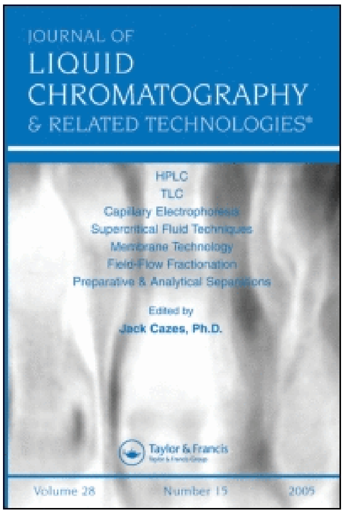

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Anthony H. Harakuwe[a]; Paul R. Haddad[a]; Rudolf Thomas[a]
[a] Department of Chemistry, University of Tasmania, Hobart, Australia

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THE EFFECT OF BUTAN-1-OL ON THE SEPARATION OF INORGANIC ANIONS USING CAPILLARY ZONE ELECTROPHORESIS WITH REVERSED ELECTROOSMOTIC FLOW

Anthony H. Harakuwe,* Paul R. Haddad, Rudolf Thomas

Department of Chemistry
University of Tasmania
GPO Box 252-75
Hobart 7001, Australia

ABSTRACT

The separation selectivity of inorganic anions in capillary zone electrophoresis with reversed electroosmotic flow was altered by incorporating ≤7.5% v/v butan-1-ol in a chromate-based background electrolyte (BGE). Pronounced selectivity changes occurred for lipophilic anions, whereas, for the common inorganic anions, the changes were minor. The likely causes for these selectivity changes are discussed. Furthermore, BGEs with butan-1-ol yielded separations with (i) short times for lipophilic anions, (ii) smoother baselines, (iii) better resolutions, (iv) increased peak heights for iodide and thiocyanate, and (v) good reproducibility (≤4% RSD, n = 11) for absolute migration time, peak area, and peak height.

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INTRODUCTION

In “normal” capillary zone electrophoresis (CZE) using bare fused silica capillaries, the separation time for inorganic anions is long because the electroosmotic flow (EOF) typically is against the anions. To shorten the time, the EOF is commonly reversed by adding a cationic surfactant to the BGE.[1] Apart from time, surfactants also influence the separation selectivity.[2] The selectivity achieved with the aid of surfactants can be altered through secondary effects, e.g. by adding organic solvents to the BGE. A wide range of organic solvents can be used in CZE and for this study, butan-1-ol was chosen because; (i) its use in manipulating the selectivity of inorganic anions in CZE with reversed EOF is unreported, (ii) only small amounts are required[3,4] in contrast to other solvents where up to 30% v/v[5] or more are needed to effect selectivity changes, (iii) it was compatible with the detection mode used, (iv) it has some solubility in water, and (v) it stabilizes the EOF.[3] This article discusses the influence of butan-1-ol on the separation selectivity of inorganic anions in CZE with reversed EOF using a chromate-based BGE with tetradecyltrimethylammonium bromide (TTAB). Also, the effect on absolute migration time (AMT), limit of detection (LOD), and precisions of AMT, peak area, and peak height will be discussed.

EXPERIMENTAL

Instrumental

A Quanta 4000 CZE instrument (Waters, Milford, MA, USA) interfaced with a Maxima 820 data station was used. The conditions in Table 1 were used throughout. BGE pH was measured with a model 8520 digital pH meter (Hanna Instruments, Singapore).

Reagents and Procedure

Anions

The following anion sources were (except where noted) sodium salts, of AR grade, purchased from Ajax Chemicals (Sydney, Australia), and dried before use: chloride (BDH, Victoria, Australia), fluoride and sulfate (Rhône-Poulenc, Manchester, UK), potassium iodate (Fluka AG, Switzerland), iodide (Merck, Darmstadt, Germany), thiocyanate (GPR, Hopkin & Williams, UK), trisodium phosphate.$12H_2O$ (undried), potassium bromate, carbonate, nitrate, and nitrite. Two mixtures were made to study (i) the effect on selectivity and LOD, and (ii) the precision of AMT, peak area, and peak height, respectively. The compositions of the mixtures are shown under the appropriate captions.

Table 1

Instrumental Conditions Used in This Study

Capillary	
Type:	Bare fused silica
Inner Diameter:	0.075 mm.
Outer Diameter:	0.365 mm.
Effective Length:	520 mm.
Total Length:	600 mm.
Detection	
Mode:	Indirect UV
Wavelength:	254 nm.
Range:	0.001 AUFS.
Time Constant:	0.1 second
Polarity:	Reversed
Others	
Sampling:	100 mm for 30 s.
Voltage:	-20kV.
Data Acquisition:	20 Hz.
Purge Time:	5 minutes
Temperature:	Ambient

Background Electrolyte

Sodium chromate and butan-1-ol (LR, Ajax, Sydney, Australia), TTAB (AR, Aldrich, Milwaukee, WI, USA) dried at 100°C for ≥1 hour, and NaOH (AR, BDH, Victoria, Australia) were required.

