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Capillary electrophoresis of inorganic anions and organic acids using suppressed conductivity detection Strategies for selectivity control

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Abstract

The use of suppressed conductivity as a detection scheme for capillary electrophoresis (CE) is described. A comparison is made between several electrolytes for CE with suppressed conductivity detection (CESC) in terms of efficiency of separation and peak shape. The ability to modify electrophoretic mobility and selectivity as a function of temperature and electrolyte ionic strength is demonstrated. The separation of a variety of low-molecular-mass organic acids is optimized using the addition of metal ions to the separation electrolyte.

1. Introduction

The traditional method of ion analysis, ion chromatography, has benefited greatly from the wide range of selectivity available from different stationary phases. The availability of stationary phases with differing selectivity has provided the analyst a range of options for solving difficult analytical problems. Isotachophoresis has also been described as a separations method for the determination of inorganic ions but suffers from poor detection limits [1–3]. Capillary electrophoresis (CE) has been attracting interest in recent years as a promising tool for the analysis of inorganic anions and low-molecular-mass organic acids. Unlike chromatography, however, separations using CE do not rely on interaction with a stationary phase but rather on differences in electrophoretic mobility between analyte ions. The electrophoretic mobility of an ion is often viewed as a stable property and thus CE would have difficulty separating ions with similar electrophoretic mobilities. Separation of some species can be accomplished by changing electrolyte pH. This strategy, however, is effective in changing selectivity only if the electrolyte pH is changed in the vicinity of the analyte's pK_a, thereby changing the analyte's charge to mass ratio. For inorganic anions, which often have a pK_a less than 2, changing the electrolyte pH to modify selectivity is not practical. At low pH, the electroosmotic flow (EOF) in a silica capillary is too low to carry inorganic anions toward the detector when operating in a source-vial-positive-polarity configuration. It is possible to reverse the polarity so that the anions are moving in the same direction as the EOF, but the current generated at an electrolyte pH of less than 2 would make operation difficult, if not impossible.

The separation of inorganic anions using capillary electrophoresis has been the subject of many

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publications during the past five years [4–12]. For detection of these analytes, many researchers have turned to indirect UV detection. The method of indirect UV is attractive because it is a universal detection scheme for non-UV-absorbing ions and it uses existing instrumentation. However, it suffers from a high background, and consequently, high noise [11]. In addition, the concentration detection limits, linear range, and dealing with matrix effects are inferior to chromatographic methods. For these reasons, other detection schemes have been devised for capillary electrophoresis of inorganic anions. Several publications describe the use of electrochemical detection for capillary electrophoresis, including amperometry [13–18], conductivity [19–23], and suppressed conductivity [24,25]. Sensitivity of electrochemical techniques is not dependent on detector cell size, as is the case with UV detection, so there is no loss of sensitivity as a result of scaling down in size. Conductivity detection is also nearly universal for detection of inorganic anions.

Optimization of conditions for determining anions with CESC has not been studied in detail. For example, the effects of electrolyte concentration, temperature, and chemical composition have not been described for CE using suppressed conductivity detection. Modification of relative electrophoretic mobilities for aminobenzoic acids with UV detection has been described as a function of temperature [26]. The effect of buffer concentration on electrophoretic mobility and migration time has been reported by several researchers [27–31]. Selectivity modification using chelating agents in the electrolyte has been used as a means of separating metal ions [32–34]. The addition of metal ions to the leading electrolyte in isotachophoresis (ITP) has been described for selectivity control during ITP separations of inorganic anions but with mixed results [1–3]. Complexation has not been extensively developed for modifying anion selectivity in capillary zone electrophoresis.

This article describes efforts toward optimizing selectivity for capillary zone electrophoresis with suppressed conductivity detection for determining inorganic anions and organic acids by adding metal ions to the electrolyte. Also described are the variations in electrophoretic mobility for common inorganic anions as a function of temperature, electrolyte ionic strength, and the addition of metal additives to the separation electrolyte.

2. Experimental

2.1. Apparatus

The apparatus used for CE with suppressed conductivity was a modified version of one described previously [24]. A schematic of the assembly is shown in Fig. 1. Unless otherwise indicated, all work was done on the apparatus shown in Fig. 1. The separation capillary was a 60-cm long, 75 μm I.D., 360 μm O.D. fused-silica capillary (Polymicro Technologies,

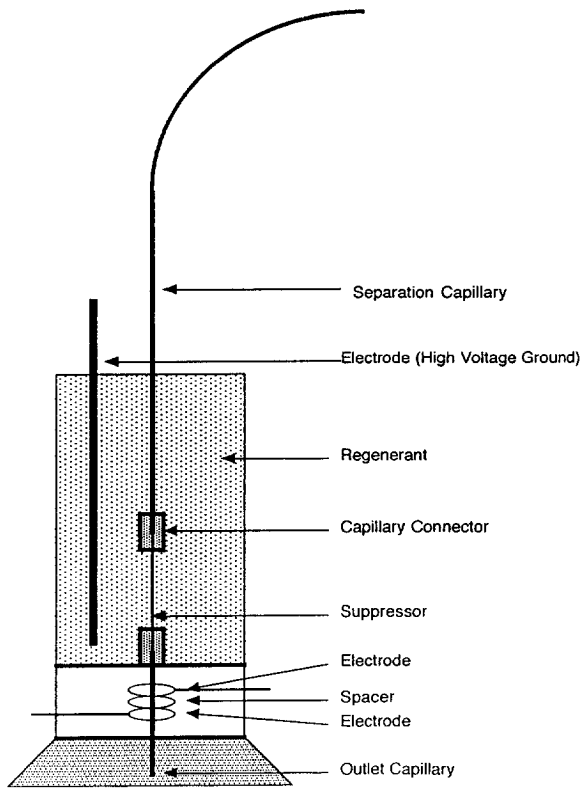

Fig. 1. Schematic of capillary–suppressor–conductivity cell assembly.

