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Capillary electrophoresis of organic cations at high salt concentrations

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Abstract

At concentrations of 100 mM or higher the chemical nature of both the cation and anion in the background electrolyte (BGE) can be varied to manipulate the migration times of protonated aniline cations. Significant differences were noted with Li^+, Na^+ and K^+ for capillary electrophoretic runs carried out at pH 3. However, much greater differences in migration times were observed at acidic pH values when the BGE contained protonated cations of aliphatic amines. Analyte migration became progressively slower in the series: methylamine, diethylamine, diethylamino ethanol and triethylamine. A major part of this effect was attributed to an opposing electroosmotic flow (EOF) resulting from a positively-charged coating of the capillary surface with the amine cations in the BGE via a dynamic equilibrium. The amine cations also interact in solution with the analyte ions to reduce their electrophoretic mobilities. Migration times of anilines could be varied systematically over a broad range according to the BGE amine cation selected. Excellent separations of seven closely-related anilines were obtained with the new system.

Keywords: Background electrolyte composition; Anilines; Amines

1. Introduction

In order to obtain reproducible migration times in capillary electrophoresis (CE), it is necessary to maintain a clean, reproducible inner surface on the fused capillary. In particular, variations in the surface can affect the electroosmotic flow (EOF) and hence the analyte migration times [1]. The coating of a fused-silica capillary with a water-soluble polymer is a simple procedure that has been used to provide a stable positively charged surface for the separation of proteins [2–7]. Fritz and Steiner [1] described a simple 8 min procedure for preparing capillaries for CE that included coating with poly(diallyldimethyl ammonium chloride) ($PD^{+)}$. This treatment resulted in a capillary with a strong, constant anodic EOF over a broad pH range that gave very reproducible migration times for sample anions. Graul and Schlenoff [7] showed that capillaries modified with alternate surface layers of positively- and negatively-charged polymers are particularly effective for separation of proteins and other bioorganic substances.

In a previous paper using a capillary coated with PD^+, it was noted that a concentration of at least 100 mM sodium chloride in the background electrolyte (BGE) was needed to provide sharp peaks in the separation of anions [1]. This observation runs counter to the accepted principle that even a moderately high ionic concentration in the BGE would cause Joule heating and serious peak distortion. However, there are a growing number of instances, often buried in the experimental details of a paper, where a high concentration has been used to advantage in the BGE. Thus, in the enhanced resolution of short-chain oligonucleotides the buffer contained 240 mM borate plus 40 mM of the phytic acid sodium salt [8].

In 1998 a comprehensive paper demonstrated that anions could be separated efficiently by CE in samples of high salt content, such as seawater, provided the salt content of the BGE was at least three times more concentrated [9]. Other papers confirmed that anions could be determined in

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undiluted seawater by CE [10–13]. We now study the effect of high salt concentration in the BGE on the separation of organic cations by CE.

In our initial research with alkali metal salts in the BGE, the type of both the cation and anion, as well as the concentration used, was found to have a major effect on the migration of sample cations. A much larger effect on the migration of protonated anilines was experienced when the BGE contained a 100 mM concentration of an aliphatic amine cation at an acidic pH. Migration times of the anilines could be varied over a broad range by selecting one of a series of amine cations for use in the BGE.

2. Experimental

All inorganic acids, bases and salts were obtained from existing laboratory stock or purchased from Fisher Scientific (Fairlawn, NJ, USA) and were of reagent grade quality or better. PDAC, mesityl oxide and anilines were purchased from Aldrich (Milwaukee, WI, USA) and were used as received. All solutions were prepared in purified 18.2 MΩ water from a Barnsted nanopure II water purification system (Barnsted Thermolyne, Dubuque, IA, USA). Analyte solutions were typically made up in acetonitrile and purified water in a concentration range of 5000 ppm and were diluted by a factor of 10 in 0.1 M HCl for the injected solutions.

To prepare the BGE a 100 mM (or another concentration) solution of an alkali metal salt or an aliphatic amine in purified water was treated with HCl to obtain a pH of 3.0. When a different pH value was used, the BGE also contained 5 mM phosphate or 10 mM citric acid as a buffer, and HCl was added to obtain the desired pH using a Corning 440 pH meter (Corning, NY, USA).

