Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Chromatography A, 1095 (2005) 164–171
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

A new ionic liquid dimethyldinonylammonium bromide as a flow modifier for the simultaneous determination of eight carboxylates by capillary electrophoresis

Pirkko-Leena Laamanen*, Sara Busi, Manu Lahtinen, Rose Matilainen

Department of Chemistry, University of Jyväskylä, PO Box 35, FI-40014, University of Jyväskylä, Finland

Received 27 June 2005; received in revised form 26 July 2005; accepted 27 July 2005
Available online 5 October 2005

Abstract

Two new methods of capillary zone electrophoresis based on aqueous phosphate running buffers with UV spectrophotometric detection were developed and optimized for the determination of eight carboxylates as copper complexes. Metalcomplexes are negatively charged, so measurements were made as anion analyses with flow reversal in the capillary. Two flow modifiers were used: a common tetradecyltrimethylammonium bromide (TTAB) and a new ionic liquid dimethyldinonylammonium bromide (DMDNAB). The methods were compared to each other. Better separation was achieved with DMDNAB as the flow modifier. Method development was done using a fused silica capillary (61 cm × 50 μm i.d.).Optimization was done using 95 mmol L^{-1} phosphate buffer with TTAB or DMDNAB in the concentration 0.5 mmol L^{-1} at pH 7.1. A −20 kV voltage and direct UV detection at 254 nm was used in measurements. In both CE methods all the peaks in the electropherograms were properly separated, the calibration plots gave good correlation coefficients and all eight carboxylates were detected in less than 7.5 min. The two methods were tested with natural water samples and a paper mill sample, and proved to be feasible.

Keywords: Chelating agents; Capillary electrophoresis; Dimethyldinonylammonium bromide; Ionic liquid; TTAB

1. Introduction

Aqueous and nonaqueous capillary electrophoresis techniques are nowadays widely used in research and have attracted a growing interest in industry. The advantages of CE methods compared to other analytical methods are, e.g. the short analysis time, the small sample size and small amount of electrolytes needed for the analysis, and the simplicity of the procedure. When using the capillary zone electrophoresis technique, the polarity can be chosen according to the requirements. If the main interest lies in cation analysis positive polarity is a natural choice, but in anion analyses negative polarity allows a shorter analysis time. When negative polarity is chosen, the flow in the capillary must also be reversed. Flow reversal can be done either by dynamic coating of the capillary [1,2] or by using a coated capillary [3–5]. Commercial coated capillaries are available [5] or the capillary could be coated in the laboratory [3,4]. The most common reagents used in dynamic coatings are quaternary alkylammonium bromides, e.g. cetyltrimethylammonium bromide (CTAB) and chloride (CTAC), and tetradecyltrimethylammonium bromide (TTAB) [6].

Ionic liquids, also called molten salts, are liquids at ambient temperatures and consist only of ionic species [7,8]. Ionic liquids are environmentally benign, nonvolatile and nonflammable, and in addition they have high thermal stability [9]. In addition ionic liquids are good solvents for both organic and inorganic materials [9]. Partly because of this, these reagents have been found useful in wide range of applications in chemistry and interest in them is growing very fast. Thus, they have been used in, e.g. liquid based extractions [10–14] organic synthesis [15–18], electrochemistry [19–21] catalysis [22,23], mass spectrometry [24] and separations [2–4,7–9,25–29]. The widespread use of ionic liquids leads

* Corresponding author. Tel.: +358 14 260 2612; fax: +358 14 260 2501.
E-mail address: pirlaam@cc.jyu.fi (P.-L. Laamanen).

0021-9673/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2005.07.111

also to their drift into the environment. Analytical extraction and analysis methods for measuring their concentrations in natural waters are needed and in fact the development of such methods has already started [30].

At the focus of capillary electrophoresis, ionic liquids can be used as electrolytes [3,4,7,9,28], as additives in electrolytes [2,8,27] and as covalent coating reagents of the capillary [3,4]. The use of ionic liquids is not limited only to aqueous systems [3,4]; they are also useful in nonaqueous systems [27,28]. Dialkylimidazolium based ionic liquids have recently been used in capillary electrophoresis [2–4,7–9,27,28]. In addition to these common ones, new recently synthesized ionic liquids may be potential reagents for analytical chemists in achieving better separations and easier analytical methods. The use of ionic liquids in separation science will grow along with the speed of the synthesis work done on these analytes.

Our previous study discussed the simultaneous determination of diethyltriaminepentaacetic acid (DTPA), ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) by capillary electrophoresis [1]. These three aminopolycarboxylic acids are the most common chelating agents used in industry, but there are many more carboxylates and phosphonates that also have powerful properties. In this study we expanded the number of chelating agents in one analysis and concentrated on carboxylates only, as according to the literature several metalcarboxylates are not analyzed simultaneously by capillary electrophoresis. We demonstrate that it is possible to separate a higher number of chelating agents in one measurement in a short analysis time and to improve separation with a new ionic liquid as a flow modifier compared to a common additive. The new chelating agents included in our current research are *trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetic acid (CDTA) hydroxyethylethylenediaminetriacetic acid (HEDTA), iminodiacetic acid (IDA) 1,3-propylenediaminepentaacetic acid (PDTA) and triethylenetetraminehexaacetic acid (TTHA). All of these analytes, including DTPA, EDTA and NTA, are synthetic chelating agents and they are used in industrial applications due to the following advantages: they prevent the formation of metal precipitates; they hinder metal ion catalysis of unwanted chemical reactions; and they remove metal ions from the system or they make metal ions more available by keeping them in solutions [1,31–33]. Because almost all aminopolycarboxylates have high polarity and low degradability, they enter creeks, rivers and lakes mainly via industrial and domestic waste water [32]. The extensive use of these acids necessitates the development of an analytical method for industrial and natural water samples.

