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Separation of inorganic and organic anionic components of Bayer liquor by capillary zone electrophoresis I. Optimisation of resolution with electrolyte-containing surfactant mixtures

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Abstract

The simultaneous separation of chloride, sulfate, oxalate, malonate, fluoride, formate, phosphate, carbonate and acetate in Bayer liquor using capillary zone electrophoresis with indirect detection is demonstrated using electrolytes comprising binary mixtures of the surfactants tetradecyltrimethylammonium bromide (TTAB) and dodecyltrimethylammonium bromide (DTAB). Two optimal electrolyte compositions were identified, namely 3 m*M* TTAB, 3 m*M* DTAB and 7.5 m*M* chromate at pH 9 (optimum 1) and 5 m*M* TTAB, 1 m*M* DTAB and 5.5 m*M* chromate at pH 9 (optimum 2). The separation selectivities of these electrolytes differ and the choice between them rests on consideration of the relative concentrations of the ionic species in the sample. Best results were obtained when the Bayer liquor sample was diluted by a factor of 500 before analysis. Linear calibrations were achieved in the working concentration range (1–10 μg/ml) and detection limits fell in the range 0.09–0.34 μg/ml for optimum 1 and 0.16–0.88 μg/ml for optimum 2. Recoveries of ions added to the diluted sample were close to quantitative, except for phosphate which showed low and variable recovery, and carbonate which was also variable due to absorption of carbon dioxide by the sample. Tartrate and succinate could not be resolved with either of the optimal electrolyte compositions.

1. Introduction

Pioneered by Jorgenson and co-workers in the 1980s [e.g. 1–3], capillary zone electrophoresis (CZE) is a differential migration separation technique that separates solutes according to their charge-to-mass ratios under an applied electric field. For the rapid separation of inorganic anions and low-molecular-mass organic acids, a suitable cationic surfactant (e.g. tetradecyltrimethylammonium bromide) is normally incorporated in the running electrolyte [4–6] to enable the electroosmotic flow (EOF) and the migrating anions to move in the same direction. Detection is usually performed in the indirect UV absorption mode since most inorganic anions show insufficient UV absorbance to permit sensitive direct detection. The high separation power, speed, quantitative reliability and unique selectivity of CZE make it attractive for the sepa-

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ration of samples containing inorganic anions and short-chain carboxylic acid anions, such as Bayer liquors.

Bayer liquors are by-products of alumina (Al_2O_3) and aluminium metal production. Alumina is made from bauxite ore via the cyclic Bayer process, and in the production of aluminium metal, the alumina is reduced electrolytically using the Hall–Héroult process (see [7]). Liquors from these processes are typically of high pH and ionic strength and contain numerous anions such as chloride, sulfate, phosphate, fluoride, oxalate, silicate, succinate, malonate and formate [8,9].

The analysis of anions in Bayer liquor is vital for two main reasons, namely process monitoring (including quality control and optimisation of product yield and purity) and toxicology and environmental impact monitoring. On the process monitoring side, sodium ions associated with fluoride, chloride, sulfate and carbonate interfere with alumina precipitation in the Bayer process, increase liquor viscosity and reduce oxalate stability, making removal of the latter from process liquor difficult [8,10]. Low levels of gluconic and tartaric acids also inhibit precipitation [10]. The rapid determination of fluoride is important for the determination of cryolite ratio ($NaF:AlF_3$) [11], with a ratio of 2–3 needing to be maintained for optimal operation [12]. On the environmental monitoring side, fluoride is a universal toxin affecting humans, plants and animals. Free and complex cyanides are also present [11].

Ion chromatography (IC) is the only technique comparable to CZE for simultaneous separation of multiple anions. However, analysis of Bayer liquor using IC is not used routinely most probably due to co-elution of weakly retained species [6,7]. Furthermore, Bayer liquor is of high ionic strength and pH and is extremely difficult to separate by IC without clean-up or pre-treatment, for example by dialysis [13]. When injected directly, untreated samples reduce column life and performance [14], the latter being due primarily to severe disturbance of the acid–base equilibria in the system. The simultaneous and fully resolved separation of chloride, oxalate, malonate, fluoride, formate, carbonate, phosphate, acetate and citrate in Bayer liquor using IC is yet to be reported.