A Waters Quanta 4000 capillary electrophoresis system (Waters, Milford, MA, USA) was used with a positive power supply installed. Polyimide coated fused-silica capillaries (Polymicro Technologies, Phoenix, AZ, USA) were 50 cm in length with effective length to the detector being 42.5 cm. The capillaries used were 50 μm inside diameter. For studies using an uncoated capillary wall, a new capillary was prepared by rinsing the complete column volume three times each with 1 M hydrochloric acid, purified water, and finally with the BGE. A single rinse consisted of filling the column volume with the rinse solution and purging the column of the rinse solution using air. This single rinse takes approximately 30 s and makes the total column preparation approximately 5 min.

In some studies, the EOF was compared with the HCl pretreatment and by substituting 0.1 M sodium hydroxide for HCL in the pretreatment regimen.

Direct UV detection at 214 nm and hydrodynamic injection for 5–30 s at 10 cm height were used for all separations. Electropherograms were sampled at a rate of 10 points/s by the Chromperfect data acquisition system (Justice Innovations, Mountain View, CA, USA).

3. Results and discussion

3.1. Effect of BGE composition

At pH 3.0–3.5 the EOF is quite small on an uncoated silica capillary and aniline cations should migrate according to their electrophoretic mobilities. However, previous work on the separation of anilines [14] and amino acid cations [15] noted that very poor peaks were obtained unless 30–50 mM ethanesulfonic acid or octanesulfonic acid was added to the BGE. The alkanesulfonic acid was believed to inhibit interaction of the analyte cations with the capillary surface. However, the ionic strength of the BGE was too low for electrostacking to occur until the alkanesulfonic acid was added.

The separation of three anilines aniline (AN), 3-ethylaniline (EA) and 4-*tert*-butylaniline (BA) was studied with a BGE containing an aqueous solution of 100, 200 or 300 mM alkali metal chloride, buffered at pH 3.0. We used a new fused-silica capillary after only a brief treatment with 1 M hydrochloric acid (three rinses, 1 min each), followed by rinses with water and BGE. A satisfactory separation of the three aniline derivatives was obtained (Fig. 1). The data in Table 1 show that the current was substantially lower for 200 mM LiCl than for the same concentration of NaCl or KCl. The migration times were also significantly longer in LiCl than in NaCl. Some differences were also noted when different anions were used. In particular, migration times were longer with lithium or sodium acetate than with the metal chloride salts.

A very dramatic change in migration behavior of the three test aniline derivatives was observed when an alkylammonium chloride was used in the BGE instead of an alkali metal chloride. Table 2 shows a large increase in the observed migration times as the molecular weight and bulk of the protonated amine becomes larger. Additional experiments were run with the protonated chloride salts of methylamine (MA), diethylamine (DEA) and triethylamine (TEA) to provide further details as to what was happening. Runs with mesityl oxide (MO) as a neutral marker with a reversed (negative) power supply showed a substantial anodic EOF that increased with the molecular mass of the amine salt. Calculations then showed that the electrophoretic mobility of the aniline cations, which was cathodic, decreased according to increasing molecular mass of the amine salt in

Table 1
Separation of aniline derivatives on an uncoated silica capillary

BGE/concentration	Current (μA)	Migration time (min)		
		Peak 1	Peak 2	Peak 3
KCl/200 mM	220	6.07	7.33	8.45
NaCl/200 mM	200	5.69	6.56	7.80
LiCl/200 mM	120	6.21	7.34	8.46

Capillary, 50 cm (42 cm to detector) × 50 μm i.d., $E = +15$ kV, BGE pH = 3. Peak 1 = aniline, peak 2 = 3 ethylaniline, peak 3 = 4-*tert*-butylaniline.

