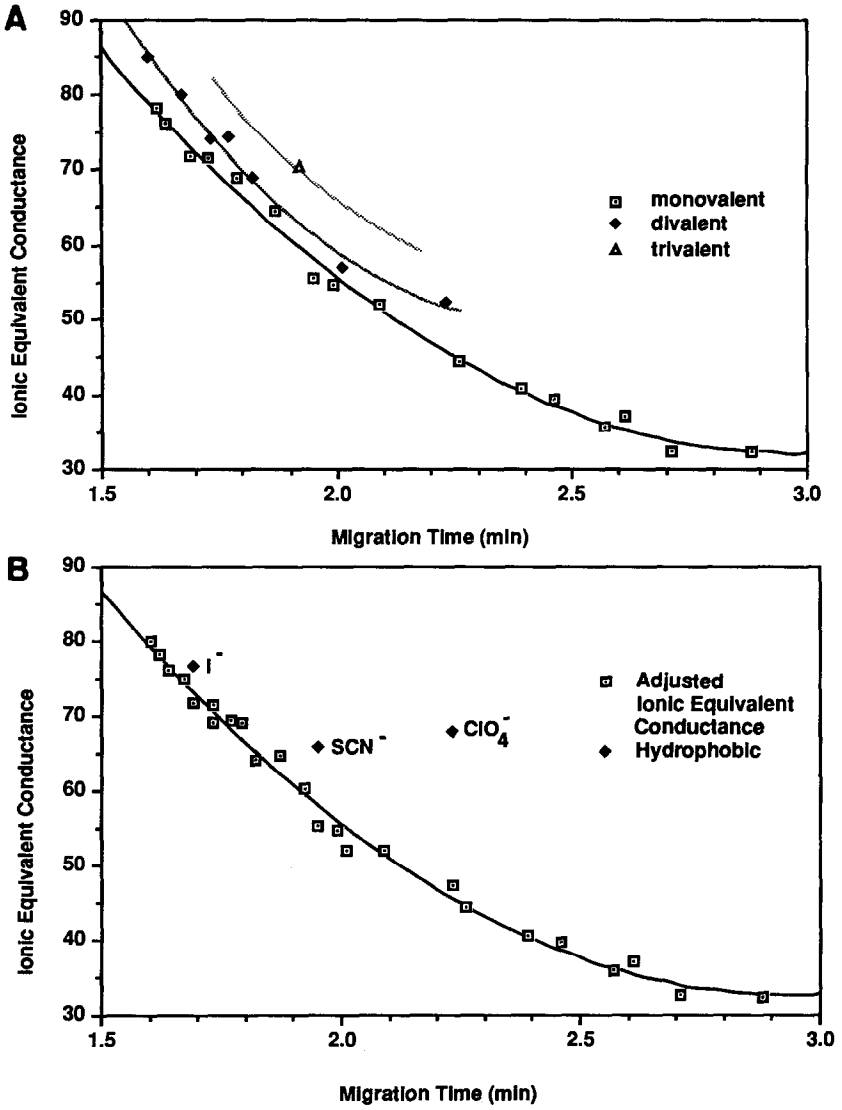

Fig. 5. (A) Migration times of anions plotted against ionic equivalent conductance values with individual second-order polynomial curve fits calculated separately for monovalent and divalent anions. The curve shown for the trivalent anion citrate was chosen to have a similar shape from the behavior of the mono- and divalent anion data. Upper curve: $y = 370.19 - 266.63\,x + 55.532\,x^2$; $R^2 = 0.989$; lower curve: $y = 254.15 - 149.75\,x + 25.270\,x^2$; $R^2 = 0.993$. (B) Migration times of the more hydrophilic mono-, di- and trivalent anions plotted against the adjusted ionic equivalent conductance values (see eqn. 2). $y = 258.79 - 154.26\,x + 26.312\,x^2$; R^2 is improved to 0.992 from the original value of 0.967 obtained from the unadjusted ionic equivalent conductance data found in Fig. 4. The more hydrophobic anions iodide, thiocyanate and perchlorate are also shown, but are not included in the curve fit. A separate ionic equivalent conductance adjustment to account for hydrophobic character is called for to normalize the migration times of lipophilic anions.