Phoenix, AZ, USA). All work was done on Dionex's CES-I with an ED40 electrochemical detector or CDM-II conductivity detector (Dionex, Sunnyvale, CA, USA). Data were collected and processed using a Dionex AI-450 chromatography workstation. Temperature control of the separation compartment was accomplished using a microprocessor controlled temperature controller, heater, and thermocouple (Omega Instruments, Stamford, CT, USA).

2.2. Reagents

High-purity sodium tetraborate, anhydrous (Aesar/Johnson-Matthey, Ward Hill, MA, USA), glycine (Sigma, St. Louis, MO, USA), taurine (Serva, Crescent Chemical, Hauppauge, NY, USA), and 4-cyanophenol (Aldrich, Milwaukee, WI, USA) were used as electrolytes for CE separations. Sulfuric acid regenerant concentrate, 500 m*M*, (Dionex) was used to prepare the working 5 m*M* regenerant. Sodium hydroxide (50%) (Fisher Scientific, Pittsburgh, PA, USA) was used to prepare titrant for pH adjustment of buffers. Anion standards were prepared using sodium salts from Fisher Scientific.

3. Results and discussion

3.1. Anion separations using CESC

The separation of anions using CE depends on the magnitude and direction of electroosmotic flow (EOF), and the electrophoretic mobility (μ_a) of the analyte ions. Both the electroosmotic flow and the electrophoretic mobility are vector quantities and are additive. In the case of anion analysis using an unmodified silica capillary, these two vectors are in opposite directions. The convention used for the sign of the vector is a positive number for migration toward the cathode, and a negative number for migration toward the anode. The magnitude of the electroosmotic flow is highly dependent on the buffer pH, ionic strength, and temperature of the separation.

At low buffer ionic strength (less than 5 m*M*) and high pH (greater than pH 9), the magnitude of the electroosmotic flow in a typical capillary is in the range of $85 \cdot 10^{-5}$ to $110 \cdot 10^{-5}$ $cm^2/V \cdot s$. The electrophoretic mobilities (at infinite dilution) of common inorganic anions are shown in Table 1. Some inorganic anions can have mobilities as high as $-85 \cdot 10^{-5}$ $cm^2/V \cdot s$, while lower-mobility inorganic anions and organic acids generally have mobilities less than $-60 \cdot 10^{-5}$ $cm^2/V \cdot s$. Because the EOF and electrophoretic mobility are additive vectors, it is necessary for the magnitude of the EOF to exceed the analyte's electrophoretic mobility by at least $10 \cdot 10^{-5}$ $cm^2/V \cdot s$ so that the analyte's net migration velocity is toward the detector, as shown in Fig. 2. If an anion's net mobility is less than $10 \cdot 10^{-5}$ $cm^2/V \cdot s$, the time required to detect the analyte will become excessively long.

Fig. 3 shows a separation under optimized conditions using 2 m*M* sodium tetraborate, pH

Table 1
Limiting ionic conductance and electrophoretic mobility at infinite dilution

Anion	Limiting ionic conductance[a] (cm^2/Ohm-equivalent)	Electrophoretic mobility ($cm^2/V \cdot s$)
Fluoride	54.4	$-56.3 \cdot 10^{-5}$
Phosphate (HPO_4^{2-})	57	$-59.1 \cdot 10^{-5}$
Nitrate	71.4	$-74.0 \cdot 10^{-5}$
Nitrite	71.8	$-74.4 \cdot 10^{-5}$
Sulfate	80.0	$-82.9 \cdot 10^{-5}$
Chloride	76.35	$-79.1 \cdot 10^{-5}$
Bromide	78.1	$-80.9 \cdot 10^{-5}$

[a] From Ref. [44].

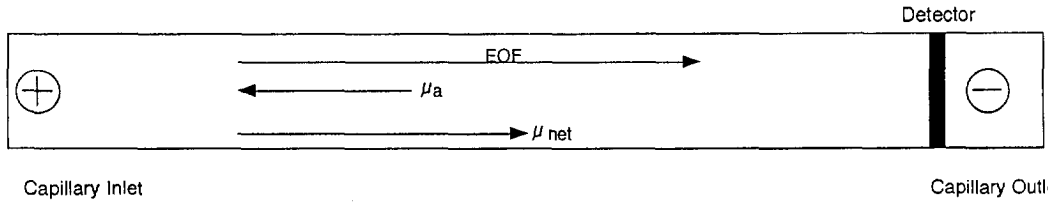

Fig. 2. Magnitude and direction of electroosmotic flow (EOF), electrophoretic mobility (μ_a), and net mobility [μ_{net} or μ_a (observed)]. Under the conditions used for separation of anions, the EOF is greater than and in the opposite direction of the electrophoretic mobility. This results in a net migration velocity of anions toward the cathode.

9.2, as an electrolyte. The EOF as measured by the water (neutral) dip is $97.3 \cdot 10^{-5}$ cm^2/V·s. The highest-mobility analyte, bromide, has an electrophoretic mobility of $-76.0 \cdot 10^{-5}$ cm^2/V·s and thus, a net mobility of $21.3 \cdot 10^{-5}$ cm^2/V·s toward the detector. This results in an overall migration time of 11.7 min for bromide. Note that when using this mode of separation, lower electrophoretic mobility analytes are detected first, whereas those with higher electrophoretic mobility are detected later.