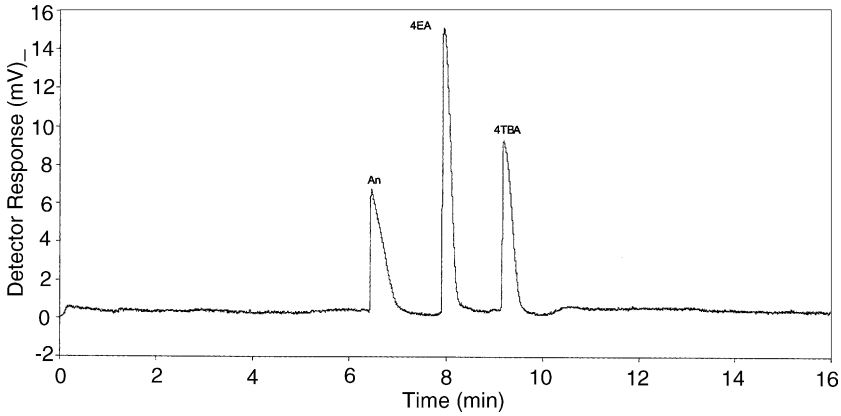

Fig. 1. Electrophoretic separation of aniline (AN), 3-ethylaniline (3EA), and 4-*tert*-butylaniline (4TBA) at pH 3.0 with 100 mM LiCl and 5 mM citrate as BGE.

Table 2
Effect of electrolyte cation on migration times of anilines

Cation	t_M (min)			Current (μA)
	AN	EA	BA	
Li^+	6.9	8.2	9.6	90
Na^+	7.0	8.4	9.9	88
Methylamine	7.8	9.7	11.8	108
Ethanolamine	8.0	9.8	11.8	86
Diethylamine	10.8	14.0	18.1	84
2-Diethylaminoethanol	12.2	16.3	22.2	–
Triethylamine	13.5	18.5	27.5	85

Conditions: BGE contains 100 mM of a cation chloride salt at pH 3.0. Capillary length 50 cm (42 cm to detector) × 50 μm i.d., +15 kV. Migration times (t_M) are the average of 2–3 runs, AN: aniline, EA: 3-ethylaniline, BA: 4-*tert*-butylaniline.

the BGE (see Table 3). The decrease from MA to DEA was much larger than from DEA to TEA.

The observed mobilities listed in Table 3 translate into substantial differences the migration times of the three test anilines. There was also a substantial improvement in peak sharpness and symmetry compared to that with lithium chloride or sodium chloride. For example, the following retention times were obtained at pH 3.0 with 100 mM DEA in the electrolyte: aniline, 12.0 min; 3-ethylaniline, 15.9 min; 4-*tert*-butylaniline, 21.0 min. The actual theoretical plate numbers, *N*, of the test anilines were 80 000, 74 000, and 57 000, respectively (160 000, 148 000 and 114 000 plates/m).

Table 3
Effect of electrolyte cation on mobility at pH 3.0

Electrolyte, 100 mM	μ_{os}	AN		EA		BA	
		μ_{OB}	μ_{ep}	μ_{OB}	μ_{ep}	μ_{OB}	μ_{ep}
Methylamine	−0.83	3.01	3.84	2.42	3.25	1.99	2.82
Diethylamine	−1.21	2.18	3.39	1.69	2.90	1.30	2.51
Triethylamine	−1.53	1.40	2.93	1.26	2.79	0.87	2.40

Conditions as in Table 1. μ_{os}: electroosmotic mobility, mesityl oxide marker; μ_{ep}: electrophoretic mobility; μ_{OB}: observed mobility. All mobilities, $\times 10^{-4}$ cm^2 V^{-1} s^{-1}.

The better peak sharpness and symmetry observed with amine salts compared with a sodium chloride BGE is likely the result of a closer match in mobility between the amine cation and the protonated aniline sample ion. Mikkers et al. concluded that symmetrical peaks are obtained only when the mobility of the carrier co-ion closely matches that of the analyte ion [16].

The effect of electrolyte concentration was studied briefly. A BGE containing 50 mM diethylammonium chloride rather than 100 mM gave similar migration times for the anilines tested but the average plate number was approximately 32% lower for the 50 mM concentration. Electrophoretic runs made with 200 mM DEA were generally satisfactory, but the current was higher than before and the peak sharpness was no better than with 100 mM electrolyte.