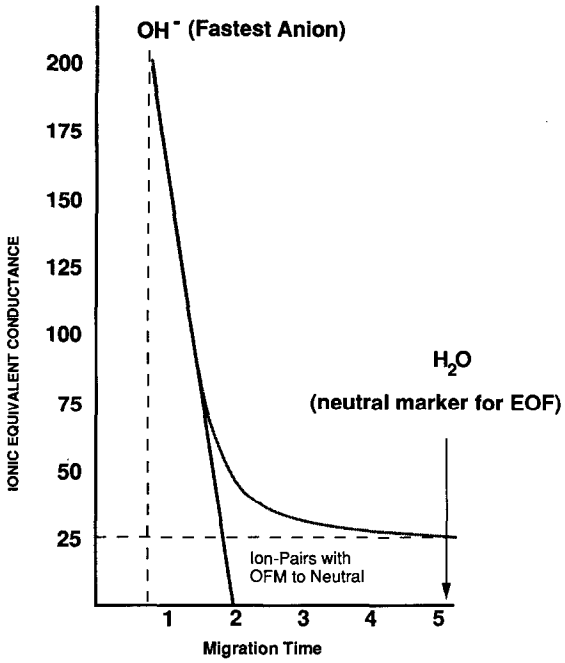

Fig. 6. This graph represents the migration time *vs.* the ionic equivalent conductance values for the entire range of mobilities found for anions in the chromate electrolyte from hydroxide to neutral water. No anion faster than hydroxide will be found to the left of the dashed vertical line and no anion will be found below the dashed horizontal line due to assumed ion pair formation with the electroosmotic flow modifier (OFM). See the corresponding discussion in the text.

interactions and ion pairing. The best fit for complete set of experimental data is given by the empirical eqn. 2:

$$\Lambda_{adj} = 258.79 - 154.26\ T_m + 26.312\ T_m^2, \quad (2)$$

where Λ_{adj} = ionic equivalent conductance $- 5(V - 1)$, V is the ionic charge of an analyte and T_m the migration time. Without polyvalent adjustment (ionic equivalent conductance to Λ_{adj}) the prediction of migration sequence is only 59% correct, with adjustment 78% correct. Individual linear adjustments for ionic equivalent conductance are required for lipophilic interactions to normalize the hydrophobic anions. Practical usefulness of eqn. 2 would be limited without a good precision of migration times. With 15 consecutive hydrostatic injections of an eight-anion standard the T_m relative standard deviation (R.S.D.) ranged from 0.331 to 0.751%. Normalizing T_m with respect to bromide, the first peak of the separation, yields an R.S.D. range of 0 to 0.422% with an average of 0.099%. It can be concluded that the reproducibility of EOF of the electrolyte is quite consistent and comparable to the reproducibility of flow-rates in high-performance liquid chromatography. Note that the EOF for a 50 μm I.D. capillary at 30 kV, using the reference chromate electrolyte (5 mM chromate, 0.5 mM EOF modifier) is 0.2 μl/min with a linear velocity of 10.2 cm/min.

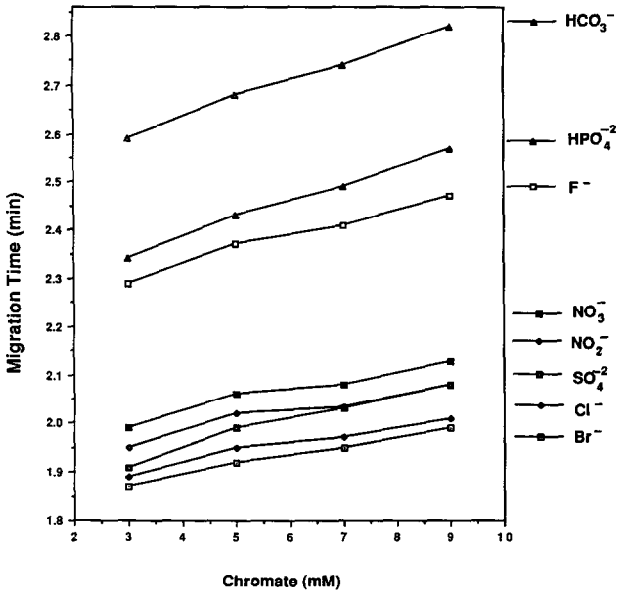

Fig. 7. Increases of chromate concentration in an electrolyte containing 0.5 m*M* EOF modifier *vs.* migration times; pH value is kept constant at 8.0. Plotted are migration times of eight common anions. Sulfate exhibits a subtle selectivity change of increasing migration time as chromate electrolyte concentration increases.