3.2. Suppressible buffers for CESC

The use of suppressed conductivity detection imposes certain restrictions on the nature of the electrolyte that can be used. A variety of electrolytes are candidates for use with suppressed conductivity detection. While many electrolytes such as sodium carbonate, sodium borate, and sodium *p*-cyanophenate have been well characterized as eluents for ion chromatography [35], amino acid electrolytes such as taurine and glycine are less well known [36–38].

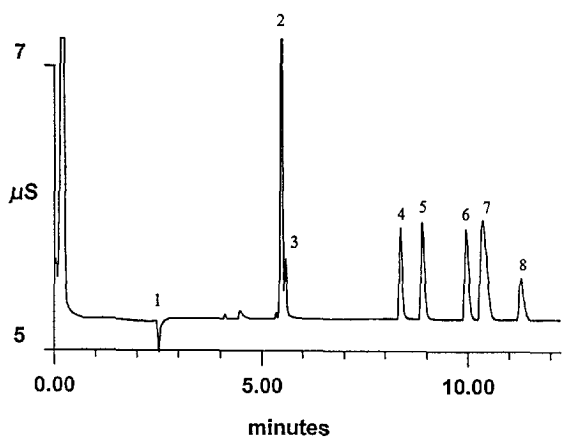

Fig. 3. Separation of anions using CESC. Electrolyte: 2.0 m*M* sodium tetraborate (ultrapure); capillary: 60 cm × 75 μm I.D. fused-silica; voltage: +24 kV, detector-end cathodic; hydrostatic injection: 40 mm/5 s; regenerant: 5 m*M* sulfuric acid; detection: suppressed conductivity; temperature: 30°C. Sample injected from water. Peaks (all at 1.0 ppm): 1 = water dip; 2 = fluoride; 3 = phosphate; 4 = nitrate; 5 = nitrite; 6 = sulfate; 7 = chloride; 8 = bromide.

A suitable buffer for CESC has some unique constraints. The peak shape obtained for analytes in CE has been shown to depend on a close match of electrophoretic mobility of electrolyte ions and analyte ions [19]. Although no single electrolyte will match all analytes, the electrolyte should have an electrophoretic mobility similar to that of the analytes being separated to result in a good peak shape. In addition to these requirements, the use of suppressed conductivity detection for anions dictates that the electrolyte be convertible to a weakly conducting species when passed through a cation exchanger in the hydronium form. The mechanism of chemical suppression is well documented [39–41] and is analogous to chemical suppression in ion chromatography. These two constraints, the ability to be suppressed to a weakly conducting species and a suitable electrophoretic mobility, are the major considerations in picking an electrolyte for CESC.

For efficient separation of inorganic ions and organic acids, a suppressible electrolyte with electrophoretic mobility similar to the analytes is desired. The following compounds are potential candidates for CESC electrolytes: sodium tetraborate, sodium glycinate, sodium taurinate, sodium bisulfide, sodium phenate, sodium cyanide, sodium 4-cyanophenate and sodium carbonate. Although there are other suppressible electrolytes, primarily amino acids, only those listed above are expected to have sufficiently high

electrophoretic mobility. Due to the toxicity of sodium cyanide, sodium sulfide, sodium phenate, sodium 4-cyanophenate, and their suppression products, these electrolytes are considered inappropriate. Electropherograms using some of these electrolytes for CESC are shown in Fig. 4. The tailing of later migrating peaks in the electropherograms is indicative of a mismatch of electrophoretic mobilities between the electrolyte and analytes. The mismatch of electrophoretic mobility for the slow migrating electrolyte species is concurrent with an increase in efficiency for early migrating peaks. Therefore, while no single electrolyte will give a perfect peak shape for all analytes, an electrolyte suitable for the analytes of interest can be selected if we know relative electrophoretic mobilities. For the analysis of inorganic anions, borate and glycinate appear to be best suited.

3.3. Ionic strength effects on selectivity

The effect of electrolyte ionic strength on selectivity in CESC was examined using sodium tetraborate, pH 9.2, as an electrolyte. A seven-anion test mixture was run repeatedly and the electrophoretic mobilities of the anions were calculated using the following formulas:

$$\mu_{EOF} = l_d l_t / t_w V \quad (1)$$

$$\mu_a(\text{observed}) = l_d l_t / t_a V \quad (2)$$

$$\mu_a(\text{actual}) = \mu_a(\text{observed}) - \mu_{EOF} \quad (3)$$

where μ_{EOF} is the electroosmotic flow, μ_a (observed) is the net electrophoretic mobility, and μ_a (actual) is the inherent electrophoretic mobility of the analyte ion. Further, l_d is the distance from the inlet to the detector, l_t is the total capillary length, t_w is the migration time of the water dip in seconds, t_a is the migration time of the analyte peak in seconds, and V is the separation voltage.

To examine the effect of ionic strength on selectivity, a series of electrolytes with different ionic strengths were run. The ionic strength of a dilute sodium tetraborate solution was calculated as simply twice the molar concentration. This simplification is appropriate at low millimolar concentrations of borate ion [42]. The range of total electrolyte ionic strength was from 2.0 to 10