The increased efficiency at 100 mM concentrations in the BGE compared to the lower conventional concentrations is due to improved sample stacking at higher ionic strength [17].

The large difference in the migration times of the three test anilines with an aliphatic amine salt in the BGE suggested that resolution of a much more complex mixture of analytes should be possible. A 100 mM solution of diethylammonium chloride was selected for this study with a low concentration of a citrate buffer also present to maintain the desired pH. After a few exploratory experiments, it was found that a mixture of seven alkyl-substituted anilines could be completely resolved at pH 3.35 (Fig. 2). This separation is quite remarkable in that position isomers, 4-ethylaniline and 3-ethylaniline, as well as the isomeric 2-propylaniline and 2-isopropylaniline derivatives, were baseline resolved.

The EOF of a fused silica capillary is normally cathodic owing to the negative surface resulting from partial ionization of silanol groups. However, a cathodic direction of electroosmotic flow is observed when the BGE contains DEA rather than a more conventional alkali metal salt.

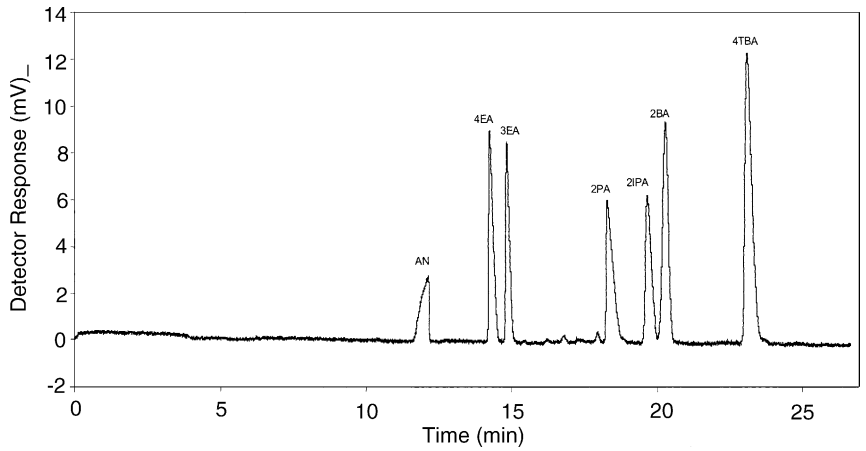

Fig. 2. Separation of anilines at pH 3.35. BGE: 100 mM DEA, 10 mM phosphate buffer. Capillary length 50 cm (42 cm to detector), 50 μm i.d.; +15 kV applied potential. Peak identification—A: aniline, EA: ethylaniline, P: propylaniline, IPA: isopropylaniline, BA: butylaniline, TBA: *tert*-butylaniline.

The observed EOF is a balance between the negative charge of the silanols and the protonated cations that are most likely adsorbed onto the capillary surface by a dynamic equilibrium. The effect of pH on electroosmotic mobility was determined with 100 mM DEA in the BGE and with a new capillary pretreated briefly with HCl, as described in the Experimental section. The anodic EOF, which is counter to the cathodic electrophoretic migration, increases rapidly going from pH 4 to 3, and then at a much slower rate down to pH 1.5 (see Fig. 3). These changes may be attributed to an increasingly positive surface resulting from adsorption of both $R_2NH_2^+$ and H^+. Even at pH 4 where a negative surface from ionized silanol groups would be expected, adsorption of $R_2NH_2^+$ gives a positive surface and a moderate anodic EOF.

EOF measurements were then made under the same conditions as before but with a new capillary treated briefly with 0.1 M sodium hydroxide instead of HCL. The EOFs were similar with both treatments between pH 4 and pH 3, but the EOF was significantly higher with the sodium hydroxide treatment at the more acidic pH values (Fig. 3).