BGEs were prepared fresh using the following procedure, filtered (0.45 μm) and degassed by ultrasound before use: The required amounts of TTAB and butan-1-ol were combined, diluted to ~80% of final volume, and stirred until there was no sign of emulsion. The pH was then adjusted to ~8 with 0.5 M NaOH, chromate added, and the solution mixed. Addition of chromate lowered the pH of the BGE. The pH was re-adjusted to 8.03 before dilution to final volume.

Prior to separation with each BGE, the capillary was conditioned according to the procedure in reference 4. Milli-Q® water from a Millipore (Bedford, MA, USA) purification system was used in all instances.

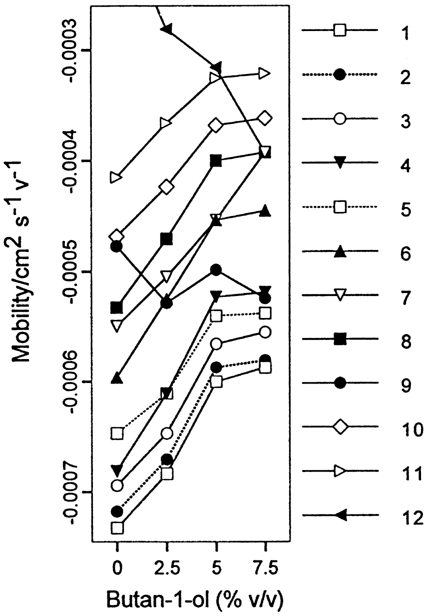

Figure 1. Effect of butan-1-ol on the separation selectivity of inorganic anions. Conditions: Apart from the varying amounts of butan-1-ol, all BGEs contained 5 mM chromate and 2.5 mM TTAB at pH 8.03. The other conditions were as in Table I. Negative mobilities denote migration to the anode, and were calculated according to Reference 16. Anions (μg mL^{-1}): 1 = chloride (8), 2 = system peak, 3 = nitrite (6), 4 = sulfate (8), 5 = nitrate (10), 6 = fluoride (5), 7 = bromate (7), 8 = hydrogenphosphate (12), 9 = iodide (10), 10 = hydrogencarbonate (10), 11 = iodate (10), and 12 = thiocyanate (10).

RESULTS AND DISCUSSION

Firstly, note that no application is shown here. However, analyses utilizing the trends from this study are being carried out on iodine speciation and quantification in table salt and seawater, and will be reported later.

Secondly, the chromate and TTAB concentrations were kept constant at 5 mM and 2.5 mM, respectively. The former is the 'standard' chromate concentration in CZE.

The latter was chosen as it afforded a selectivity where the interference from the system peak on adjacent anions was minimal, gave a separation time of <10 min, and the AMT was stabilized relatively quickly.[6]

Effect on Selectivity

The effect of increasing amounts of butan-1-ol on the selectivity of inorganic anions is shown in Fig. 1. Major selectivity changes occurred for lipophilic anions, iodide, and thiocyanate. Minor changes occurred for sulfate, nitrate, and bromate. The possible causes for the observed selectivity changes are discussed below.

Lipophilic anions

The TTAB in the BGE dynamically coats the capillary surface and forms a double-layer. This layer may act as a "quasi" stationary phase and retard the lipophilic anions through formation of ion-pairs[7,8] or by ion-exchange effects.[9] When the capillary surface is also occupied by butan-1-ol,[3] the double-layer thickness and charge density of the "quasi" stationary phase are reduced. This would weaken the retardation effect and allow the lipophilic anions to migrate faster. The EOF decreased with increasing amount of butan-1-ol in the BGE, which indicated a reduction in the thickness and/or charge density of the double-layer and gives support to the above discussion. Further support is given by the increase in migration time for the non-lipophilic anions. Also, the lipophilic anions may form ion-pairs with the free TTAB in the BGE which the butan-1-ol may partially suppress,[10] increasing the effective charge and thus producing a faster migration rate.