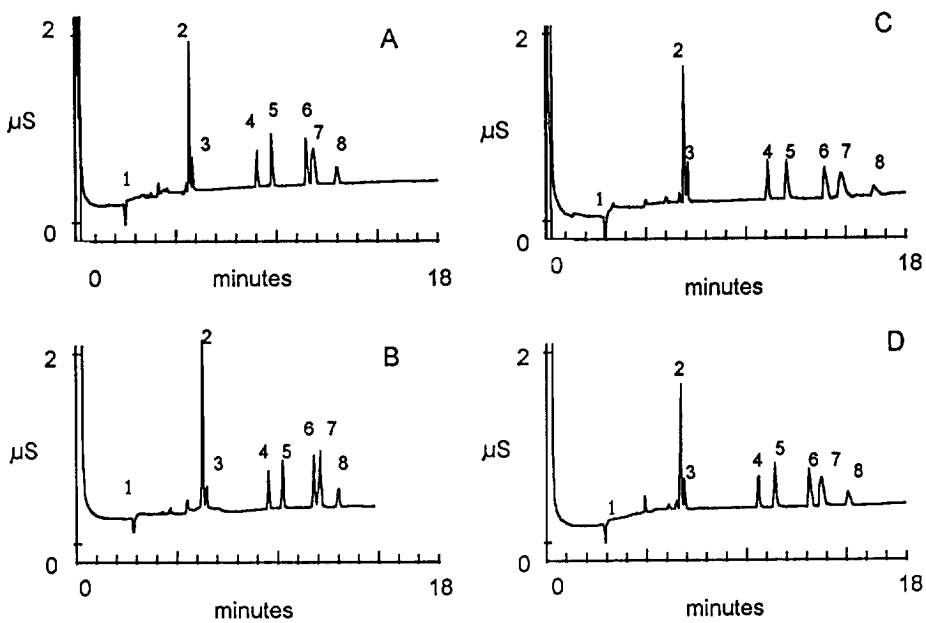

Fig. 4. Comparison of electrolytes for CESC. Conditions and peak identification same as Fig. 3, except for different electrolytes and voltages as follows: (A) 2.0 m*M* sodium tetraborate (pH 9.2), 24 kV; (B) 4.0 m*M* sodium glycinate (pH 10.5), 20 kV; (C) 4.0 m*M* sodium taurinate (pH 10.5), 20 kV; (D) 4.0 m*M* sodium *p*-cyanophenate (pH 10.5), 20 kV.

m*M* (1.0 to 5.0 m*M* $Na_2B_4O_7$). The resulting electropherograms are shown in Fig. 5. The front shoulder on the chloride peak observed at higher electrolyte ionic strength was previously reported to be the ^{37}Cl isotope [24].

Calculated electrophoretic mobility [μ_a (actual)] as a function of ionic strength is plotted in Fig. 6. As the ionic strength of the electrolyte increases there is a decrease in EOF. The decrease in EOF with increasing electrolyte ionic strength is well documented [27–31] and is attributed to a decrease in zeta potential due to compression of the electrical double-layer. The overall migration time also increases as the ionic strength is increased, but the overall migration time is the vector sum of the EOF and an ion's inherent electrophoretic mobility. The calculated electrophoretic mobilities of the analyte ions become slower with decreasing ionic strength and individual ions show differences in their response to changing ionic strength. At the highest ionic strength studied, the calculated electrophoretic mobilities of the analyte ions approach the values predicted by their limiting ionic conductance. Ionic strengths higher than 5 m*M* sodium tetraborate could not be studied because the low EOF at high ionic strength results in an excessively long run time. The observed behavior, a direct relationship between ionic strength and inherent mobility, is contrary to what is expected based on Kohlrausch's Law. Kohlrausch's Law predicts that the equivalent conductivity of an ion should have an inverse linear relationship with the square root of concentration [43]. The law also predicts a negative slope for a plot of equivalent conductivity versus concentration. Equivalent ionic conductance is directly related to electrophoretic mobility by the Faraday constant [43],

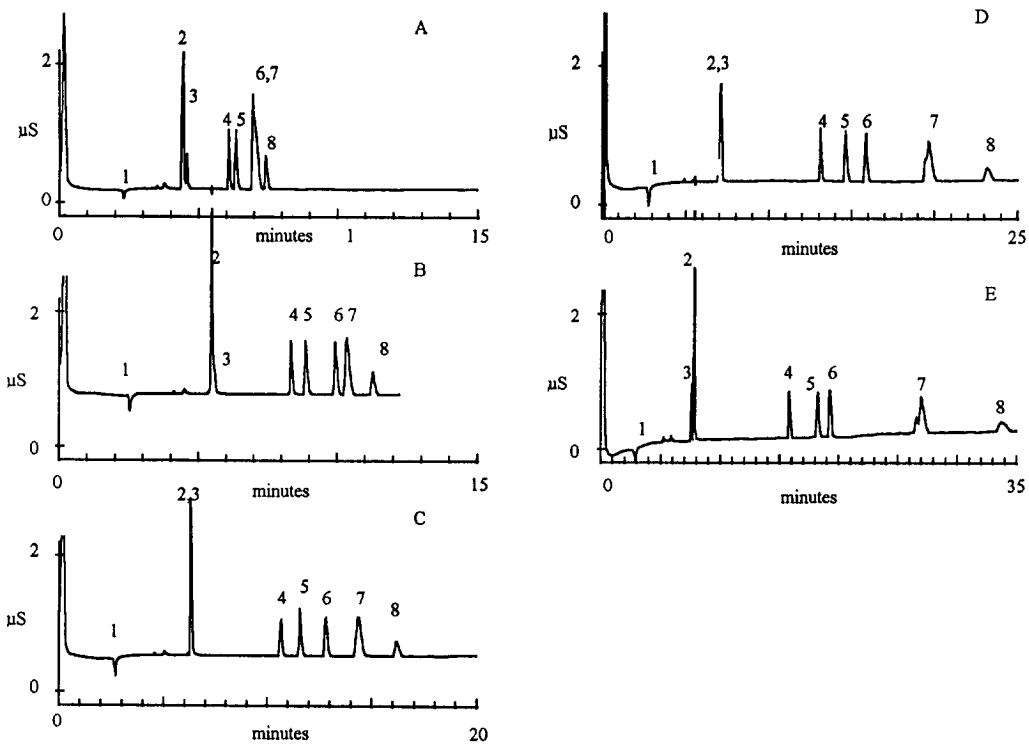

Fig. 5. Anion separation at different electrolyte ionic strengths. Conditions and peak identification same as Fig. 3, except for different electrolyte ionic strengths as follows: (A) 1.0 m*M* sodium tetraborate; (B) 2.0 m*M* sodium tetraborate; (C) 3.0 m*M* sodium tetraborate; (D) 4.0 m*M* sodium tetraborate; (E) 5.0 m*M* sodium tetraborate.