Separation by CZE of common anions in samples with simple matrices (e.g. tap water) poses few practical problems. However with complex and difficult matrices like Bayer liquor, anion separation can be problematic. Extreme pH is detrimental to bare capillaries [15] and the capillary surface may potentially be altered [16] with a resultant effect on EOF. Like IC, literature related to separation of anions in Bayer liquor using CZE is limited, but the separation of chloride, sulfate, oxalate [8] and fluoride [17] has been reported previously. However the optimised simultaneous separation of the above anions as well as malonate, formate, carbonate and acetate has not been reported to date. The main impediments appear to be inadequate resolution of a closely migrating cluster of anions comprising tartrate, succinate, fluoride, phosphate and formate; and deterioration of the baseline. Furthermore, resolution of fluoride and phosphate is acknowledged as being problematic [18].

In all of the above studies, a single cationic surfactant species has been used to reverse the EOF. In a previous paper, we have noted that certain selectivity effects in the separation of inorganic and organic anions arise when a binary mixture of surfactants is used [19]. The aim of the present work was to exploit these selectivity effects with a goal of achieving a fully resolved separation of the inorganic and organic ionic components of Bayer liquor using CZE.

2. Experimental

2.1. Instrumentation

A Waters Quanta 4000 automated CZE system coupled to a Maxima 820 data station (Dynamic Solutions, Ventura, CA, USA) was used to acquire all electropherograms. A polyimide-coated fused-silica capillary (Polymicro Technologies, Phoenix, AZ, USA) measuring 60 cm total length (52 cm effective length) × 75 μm I.D. was used throughout. A Model 8520 digital

pH meter (Hanna Instruments, Singapore) was used for all pH measurements.

2.2. Reagents and standards

Water from a Milli-Q (Millipore, Bedford, MA, USA) water-purification system was used throughout. Unless specified, all reagents were of analytical-reagent grade and sourced from Ajax Chemicals (Auburn, Australia). Tetradecyltrimethylammonium bromide (TTAB) and dodecyltrimethylammonium bromide (DTAB) were obtained from Aldrich (Milwaukee, WI, USA). Other reagents required were sodium chromate (laboratory-reagent grade, LR) for electrolyte preparation and potassium hydroxide (LR) for pH adjustment and capillary conditioning.

Standard stock solutions (1000 μg/ml) of each of the analytes were made from analytical-reagent grade sodium salts which had been dried at 100°C overnight (except where indicated). The salts used were *d*-gluconate (Fluka, Switzerland), malonate (undried; LR, BDH, Poole, UK), succinate (undried; LR, BDH), citrate (By-Products and Chemicals, Auburn, Australia), formate, acetate (anhydrous; Strem Chemicals, Newburyport, MA, USA), tartrate (Mallinckrodt, St. Louis, MO, USA), phosphate ($Na_3PO_4 \cdot 12H_2O$, undried), chloride (Rhône Poulenc, Victoria, Australia), nitrate, sulfate (May & Baker, Manchester, UK), fluoride (Rhône Poulenc, Manchester, UK) and carbonate (anhydrous). An oxalate standard solution was made by dissolving 0.3583 g undried $H_2C_2O_4 \cdot 2H_2O$ (Mallinckrodt) and titrating with NaOH to pH 6.1 and dilution to 200 ml. An adipate standard was made similarly by titrating 0.2535 g adipic acid (LR) to pH 8.6 and dilution to 200 ml. Working standards between 1 and 10 μg/ml were made by appropriate dilution of the stock solutions.

2.3. Procedures

Running electrolytes were prepared daily using accurately weighed amounts of TTAB and/or DTAB dried at 100°C for 1 h. After dissolution of the solid material and dilution to ca. 80% of final volume, the appropriate aliquot of 100 m*M* chromate was added and the pH adjusted to 9 ± 1 with HNO_3 or NaOH. Final dilution of the electrolyte was used to produce 5 m*M* chromate and the desired concentration(s) of surfactant(s).