For a 75 μm I.D. capillary at 20 kV using the same electrolyte the EOF is 0.32 μl/min and linear velocity is 7.42 cm/min.

Influence of ionic strength on selectivity in chromate electrolytes

Ionic strength of the background electrolyte plays three different roles in the CE separations. Firstly, increasing concentration of background electrolyte decreases the EOF, secondly it increases efficiency due to higher field strength [5] and thirdly it yields subtle but important selectivity changes as shown in Fig. 7. Here the chromate concentration is varied while keeping the EOF modifier at 0.5 m*M* and pH at 8.0. It is seen that the sulfate anion begins to comigrate with the nitrite anion at higher chromate concentrations.

pH of chromate electrolytes and selectivity

The effect of electrolyte pH on analyte mobility is predictable and most pronounced for weakly acidic anions [15]. Eight anions plus borate were evaluated using a 5 m*M* chromate–0.5 m*M* EOF modifier with a pH starting at 8.0 and increasing in increments of 0.5 pH units to 12. The T_m values of the more strongly acidic anions with pK_a below 8 are unaffected by electrolyte pH changes between pH 8 and 10 (Fig. 8). Borate, carbonate and phosphate, on the other hand, exhibit a gradually increasing mobility (shorter T_m) as the pH of the electrolyte increases. As expected [15], the shape of the dependency (T_m *vs.* pH) resembles a pH titration curve. Fluoride and phosphate are best resolved at pH 8 with a total comigration occurring from 9.5 to

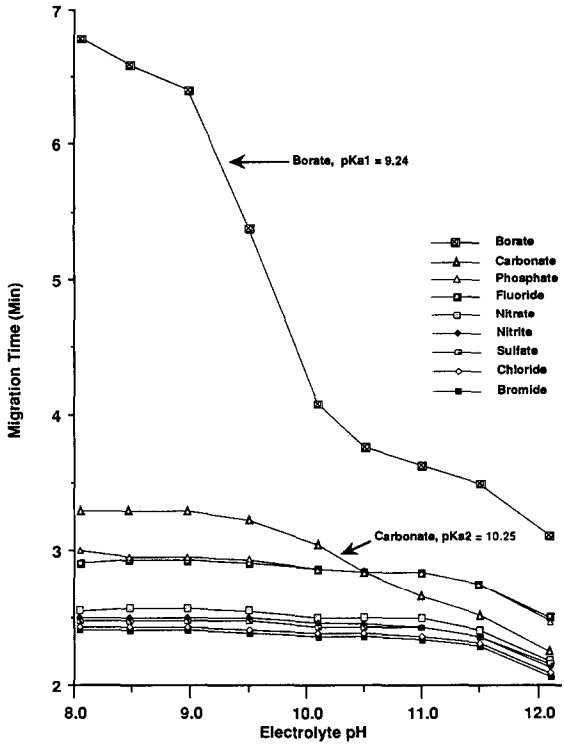

Fig. 8. The migration times of nine anions are plotted against the pH of the electrolyte 5 m*M* chromate–0.5 m*M* EOF modifier. Weak acids such as borate, carbonate and phosphate exhibit increasing ionization as the pH increases and correspondingly the migration times for these weak acids decreases in going from alkaline to more acidic pH values.

11.5. Above pH 11.5 phosphate begins to approach its third pK_a and moves ahead of fluoride. Carbonate comigrates with fluoride and phosphate at pH 10.5. As it converts to its dibasic form above pH 12 it eventually migrates just after nitrate. Interestingly, even a partial ionization is sufficient to give an analyte a higher mobility than that of neutral water peak migrating at 7 min in the chromate electrolyte and 0.5 m*M* EOF modifier. This is exemplified by borate with first pK_a at 9.24. Borate, a Lewis acid [16], is found in mildly alkaline solutions as $B(OH)_4^-/B(OH)_3$ exhibiting anomalous CE peak symmetry contrary to that predicted by Mikkers *et al.* [17]. As long as there is boric acid in the borate–boric acid mixtures (pH 8 to 10.5) the CE peak for borate shows fronting rather than the anticipated tailing. This fronting increases as the electrolyte pH approaches the first pK_a of 9.24. The tailing predicted by theory occurs only at pH values greater than 10.5 (see Fig. 9). The explanation for this unusual behavior can be derived from the fact that the borate anion is in transition between two valence states: at pK_{a1} 50% is $B(OH)_3$ and 50% is $B(OH)_4^-$. To be consistent with the electrophoretic diffusional process described by Mikkers *et al.* [17], the borate must be moving faster than the chromate electrolyte. Since borate is a Lewis acid it forms a polar bond with hydroxide ions which are in a relative surplus as the electrolyte pH is