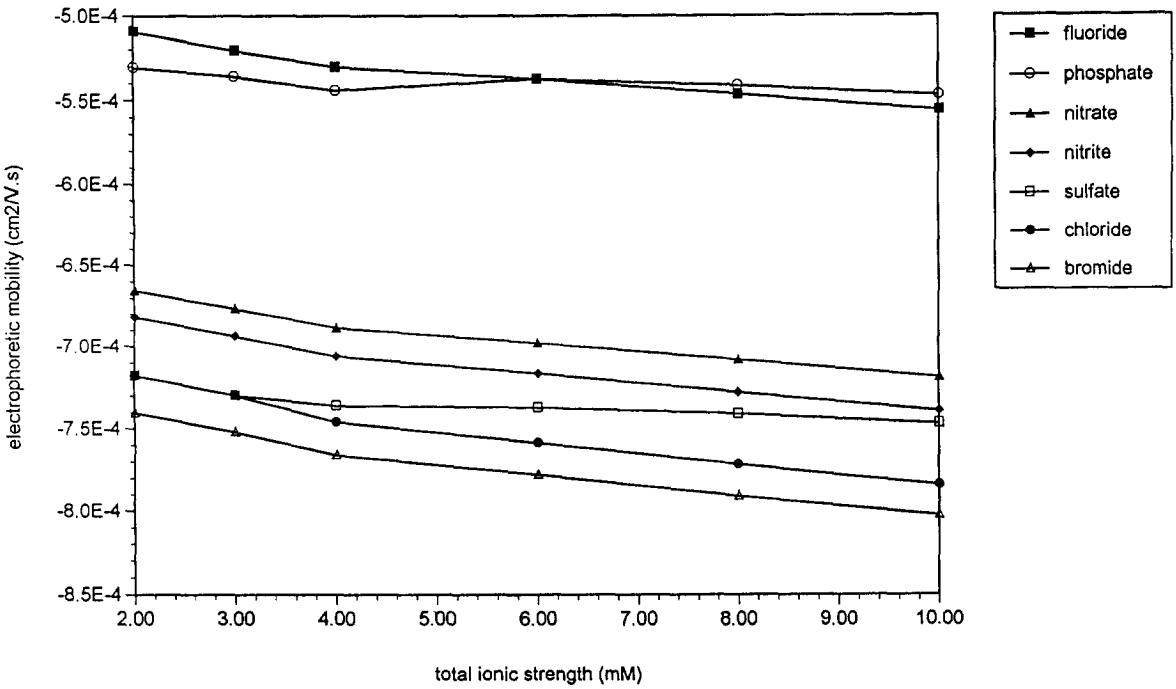

Fig. 6. Inherent electrophoretic mobility as a function of electrolyte ionic strength. Data plotted from electropherogram in Fig. 5. Electrophoretic mobilities were calculated using Eqs. 1, 2 and 3.

$$\mu = \lambda / F$$

where μ is the electrophoretic mobility in $cm^2/V \cdot s$, λ is the equivalent ionic conductance in cm^2/Ohm-equivalent, and F is the Faraday constant (96 489 C/mol).

Although Kohlrausch's Law applies to measurement of the equivalent conductivity of an ion in a solution of the same ions, it is expected to apply to the measurement of ions in a solution of a different electrolyte (as is the case in electrophoresis). It is also expected that as the ionic strength of the electrolyte decreases, the electrophoretic mobilities should approach the limiting values predicted from the equivalent ionic conductance at infinite dilution. The data in Fig. 6 show a different trend. At an electrolyte ionic strength of 10 mM, the electrophoretic mobilities of the anions are similar to those predicted from the equivalent ionic conductance at infinite dilution. As the ionic strength of the electrolyte decreases, the electrophoretic mobility of the anions appears to decrease to a value much less than predicted at infinite dilution. The data show a trend contrary to Kohlrausch's Law; as the ionic strength of the electrolyte is decreased, the inherent electrophoretic mobility of the anions toward the anode becomes slower. It is possible that at the low ionic strength conditions used for this experiment, the mobilities of ions cannot be measured correctly. However, the phenomenon of changes in relative migration order (e.g., changes in selectivity) as a function of ionic strength is useful as a tool in optimizing electrophoretic separations.

As electrolyte ionic strength decreases, the inherent electrophoretic mobility of the anions toward the anode decreases while the EOF toward the cathode increases, resulting in an overall run time decrease. The important observation from the standpoint of selectivity manipulation is that the electrophoretic mobilities of the anions change at different rates in response to ionic strength changes. Most dramatic is the change in migration order of fluoride and phosphate ions as the ionic strength changes. At low

ionic strength, fluoride has a lower electrophoretic mobility [μ_a (actual)] than phosphate and a faster net migration through the capillary. Therefore, fluoride is detected before phosphate (Fig. 5A). As the ionic strength increases, the electrophoretic mobility of fluoride and phosphate converge (Fig. 5C). At higher ionic strength, the electrophoretic mobility of fluoride exceeds that of phosphate and thus, fluoride migrates after phosphate (Fig. 5E). Large changes in sulfate and chloride resolution are also observed. As the ionic strength of the electrolyte is increased, sulfate moves away from chloride and is detected near nitrite (Fig. 5E). The use of higher ionic strength may be useful in matrices with high concentrations of both sulfate and chloride.