Prior to use, the capillary was conditioned by vacuum flushing for 5 min each with water, absolute ethanol and then water; 8 min with 0.5 *M* KOH; 5 min with water; and finally for 10 min with the running electrolyte. All injections were performed in the hydrodynamic mode by gravity feed. Detection was at 254 nm in the indirect mode using chromate as the probe. The detector polarity was reversed so that detected peaks appeared in the positive direction. A voltage of 20 kV was applied from a negative power source for all separations and data acquisition was at 20 points/s. All measurements were made in replicates of ≥ 2 using fresh running electrolyte per analysis. Peak positions were confirmed by spiking with known standards.

3. Results and discussion

We have shown previously [19] that anion selectivity in CZE can be manipulated by using binary TTAB and DTAB mixtures in the running electrolyte. The work discussed here is an extension of this approach to achieve an optimised separation of inorganic anions and short-chain organic acid anions in Bayer liquor. Separation using single surfactants was performed first to provide a basis for comparison with the use of surfactant mixtures. Migration times were determined for the species anticipated to be present in the Bayer liquors (chloride, sulfate, fluoride, phosphate, carbonate, acetate, oxalate, malonate, formate, tartrate, succinate and citrate), as well as cyanide, adipate, gluconate and nitrate. The migration time of nitrate was important since nitric acid was to be used to adjust the electrolyte pH.

3.1. Use of DTAB and TTAB as single surfactants in the running electrolyte

Fig. 1 shows the separation of diluted Bayer liquor using 2.6 m*M* TTAB (Fig. 1a) and 2.6 m*M* DTAB (Fig. 1b) as single surfactants in the

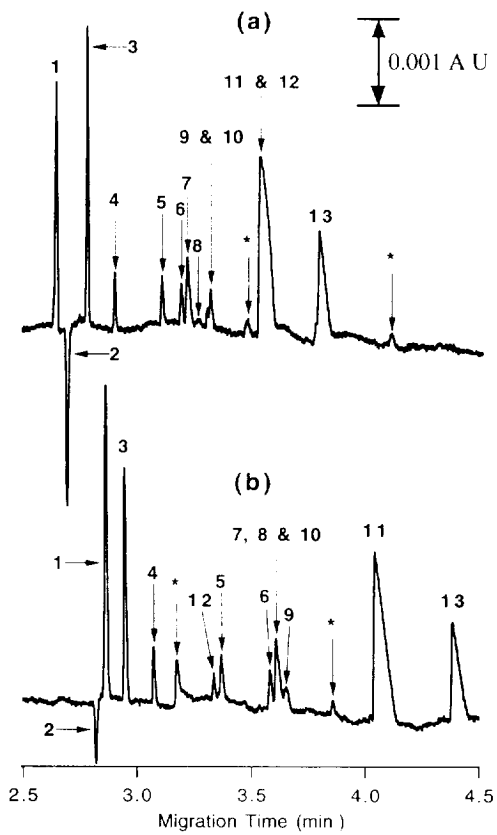

Fig. 1. Separation of 1:500 (v/v) diluted Bayer liquor using electrolytes comprising (a) 2.6 m*M* TTAB and (b) 2.6 m*M* DTAB, together with 5 m*M* chromate at pH 9.1. Injection was in the hydrostatic mode (raised 10 cm for 45 s) and detection was in the indirect spectrophotometric mode at 254 nm. A capillary of 60 cm total length (52 cm effective length) × 75 μm I.D. was used. Peaks: 1 = chloride; 2 = system (bromide); 3 = sulfate; 4 = oxalate; 5 = malonate; 6 = fluoride; 7 = formate; 8 = phosphate; 9 = tartrate; 10 = succinate; 11 = carbonate; 12 = citrate; 13 = acetate; * = unknown.

running electrolyte. The anions of interest were not fully resolved in either case, however separation using TTAB was generally superior to that obtained using DTAB. The system peak due to the presence of bromide in the electrolyte is a potential cause of interference and was observed to be larger with TTAB than for DTAB under identical conditions.