The electrophoretic mobilities of seven different anilines were measured as a function of pH with a new capillary (treated briefly with HCl) and a BGE containing 100 mM DEA and 10 mM citrate buffer. The observed mobilities (μ_{OB}) were determined from the various electropherograms. Then, the electrophoretic mobilities (μ_{ep}) were calculated by adding each μ_{OB} to the electroosmotic mobility (μ_{os}) at each pH. The μ_{ep} must be larger than μ_{OB} in order to overcome μ_{os} in the opposite direction.

Fig. 4 shows relatively small changes in the electrophoretic mobilities between pH 3.6 and pH 2.0. The decrease in electrophoretic mobilities between pH ca. 3.6–4.0 could be due to less than complete protonation of the anilines. However, subtle changes do occur that provide the best resolution of all analytes at pH 3.4–3.6 (see Fig. 2). Below pH 2.0 the current increases rapidly and all of the μ_{ep} values increase significantly. This can be attributed to

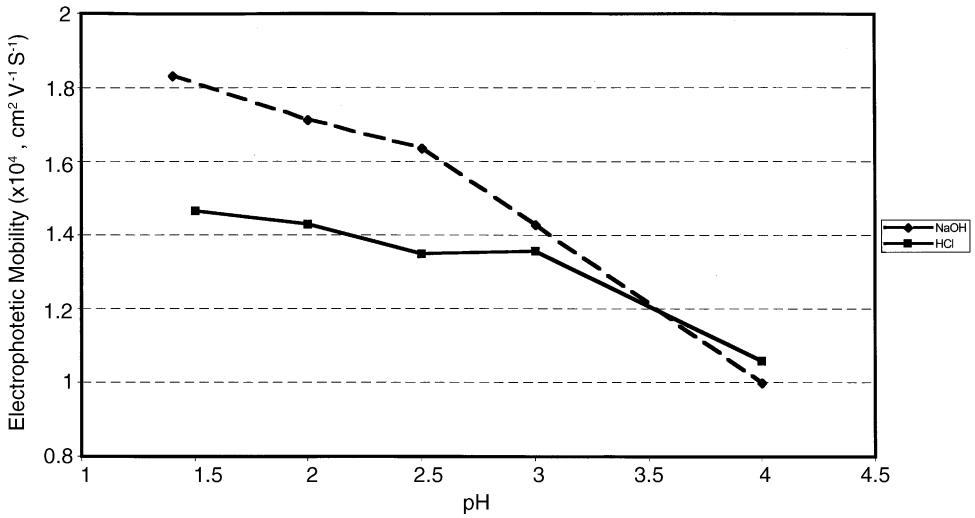

Fig. 3. Electroosmotic mobility as a function of pH. HCl preliminary treatment of silica capillary, solid line; NaOH preliminary treatment, dashed line.

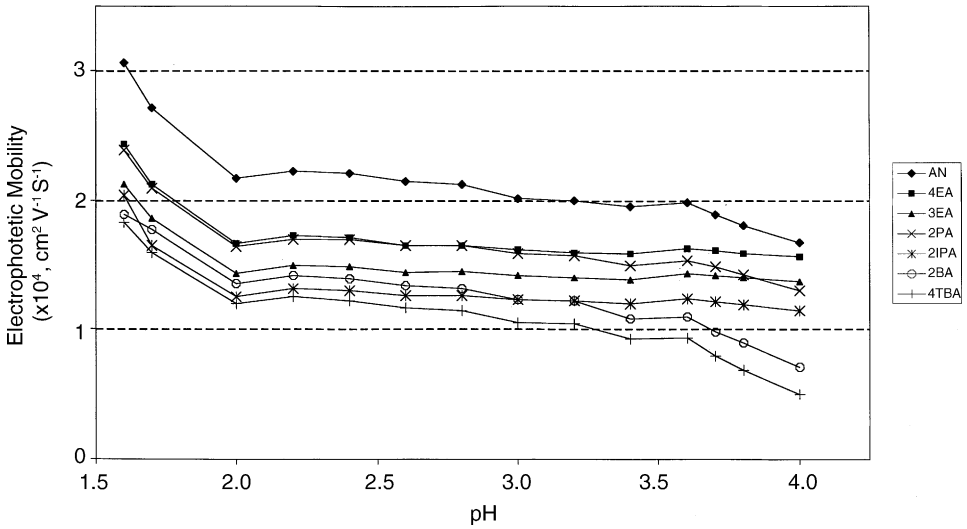

Fig. 4. Electrophoretic mobilities as a function of pH. BGE: 100 mM DEA, 10 mM citrate buffer. Preliminary treatment of capillary with HCl.