Clearly, the electrolyte ionic strength is an important parameter in controlling observed electrophoretic mobility and, therefore, selectivity in the separation of inorganic anions. Through the proper choice of electrolyte ionic strength, selectivity and run time can be manipulated and optimized for a particular separation.

3.4. Temperature effects on selectivity

The effect of temperature on electrophoretic mobility was studied using a 2 m*M* $Na_2B_4O_7$ electrolyte. The temperature of the entire separation compartment was controlled using a forced air heating device. It is known that both the EOF and the electrophoretic mobility of an individual ion are a function of temperature. The dominant effect is thought to be a decrease in viscosity as temperature is increased. If a decrease in viscosity is the only effect, the overall effect of temperature should be negligible and would affect the overall analysis time, but not the relative migration velocities of the analyte ions. However, the electropherograms in Fig. 7 show changes in the relative migration order of the test analytes. A plot of electrophoretic mobility [μ_a (actual)], versus temperature at constant ionic strength is shown in Fig. 8.

As the temperature is increased, the EOF increases at 2% per degree Celsius as predicted from the change in viscosity with temperature. However, the overall run time decreases as the temperature is increased. This implies that the increase in EOF is greater for a given change in temperature than the change in analyte electrophoretic mobility for the same temperature change. If the magnitude of the change were the same for both the electrolyte and analyte, the two effects would cancel and the overall run time would be independent of temperature. Because the electroosmotic flow increases at a faster rate than the electrophoretic mobility of the analytes, the overall run time decreases as the temperature is increased.

The effect of increasing temperature is not simply limited to faster analysis times; the relative migration order of the analyte ions and, therefore, the selectivity of the system, changes as the temperature is increased. The resolution of fluoride and phosphate increases with increasing temperature because their electrophoretic mobilities change at different rates. Most interesting is the change in the migration order of sulfate, chloride, and bromide. Sulfate, which initially migrates before chloride and bromide, shows a relative increase in electrophoretic mobility as the temperature is increased. At the highest temperature studied (54.4°C), the electrophoretic mobility of sulfate has surpassed both chloride and bromide, and sulfate migrates last in the electropherogram. At this temperature, the analytes are detected in the order predicted by their limiting ionic conductance. At 54.4°C, the EOF is $147 \cdot 10^{-5}$ $cm^2/V \cdot s$ and the total run time is less than 7 min. Nielen [26] observed similar changes in the migration order of aminobenzoic acids and explained them on the basis of chemical equilibrium changes as a function of temperature. Strong acid inorganic anions are completely dissociated at the pH of the electrolyte (pH 9.2) and should not show a significant dependence on temperature. Yet the changes in relative migration order that we have observed appear to be a result of changes in electrophoretic mobility of anions in response to temperature. It is also apparent that the electrophoretic mobilities of different ions change at different rates in response to changes in separation temperature.