In the separation using DTAB as the single surfactant, nitrate migrates between sulfate and oxalate and the system peak may interfere with chloride, especially at lower dilution (higher ionic strength). Fluoride, formate, succinate and tartrate are unresolved, and phosphate co-migrates with formate and succinate. For the separation using TTAB as the single surfactant, fluoride was resolved from the usual interfering anions (formate, tartrate, phosphate and succinate) and the clean separation of chloride, sulfate and oxalate compares well with that achieved by Grocott et al. [8]. The disadvantages evident with this electrolyte are the possible non-resolution of closely migrating adjacent anions (e.g. fluoride and formate), especially where a large disparity in concentration exists, poor resolution of succinate and tartrate, and the likelihood that elevated levels of carbonate will interfere with the determination of citrate. In addition, nitrate co-migrates with oxalate, making any adjustment of electrolyte pH with nitric acid unsuitable, and there is a tendency for rapid crystal formation in the electrolyte.

3.2. Separation using TTAB and DTAB mixtures in the running electrolyte

Fig. 2 shows the effects on the relative migration times obtained for anions in a diluted Bayer

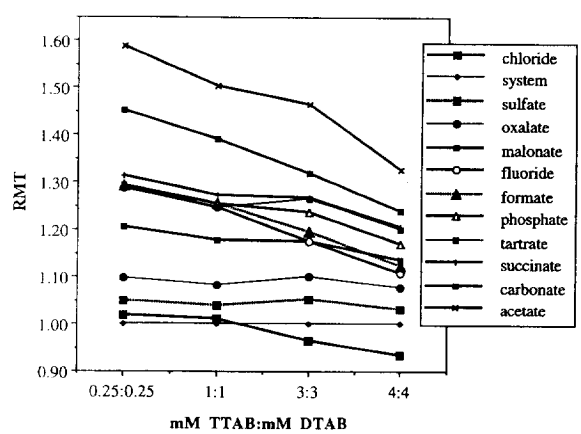

Fig. 2. Effect of electrolytes comprising equimolar surfactant mixtures on the relative migration times (RMT) for solutes in a 1:500 (v/v) diluted Bayer liquor. Conditions as in Fig. 1 except injection times and electrolyte pH were 30 s and 8.8, respectively. All migration times are normalised to the system peak.

liquor sample when various equimolar mixtures of TTAB and DTAB were used to modify the EOF. A number of selectivity effects are evident, but the general trend is that the relative migration times decrease as the total concentration of the surfactant mixture increases. The best separation occurs when both TTAB and DTAB are present at a concentration of 3 m*M*, although some species co-migrate (succinate and tartrate, fluoride and malonate). It can be noted that the migration order of the solutes using this mixture is different from that obtained with either of the two surfactants used singly (see Fig. 1). Further optimisation of the separation was investigated by changing the concentration of the chromate (present to permit the indirect UV absorbance detection of the analytes) in the electrolyte. Fig. 3 shows the results obtained when the chromate concentration was increased from 5 m*M* (as used in Fig. 2) to 7.5 m*M*. While the changes observed were only minor, the resolution of fluoride and malonate improved at the highest chromate concentration studied. It should be noted that increasing the concentration of chromate has a beneficial effect on the detection signal, as shown in Fig. 4 using chloride as the analyte anion. These studies suggested that an optimal separation could be

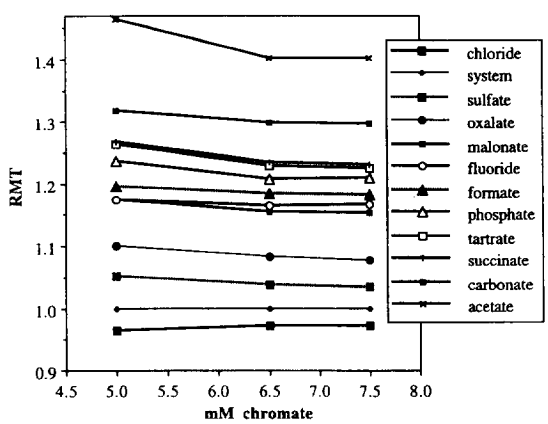

Fig. 3. Effect of chromate concentration in the running electrolyte on the relative migration times (RMT) for solutes in a 1:500 (v/v) diluted Bayer liquor. The electrolyte contained 3 m*M* TTAB and 3 m*M* DTAB. Other conditions as in Fig. 1. All migration times are normalised to the system peak.