a higher capillary temperature in this pH region. Higher electrophoretic mobilities of anions have been previously noted as the BGE ionic concentration is increased and the current becomes higher [9]. The seven aniline derivatives used in Fig. 2 could be separated at pH values as low as 1.6 in only 13 min. However, resolution of 4 EA and 3 EA was incomplete and the current was very high (277 μA).

3.2. Mechanism

Variances in EOF from run to run have been identified as a major cause of poor reproducibility in the migration times of ionic analytes in CE. Cohen and Gruska reported a large change in electroosmotic mobility (μ_{os} or μ_{eo}) during the first few runs with a silica capillary buffered at pH 6.0 with 20 mM phosphate [18]. They found that a 4–10 mM concentration of an amine, trimethyl acetic acid or an amino acid in the BGE, gave stable μ_{os} values with excellent run-to-run reproducibility. It was believed that the improved reproducibility was not due to surface adsorption. However, the value of μ_{os} at any fixed pH did vary with the different amines that were investigated.

Lauer and McManigill incorporated 2 mM putrecine (1,4-diaminobutane, mono protonated) in a buffer at pH 8.2 to inhibit surface adsorption of large biomolecules [19]. The EOF was reduced by approximately 50% and large, non-linear changes in EOF were reported in the putrecine concentration range of 0–5 mM.

Salmon, Burge and Helmer proposed a new equation to account for the factors that affect electroosmotic mobility [20].

$$\mu_{eo} = \frac{Q_0}{\eta(1 + K_{wall}[M^+]} \times \left(d_0 \frac{1}{K'[M^+]}\right)$$

where $Q_0 = [SiO^-] + [SiO^- M^+]$, $K_{wall} = [Si\ O^- M^+]/[M^+]\ [Si\ O^-]$, d_0 = compact fixed layer (Debye–Hückel) thickness in the capillary and Q = charge/unit area $= Q_0/(1 + K_{wall}[M^+])$.

It was stated that the choice of counter ion used in the buffer can have a large effect on the electroosmotic flow. In a buffer containing 5 mM 2-(*N*-morpholine)ethanesulfonic acid (MES) and 2 mM of an alkali metal cation, values of μ_{eo} ranging from 4.98 to 8.0 $cm^2\ V^{-1}\ s^{-1}$ were reported for the various cations.

These studies provide additional confirmation that relatively small organic cations are effective in stabilizing the EOF in silica capillaries. The paper by Salomon et al. strongly suggests an interaction between the electrolyte cations and the capillary wall. However, the 100 mM concentration of electrolyte ions used in our studies is much higher than that in the literature cited.

With an alkali metal salt such as sodium chloride in the BGE the EOF of a silica capillary has been reported to decrease inversely with the square root of concentration over a limited concentration range [21]. High concentrations of sodium chloride reduce EOF by more efficient shielding of the negative charges on the inner surface of the capillary wall, according to another author [8]. A sodium chloride concentration of 1.5 M gave no observed differences in the migration times of test analytes at pH 3, 7 and 12, which was taken as evidence that the electroosmotic flow was greatly suppressed by the high salt concentration [9]. In our experiments with uncoated capillaries at pH 3.0, the EOF would be expected to be quite low and it would be reduced further by the high salt concentrations used. Thus, we were unable to detect any EOF in solutions of 100 mM sodium chloride or lithium chloride.