The changes in electrophoretic mobility as a

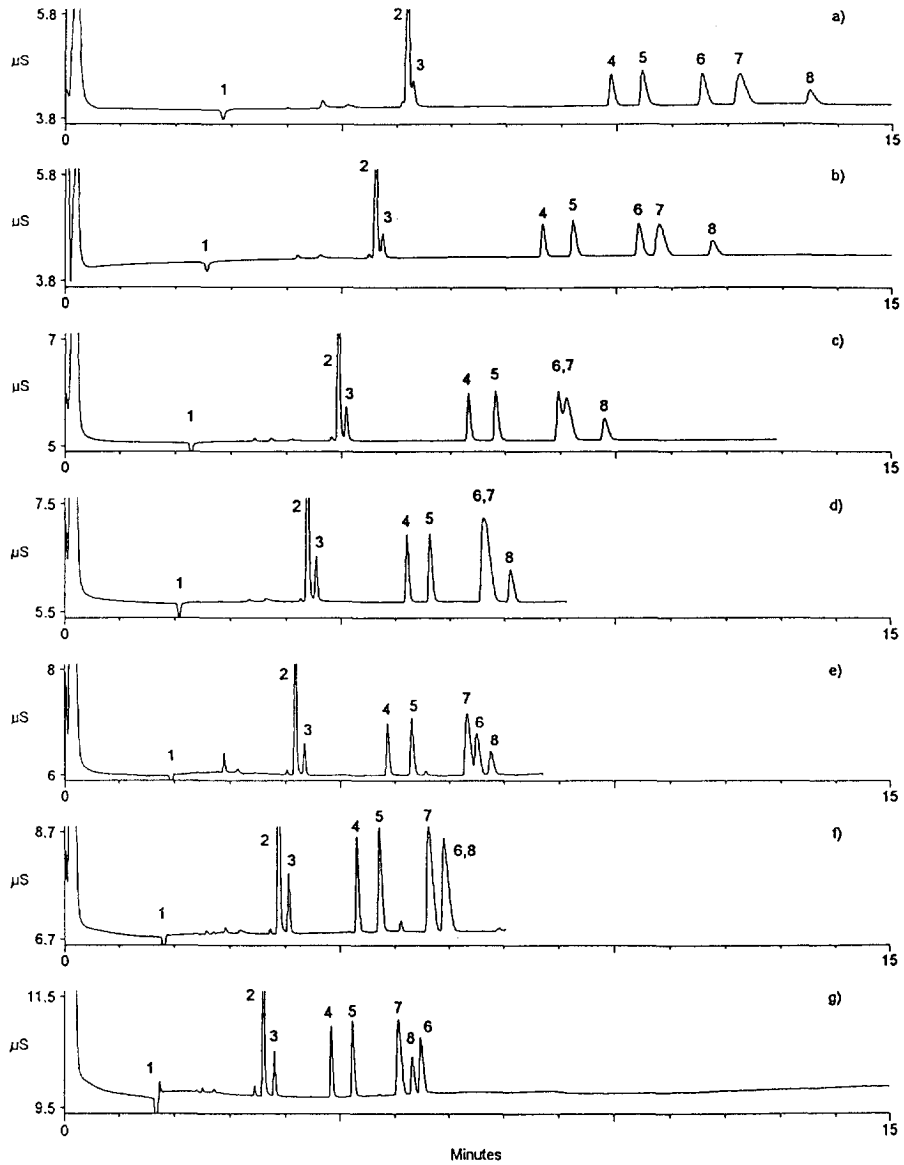

Fig. 7. Anion separations at different temperatures: (a) 21.1°C; (b) 26.7°C; (c) 32.2°C; (d) 37.8°C; (e) 43.3°C; (f) 48.9°C; (g) 54.4°C. Electrolyte: 2.0 m*M* sodium tetraborate (ultrapure); capillary: 60 cm × 75 µm I.D. fused-silica; voltage: +24 kV, detector-end cathodic; hydrostatic injection: 40 mm/5 s; regenerant: 5 m*M* sulfuric acid; detection: suppressed conductivity. Sample injected from water. Peaks (all 1.0 ppm): 1 = water dip; 2 = fluoride; 3 = phosphate; 4 = nitrate; 5 = nitrite; 6 = sulfate; 7 = chloride; 8 = bromide.

function of temperature provide a means of affecting selectivity for ions in CE. This can be exploited as a means of modifying migration order and resolution of inorganic anions. Also, the observation that for a given change in temperature the EOF increases faster than the electrophoretic mobility implies that overall run times can be shortened by running at elevated temperature. With a knowledge of the relationship between an anion's electrophoretic mobility

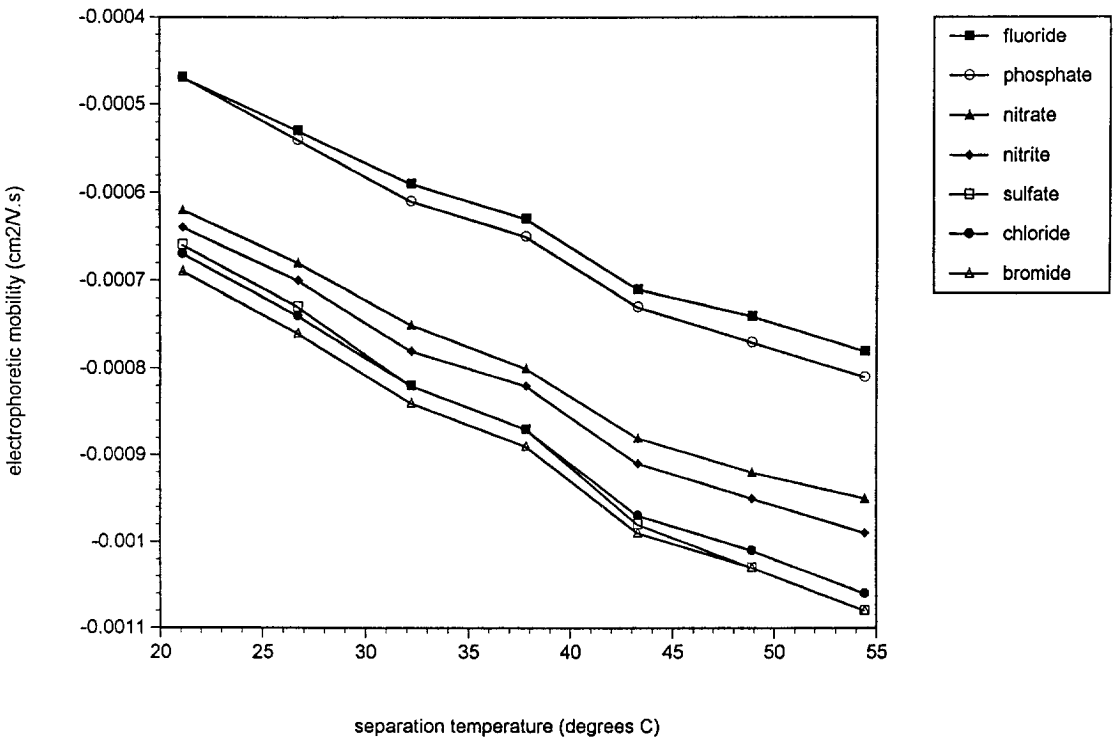

Fig. 8. Inherent electrophoretic mobility as a function of separation temperature. Data plotted from electropherogram in Fig. 7. Electrophoretic mobilities were calculated using Eqs. 1, 2 and 3.

and temperature, resolution of closely migrating analytes as well as overall run time can be optimized.

3.5. Effect of buffer additives on selectivity and resolution

The use of metal cations in the electrolyte has been reported for the purpose of mediating the mobility of selected inorganic anions using isotachophoresis. In one case, the authors used either calcium or magnesium to decrease the effective mobility of sulfate, and in another case cadmium to retard the mobility of chloride and sulfate. The result was unsuccessful due to the unacceptable change in mobility of other ions such as fluoride or to the loss of ions, probably due to precipitation, such as phosphate and fluoride, depending on the metal cation used. The use of metal cations in this work is intended to change the selectivity of the system for inorganic anions versus organic acids.