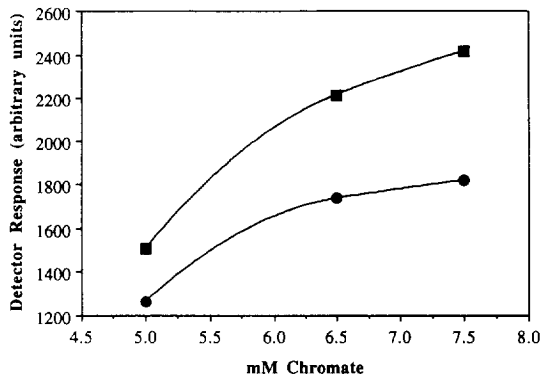

Fig. 4. Effect of chromate concentration variation on the detector response for chloride using electrolytes containing 3 m*M* TTAB and 3 m*M* DTAB. Other conditions as in Fig. 1. ● = Peak area; ■ = peak height.

achieved using an electrolyte containing 3 m*M* of both TTAB and DTAB and 7.5 m*M* chromate. An electropherogram obtained using this electrolyte (which will be designated as optimum 1) is shown in Fig. 5. A potential problem with this separation is the minimal separation of malonate, fluoride and formate which could lead to partial co-migration of these species if they were present at higher concentrations than shown in Fig. 5.

The empirical optimisation procedure described above was repeated for a wide range of mixtures of TTAB, DTAB and chromate. It was found that the separation selectivity could be manipulated to produce a desired electropherogram. For example, the resolution problem mentioned earlier for optimum 1 could be overcome using 5 m*M* TTAB, 1 m*M* DTAB and 5.5 m*M* chromate. The electropherogram obtained with this electrolyte, designated as optimum 2, appears in Fig. 6.

The two optima shown in Figs. 5 and 6 allow for some separation flexibility to be exercised, especially when there are large disparities in concentration between fluoride and adjacent anions. The two optima are also ideal for the separation of additional anions not shown in the two figures (e.g. nitrate, adipate, citrate and gluconate). Variations in the concentration of chromate in the electrolyte can be used to fine-tune the separation where necessary. The obvi-

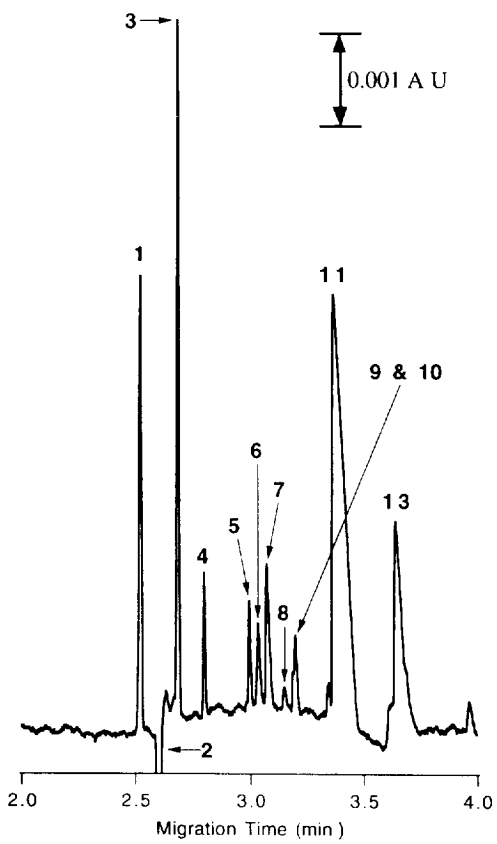

Fig. 5. Separation of 1:500 (v/v) diluted Bayer liquor using an electrolyte comprising 3 m*M* TTAB, 3 m*M* DTAB and 7.5 m*M* chromate (optimum 1). Other conditions as in Fig. 1.