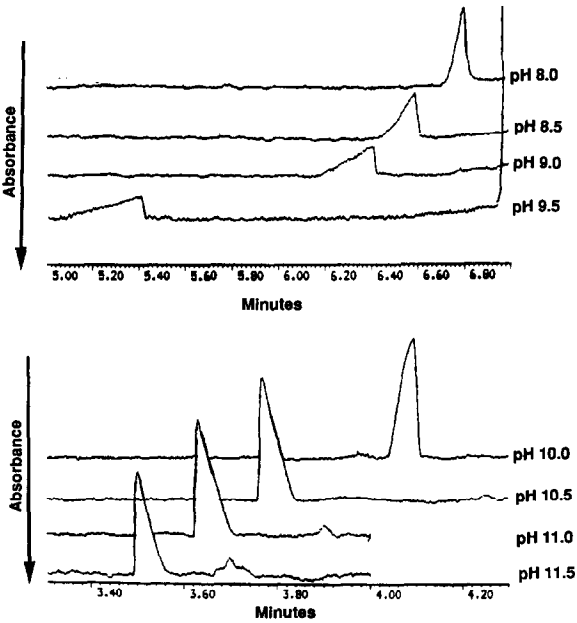

Fig. 9. Borate exhibits "anomalous" peak assymmetries. Fronting is observed as the electrolyte pH approaches the first pK_a. Peak tailing predicted by theory [ionic equivalent conductance (borate) < ionic equivalent conductance (chromate)] occurs only after the electrolyte pH increases beyond the first pK_a of borate.

increased. It is thus likely that borate acquires an increased "apparent" mobility from its association with a hydroxide ion (OH^- is the fastest anion in solution, with an ionic equivalent conductance of 198 S cm^2 $equiv.^{-1}$). Once the pH of the electrolyte is sufficiently higher than pK_{a1} of borate, the predominant form is $B(OH)_4^-$, which is no longer in transition and exhibits peak symmetry consistent with Mikkers *et al.* The relatively long T_m of borate and its unusual peak symmetry behavior make this anion an ideal indicator of electrolyte pH, if spiked into samples where a particular pH is required for resolution of closely migrating analytes.

Unexpectedly, an even weaker acid silicate was identified in the electropherogram (see Fig. 10) at electrolyte pH 11.0. The observed silicate was found to be an extractable from the borosilicate glass vial containing the standard. It is thus important to use polypropylene or polycarbonate vials as sample containers with elevated pH electrolytes.

Selectivity variations due to changing concentrations of EOF modifier

The EOF modifier reverses the natural direction of flow observed in fused-silica capillaries filled with mildly acidic or alkaline electrolytes. The modifier utilized in our experiments is an alkylammonium compound which is electrostatically attracted to the silanol groups on the inner wall of the capillary. It effectively shields these negative charges from the bulk of the electrolyte and creates a net positive wall charge. Without the addition of this modifier it is not possible to analyze highly mobile inorganic and

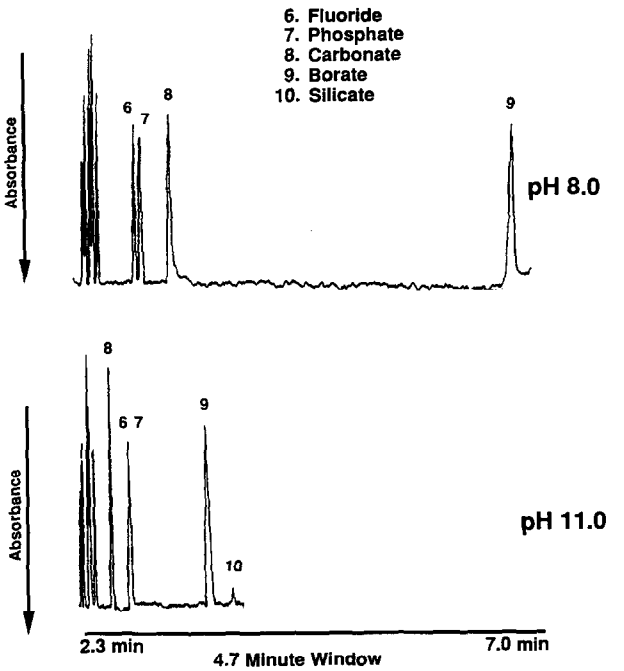

Fig. 10. Significant selectivity differences are observed for borate and carbonate as the electrolyte pH increased from 8 to 11. Peak 10 is due to silicate inadvertantly extracted from the borosilicate glass of the vial containing the sample.