This situation changes drastically when protonated amine salts were used in the BGE. Anodic electroosmotic mobilities of MA, DEA and TEA were 0.83×10^{-4}, 1.21×10^{-4} and 1.54×10^{-4} $cm^2\ V^{-1}\ s^{-1}$, respectively. It seems clear that the capillary has acquired a positive surface, most likely

by attracting the positively charged amine cations to the surface. A mechanism can be postulated whereby the amine cation is attracted to the oxygen atoms of the silica silanol groups or siloxane groups by a dynamic equilibrium.

$$RNH^+ \text{ (solution)} + \text{Si–O (surface)} :\rightleftharpoons RNH^+ : \text{O–Si (surface)}$$

$$K = \frac{RNH^+ \text{ (surface)}}{RNH^+ \text{ (solution)}}$$

As the amine salt becomes bulkier with more hydrophobic character, K becomes larger and the overall surface assumes a greater positive charge. It has been shown that with some types of molecular sieves the silica cavity is actually hydrophobic and adsorbs organic analytes from aqueous solution [22].

So, the longer migration times of aniline cations obtained with an increasingly larger amine cation in the BGE are partly explained by a stronger EOF in the direction counter to the electrophoretic migration. However, Table 3 shows that another cause of longer migration times is the decrease in electrophoretic mobilities of the aniline cations in the BGE series: MA, DEA, and TEA. Since the same anion (chloride) was used in all of the experiments with uncoated capillaries, the dramatic change in electrophoretic migration of the aniline cations must be caused by differences in the BGE cation.

In earlier work a nearly linear increase in migration times was observed between 1 and 5 M sodium chloride in the BGE [9]. The electrophoretic mobility of an ion (μ_{ep}) is related to the effective charge on the ion (q_{eff}), the viscosity of the surrounding medium (η) and the apparent dynamic hydrated radius of the sample ion R by the equation:

$$\mu_{ep} = \frac{q_{eff}}{6\pi\eta R}$$

At higher salt concentrations, μ_{ep} is smaller because q_{eff} decreases due to greater shielding [23]. Shielding of the aniline ions by 100 mM concentration of BGE cations is likely to be much greater for the amine cations than for Na^+. This could explain the slower electrophoretic mobilities of the anilines when MA, DEA or TEA electrolytes are used. In addition, it can be noted that the viscosity of aqueous solutions increases with added salts and the amines and may contribute as well to the diminished electrophoretic mobilities of the anilines in the amine solutions.

The electrophoretic mobility of a sample ion is a function of the size and shape of the solvated ion, as well as its effective charge. This would be represented rather crudely by the R term in the equation. Some attraction is likely in solution between the BGE cations, which are hydrated to some degree, and the aromatic sample cations. This would result in a larger solvation cloud around the anilines than would be the case when Na^+ was the BGE cation. Thus, a larger R term would lead to lower values for μ_{ep}.

4. Conclusions

Heretofore, mostly large molecules such as surfactants and soluble polymers have been used when it is desired to alter the migration characteristics of analyte ions in CE. These chemicals affect the EOF by forming semi-permanent surface coatings, and they may modify the electrophoretic mobility of sample ions by forming micelles in the liquid phase. Now we find that at concentrations of 100 mM or so, much smaller organic ions in the BGE will change the EOF in a controlled manner and also alter the electrophoretic migration of sample cations.

Faster separations are obtained in CE when the electrophoretic vectors and the electroosmotic flow are in the same direction (co migration). However, separation of sample ions may be incomplete in this mode and it becomes necessary to obtain longer migration times in order to improve peak resolution. This can be accomplished by reversing the direction of EOF and thus perform the separation in a counter migration mode. By selecting the electrolyte cation from a series of protonated aliphatic amines of increasing size, the migration times of the sample cations can be increased just enough to attain the desired resolution. In this way the time required for a given separation can be optimized.

The present study has been limited to the separation of protonated anilines in the pH range of 1.6–4.0. However, we anticipate that the general principles outlined here can be extended to other CE systems over a broader pH range.

The results reported here emphasize the truism that each and every chemical in the BGE has an effect on the migration of ionic analytes. The capillary surface is altered because each component of the electrolyte is in a dynamic equilibrium between the bulk solution and the capillary surface. Each component can also interact in solution with an analyte to alter its electrophoretic migration. Of course some electrolytic components have a much greater effect than others, but our results show that the effect even of “ordinary” cations and anions is not always negligible, especially when their concentration is relatively high.

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