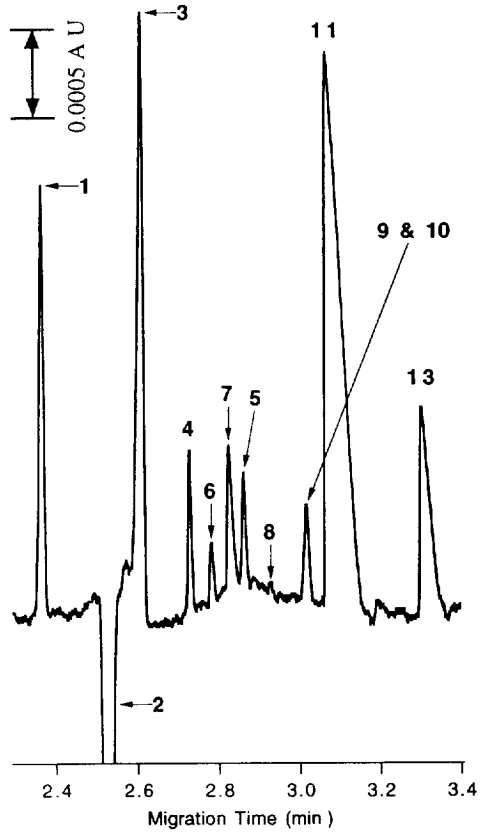

Fig. 6. Separation of 1:500 (v/v) diluted Bayer liquor using an electrolyte containing 5 m*M* TTAB, 1 m*M* DTAB and 5.5 m*M* chromate (optimum 2). Other conditions as in Fig. 1.

ous common disadvantage of both optima is the poor resolution of tartrate and succinate.

3.3. Analytical performance parameters

Using chloride as a model solute, Fig. 7 illustrates that detectability decreases with increasing (total) surfactant concentration. Whilst the responses obtained for optima 1 and 2 were less than for some of the other electrolyte compositions examined, a compromise between detectability and attainment of the desired resolution is necessary. For Bayer liquor, selectivity takes priority over detectability since the latter can easily be enhanced by using a lower sample dilution.

Table 1 summarises results related to quantification using the two optimal electrolyte compositions. For optimum 1, peak area precision was better than 6.6% R.S.D. for all solutes except carbonate, fluoride and phosphate. The high R.S.D. for the carbonate peak area is due to the absorption of carbon dioxide from air, whilst fluoride complexes strongly with iron and aluminium and low or variable values are often recorded in Bayer liquor analysis [17]. The determination of fluoride has been investigated in detail and will be reported in a subsequent publication. Phosphate was not detected at the 1:500 dilution used, so that a more concentrated sample was required. Phosphate response was noted to be very variable and this appeared to be a function of capillary conditioning regimes. All calibration plots had correlation coefficients

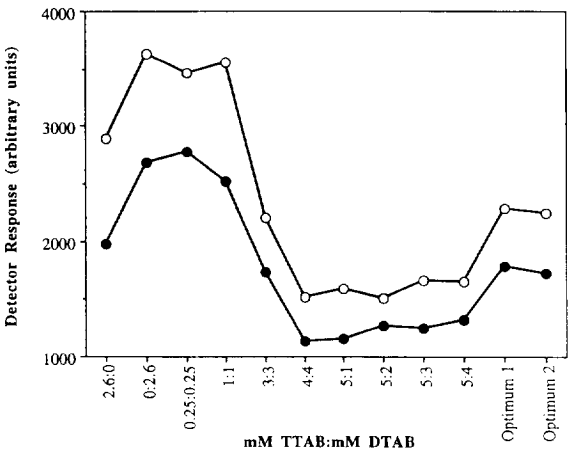

Fig. 7. Effect of surfactant combinations in the electrolyte on detector response for chloride. All electrolytes contained 5 m*M* chromate, except for optima 1 and 2. Conditions for optimum 1 and optimum 2 as in Figs. 5 and 6, respectively. Other conditions as in Fig. 1. ● = Peak area; ○ = peak height.