Other anions

The reversal of the migration order of sulfate and nitrate is similar to the result of Buchberger and Haddad.[5] Reduction in hydration volume as a major cause for selectivity change is less likely as any change would have been pronounced for the highly solvated fluoride and this was not observed. The likely causes for the reversal of the sulfate and nitrate migration order are a decrease in the effective charge:size ratio of sulfate through selective variation in the solvation shell,[11,12] or changes in ion-association.[12]

Bromate showed a migration trend that, to our knowledge, has not been reported previously for the system studied here. Since butan-1-ol forms a monolayer on the capillary surface,[3] it was thought that bromate was retarded by interacting with this monolayer. To validate this notion, a 10 μg mL^{-1} bromate standard was separated before and after extraction with butan-1-ol to see if there would be a change in the response. A reduction, which would have supported the case for bromate interacting with the monolayer, was not recorded after extraction. Solubility tests showed that bromate was more soluble in water than in butan-1-ol. These results suggested that the selectivity trend for bromate was probably due to shifts in solubility and solvation equilibria,[13] or through ion-dipole interaction with the polar solvent.[14]

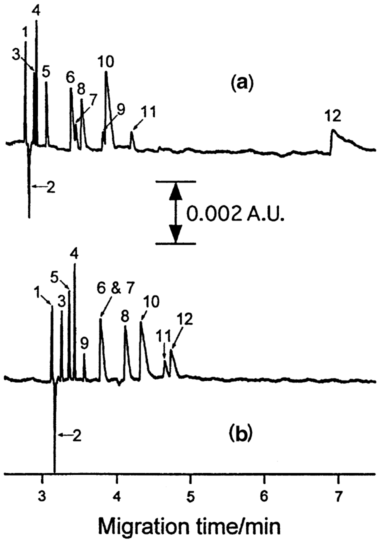

Figure 2. Effect of butan-1-ol concentration on the separation time and resolution of inorganic anions. BGEs: Both (a) and (b) had 5 mM chromate, 2.5 mM TTAB, and pH 8.03 except (b) had 5% v/v butan-1-ol. Conditions: As in Table 1. Anions: The identities and concentrations were as in Fig. 1.

Effect on Migration Time and Resolution

Incorporation of butan-1-ol in the BGE reduced the total separation time by >28% (Fig. 2) for the mixture. However, the migration times for the non-lipophilic anions were, in agreement with the observations of Benz and Fritz,[3] increased. Also, the resolution between anions was improved by having butan-1-ol in the BGE (compare Figs. 2 a and 2 b). The exception was bromate, which co-migrated with fluoride.

Reproducibility

A BGE with 5% v/v butan-1-ol was used since it gave the best overall separation (Fig. 2b). Separation using a BGE without butan-1-ol was unwarranted as there was sufficient material in the literature for comparison purposes. Precisions (RSD) for AMT, peak area, and peak height were ≤4% (Table 2) and comparable to literature values, e.g. 1-5% for AMT,[15-17] 2-56% for peak area,[15,17-19] and 3-32% for peak height.[19,20] The excellent AMT precision was indicative of a stable EOF and gave quantitative support to the report of Benz and Fritz.[3]

Table 2

Summary of Reproducibility

	% RSD Reproducibility$^{\varphi}$ (n = 11)		
Anion	**AMT‡**	**Area$^{\theta}$**	**Height$^{\beta}$**
Chloride	1.6	2.1	0.9
Sulfate	1.6	1.1	1.3
Hydrogenphosphate	1.7	4.0	1.7
Hydrogencarbonate	1.8	*	*

$^{\varphi}$ = for BGE with 5% v/v butan-1-0l and a mixture (μg mL^{-1}) with chloride (10), sulfate (20) and hydrogenphosphate (10), ‡ = absolute migration time (mih), $^{\theta}$ = μVS, $^{\beta}$ = μV, and * = the precision values for peak area and peak height were not calculated as the hydrogencarbonate was ubiquitous.

Table 3

Summary of Limit of Detection

	Limit of Detection$^{\phi}$	
Anions	**0% v/v Butan-1-ol**	**5% v/v Butan-1-ol**
Chloride	0.5	0.8
Sulfate	0.3	0.5
Hydrogenphosphate	1.3	1.4
Hydrogencarbonate	1.6	0.4
Bromate	1.5	*
Fluoride	0.5	0.6
Iodate	3.1	4.0
Iodide	4.4	2.4
Nitrate	0.8	0.7
Nitrite	0.8	0.6
Thiocyanate	3.1	2.7

$^{\phi}$ = in μg mL^{-1} calculated at 3 X baseline noise, and * not determined as it was swamped by fluoride. The mixture was as shown in Figure 1.

Limit of Detection

The LODs for BGEs with and without butan-1-ol were generally comparable (Table 3). The exceptions were iodide and thiocyanate, which showed improved LODs using the BGE with butan-1-ol due to their increased peak heights. Improvement in the LOD of bicarbonate using the BGE with butan-1-ol was likely to be an artificial effect due to ubiquitous carbon dioxide.

CONCLUSIONS

The separation selectivity of inorganic anions in CZE with reversed EOF was manipulated by using butan-1-ol as a BGE additive. Shifts in ion-pairing and ion-exchange effects were the likely causes for the major selectivity changes for lipophilic anions. Also, BGEs with butan-1-ol yielded separations with short total times, smoother baselines, improved resolution between anions, improved detectability for iodide and thiocyanate, and good precisions for AMT, peak area, and peak height.

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