The separation of a variety of organic acids has been accomplished using CESC. In fact, CESC may prove to be a superior method for the analysis of small organic acids because they are essentially separated as a class from strong acid anions. This class separation occurs because the electrophoretic mobilities of most organic acids are much lower than those of strong acid inorganic anions. This class separation can be enhanced by adding a micromolar concentration of metal ions to slow the EOF of the system. Since the electrophoretic mobility of the anions is in the opposite direction of the EOF, anions with faster mobilities will increase in migration time faster than anions with slower mobilities. The result is that essentially all of the inorganic anions in the sample are moved to a position later in the electropherogram, and the organic anions in the sample migrate first. There are,

however, certain pairs of organic acids whose electrophoretic mobilities in a particular electrolyte are too close for full resolution of the migrating bands. This problem is also addressed by the presence of micromolar concentrations of metal cations in the electrolyte, which can weakly complex some organic acids. Many organic acids are weak chelators and form complexes with metal ions in solution. The degree to which an organic acid complexes a metal is a function of the chemical environment, temperature, and the presence of competing chelators. The resulting complex has chemical properties different than the free organic acid and can include changes in charge, charge density, geometry, and relative hydrophobicity. Complexation of an organic acid with a metal cation generally decreases its charge and charge density, resulting in a slowing of the complexed acid relative to its free acid counterpart. The degree to which the analyte is slowed by complexation with the metal depends on the nature of the analyte and the stability of the analyte–metal complex. Generally, two co-migrating organic acids will not complex with a metal to the same degree and, therefore, their relative migration times are affected differently by the addition of a metal ion.

The addition of even a low concentration of di- or trivalent metal ions can significantly slow the EOF. This can be seen in Fig. 9, where the measured EOF is only $70 \cdot \times 10^{-5}$ cm^2/V·s with the addition of 0.02 m*M* barium borate, in comparison with $97 \cdot 10^{-5}$ cm^2/V·s with 2.0 m*M* sodium tetraborate electrolyte and no added metal. Under these conditions, many high-mobility inorganic anions will not be detected, but the resolution of the slower organic acids is greatly enhanced. The addition of micromolar concentrations of barium to the electrolyte has resulted in resolution of otherwise inseparable pairs of organic acids (Fig. 9). We have also

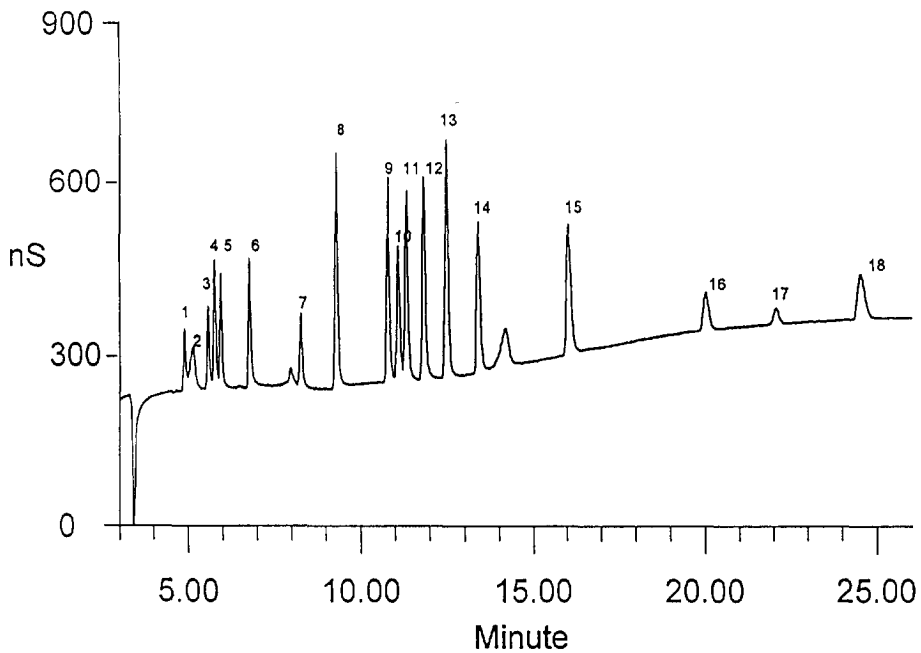

Fig. 9. Separation of organic acids with barium additive in electrolyte. Electrolyte: 2.0 m*M* sodium tetraborate (ultrapure), 0.02 m*M* barium borate; capillary: 60 cm × 75 μm I.D. fused-silica; voltage: +24 kV, detector-end cathodic; hydrostatic injection: 3 mm/3 s; regenerant: 5 m*M* sulfuric acid; detection: suppressed conductivity. Sample injected from water. Peaks (all at 250 ppb unless noted): 1 = quinate; 2 = shikimate; 3 = benzoate; 4 = salicylate; 5 = lactate; 6 = acetate; 7 = mucate; 8 = saccharate; 9 = formate (125 ppb); 10 = succinate; 11 = malate; 12 = tartrate; 13 = fumarate; 14 = maleate; 15 = malonate; 16 = isocitrate; 17 = citrate; 18 = aconitate.

observed slightly different changes in selectivity for organic acids with the addition of calcium and magnesium cations to the electrolyte.

4. Conclusion

Capillary electrophoresis with suppressed conductivity detection (CESC) is a powerful and versatile technique for the analysis of inorganic anions and low-molecular-mass organic acids. A variety of electrolytes are compatible with this technique and high efficiency separations can be optimized for analytes of differing mobilities. The electrophoretic mobility of analyte ions, often viewed as a fixed property, can be changed though judicious choice of operating conditions. Ionic strength of the electrolyte has been shown to exhibit subtle control over electrophoretic mobility and can be used as a means of modifying selectivity. Likewise, separation temperature can have a dramatic effect on selectivity in CE and may prove to be a powerful tool in optimizing separations. Finally, the addition of weakly complexing metals to an electrolyte can modify the net electrophoretic mobility of organic acid analytes and resolve otherwise co-migrating pairs. Manipulation of these parameters allows the selectivity of CE separations to be optimized for particular application problems.

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