≥99.5%, except for phosphate and acetate, and recovery values were close to quantitative for all solutes except phosphate. For optimum 2, peak area precision was better than 7.8% R.S.D. (again except for carbonate, fluoride and phosphate). The low recovery observed for sulfate is a result of interference from the system peak; especially at low sample dilution. The detection limits (determined at 3 × baseline noise) of the solute anions are listed in Table 1, which shows that with the exception of phosphate, these detection limits are more than adequate for analysis of the 1:500 diluted Bayer liquor.

The two identified optima are limited by their inability to resolve tartrate and succinate. Furthermore, poor resolution of adjacent anions is a possibility at high and disparate solute concentrations. With optimum 1, acetate is prone to interference from citrate, whereas with optimum 2, the interference is likely to be from

Table 1
Summary of analytical performance parameters using optima 1 and 2

Anion	Peak area precision, % R.S.D. (*n*)		Correlation coefficient (r^2)		Concentration (μg/ml)		Recovery (%) (*n*)		Detection limit (μg/ml)	
	1	2	1	2	1	2	1	2	1	2
Chloride	1.5 (8)	1.7 (10)	99.8	99.6	4.1	4.3	107 (6)	109 (2)	0.14	0.16
Sulfate	2.7 (10)	1.7 (10)	100.0	99.8	4.4	5.1	108 (4)	71 (3)	0.11	0.22
Oxalate	3.4 (8)	2.0 (8)	99.9	99.9	0.8	0.9	100 (6)	104 (4)	0.11	0.16
Formate	4.8 (6)	4 (10)	99.6	99.5	1.4	1.5	99 (6)	98 (4)	0.15	0.29
Fluoride	8.6 (10)	6.4 (8)	99.9	100.0	0.4	0.4	106 (3)	109 (3)	0.09	0.17
Malonate	6.6 (10)	5.5 (5)	99.8	99.7	0.9	1.0	103 (6)	99 (4)	0.16	0.23
Phosphate[a]	n.d.	n.d.	99.6	98.5	0.1	0.4	87.8 (6)	95 (6)	0.07	0.88
Carbonate	21.7 (10)	20.6 (10)	–	–	–	–	–	–	–	–
Acetate	4.0 (8)	7.8 (8)	99.6	96.4	5.0	4.7	95 (6)	113 (2)	0.34	0.58

R.S.D. = Relative standard deviation; *n* = number of replicates; 1 = optimum 1; 2 = optimum 2; n.d. = not detected. Detection limit calculated at 3 × baseline noise.

[a] 1:50 dilution used for quantification of phosphate.

adipate. There is a large disparity between the amount of phosphate detected using the two optima and this is again attributable to capillary conditioning regimes and capillary age and history. At the present time, the determination of phosphate using the methods reported in this paper is unreliable and will be examined further. The system peak is a potential source of interference for the determination of chloride and sulfate. However, the ionic strength and total surfactant concentration in the running electrolyte influence the behaviour and magnitude of the system peak. Interestingly, it has been noted that at equal concentration, DTAB yields a smaller system peak than TTAB. Where possible, maximum possible dilution of sample is advisable.

4. Conclusions

Two optimal running electrolytes able to fully resolve chloride, sulfate, oxalate, formate, fluoride, malonate, phosphate, carbonate and acetate in Bayer liquor were identified at (i) 3 m*M* TTAB, 3 m*M* DTAB and 7.5 m*M* chromate at pH 9 ± 1 and (ii) 5 m*M* TTAB, 1 m*M* DTAB and 5.5 m*M* chromate at pH 9 ± 1. Both optima employ binary surfactant mixtures in the running electrolyte and have different selectivities, allowing for some flexibility when separating samples with high and disparate anion concentrations.

Acknowledgements

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