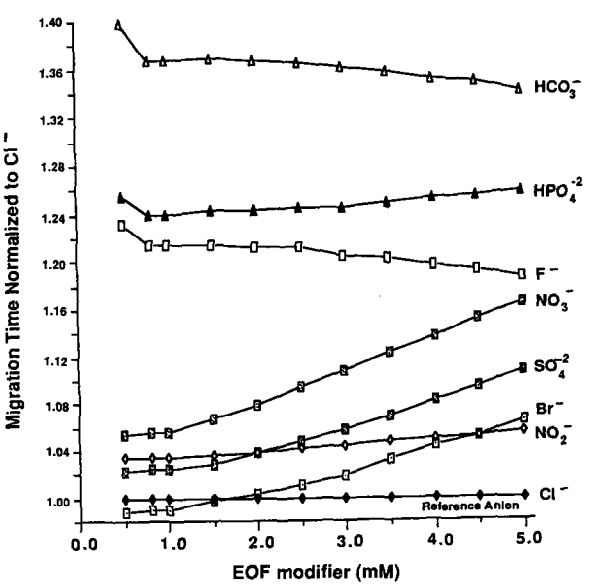

Fig. 11. Increasing EOF modifier concentration *vs.* migration times normalized with respect to chloride. The electrolyte contained 5 m*M* chromate. Bromide, sulfate and nitrate showed decreased mobility with increases EOF modifier concentration, this was attributed to ion pairing between the modifier and the analyte.

less mobile organic anions in a single run. The magnitude of the naturally occurring EOF is greater than the mobility of the majority of organic anions and some inorganic anions. Only the fastest anions such as thiosulfate, bromide and chloride would reach the detector within 30 min using 5 m*M* chromate electrolyte pH 8.0 at 30 kV. The main advantage of the EOF modifier used in this study is its ability to remain in solution with various background electrolytes (chromate included) and to contribute little to the running current of the electrolyte. Most importantly, the EOF modifier provides a stable rate of EOF, as is evident by the R.S.D. of migration times discussed in one of the preceding sections of this report, without any negative effect on the efficiency of the separation. Increasing the concentration of EOF modifier above 0.5 m*M* does not appreciably change the magnitude of the reversed EOF but does change the selectivity for three of the eight anions, namely bromide, sulfate and nitrate. Fig. 11 shows the plot of concentrations of EOF modifier *vs.* the T_m values normalized with respect to chloride.

A possible explanation of this effect involves ion pairing between the three anions and EOF modifier. This is supported by measurements comparing the conductivities of various salt forms of the EOF modifier. As an example, chloride with a lower ionic equivalent conductance than bromide would be expected to give a lower total conductivity in its salt with EOF modifier in comparison with bromide. However, our measurements have shown that in reality chloride salt is significantly more conductive than an equimolar concentration of the bromide form, suggesting that bromide unlike chloride is undergoing ion pairing with the EOF modifier. And correspondingly, the bromide and not chloride exhibits a pronounced dependency of its T_m on the concentration of EOF modifier in carrier electrolytes.

CONCLUSIONS

CE for low-molecular-weight inorganic and organic ions appears to offer a significant improvement over IC in efficiency and analysis time. Also the selectivity of the separation is predictable and can be correlated with the ionic equivalent conductances of the analytes. Variations in selectivity and resolution are achieved by modifications of the electrolyte composition —*i.e.*, the concentration of background electrolyte, pH and concentration of EOF modifiers. To direct EOF in the same direction as the analytes has been recently suggested to be counter productive, if good peak resolution is desired [5]. However, in our own observations, the EOF directed in the opposite direction to that of the analyte ions has resulted in extremely long analysis times. In the work carried out to date, satisfactory resolution was always observed in systems with EOF and analyte ions migrating in the same direction. Moreover, short run times (less than 3 min for 30 anions) and high efficiencies (500 000 plates and higher) make the discussed approach very attractive in applications for mixtures of low-molecular-weight anions. It is these authors belief that for the class of ionic species in question, there is a distinct advantage in the "going with the flow".

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