2. Experimental

2.1. Instrumentation

Electropherograms were obtained on a Hewlett-Packard CE^{3D} G1600 AX apparatus (Hewlett-Packard, Waldbronn, Germany) equipped with a photodiode array detector (DAD) and an air cooling unit for the capillary. Instrument control and data acquisition were performed with HP^{3D} Chemstation software (Hewlett-Packard, Rev 04.02.). Absorbances at 191, 210 and 254 nm were monitored for the detection of analytes. Uncoated fused silica capillary (Composite Metal Services Ltd., The Chase, Worchester, UK) was of 50 μm i.d., 375 μm o.d. and total length 61 cm (52.5 cm to the detector). The capillary cassette temperature was adjusted to 25 °C with air cooling. The operating conditions for a run included a voltage of −20 kV generated by the negative power supply resulting electric currents from −85 to −120 μA. Standards and samples were injected in hydrodynamically by overpressure (50 mbar = 5000 Pa). Depending on the experiment injection time was from 2 to 4 s. The instrument was placed in a special room with automated temperature and humidity control.

2.2. Conditioning of the capillary

Daily, before and after runs, the capillary was conditioned by sequentially purging it with 0.1 mol L^{-1} NaOH (5 min), 0.01 mol L^{-1} NaOH (5 min) and ultra pure water (20 min). In addition, before the commencement of a day's runs the capillary was purged with buffer solution for 20 min. Between all the runs the capillary was purged with buffer for 3 min. After every sixth sample, the capillary was conditioned by washing it with 0.1 mol L^{-1} sodium hydroxide for 5 min, ultra pure water for 15 min and separation electrolyte for 15 min, to assure that capillary was in good condition throughout the sequence.

2.3. Reagents and solutions

Ultra pure water was obtained by passing distilled water through an ELGA Elgastat Maxima (Elga Ltd., UK) and it had a resistivity greater than 18.2 MΩ/cm. All the chemicals used were of analytical reagent grade. Diethylenetriaminepentaacetic acid (DTPA) was obtained from Merck (Darmstadt, Germany), ethylenediaminetetraacetic acid disodiumsalt dihydrate (EDTA) from FF-Chemicals (Yli-II, Finland), and nitrilotriacetic acid trisodium salt monohydrate (NTA) and tetradecyltrimethylammonium bromide (TTAB) from Fluka Chemika (Buchs, Switzerland). Copper sulphate pentahydrate was obtained from Riedel-de Haën (Seelze, Germany). *Trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetic acid (CDTA) hydrate, iminodiacetic acid (IDA) and triethylenetetraaminehexaacetic acid (TTHA) were obtained from Sigma–Aldrich (Steinheim, Germany), 1,3-diaminopropane-*N*,*N*,*N*′,*N*′-tetraacetic acid (PDTA) from Fluka Chemika (Buchs, Switzerland) and *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetic acid (HEDTA) from Fluka BioChemika (Buchs, Switzerland). Diethyldihexylammonium bromide (DEDHAB), dimethyldipentylammonium iodide (DMDPeAI), diethyldihexylammonium iodide (DEDHAI), dimethyldinonylammonium bromide (DMDNAB)

and dimethyldioctylammonium bromide (DMDOAB) were synthesized by Busi et al. [34].

Phosphate BGE was prepared from disodium hydrogenphosphate dihydrate and potassium dihydrogenphosphate, both obtained from Merck (Darmstadt, Germany). TTAB or synthesized quaternary alkylammonium bromides and iodides were added to the buffer solution to reverse the direction of the electroosmotic flow. 0.1 M NaOH and 0.1 M HCl were added to the solutions (buffer and samples) to adjust the pH. pH, adjusted to phosphate BGE and samples, was 7.1. Buffer solution was degassed by passing helium through the solution.

The stock solutions of the complexing agents were made as mixtures of four chelating agents together at a concentration of 20 mmol L^{-1}, and the stock solution of copper was 120 mmol L^{-1}. The stock solutions of the complexing agents needed a small amount of NaOH to make them totally soluble in water. The desired amounts of stock solutions were taken and the pH of the standards/samples was adjusted to the same level as the electrolyte used. The pH adjustments of the samples were done before final buffer addition. The buffer used for sample dilution did not contain any flow modifier. The buffer and samples were filtered through a 0.45 μm membrane filter (GHP Acrodisc, Pall Corporation, USA).

Two natural water samples were used to test the suitability of method in real samples. In addition one paper mill sample (cleaned waste water, which was released back into the river) was obtained from a Finnish paper mill in Southern Finland.

All the aqueous metal complex solutions were allowed to stand overnight to ensure thermodynamic equilibrium and complete complexation prior to the CE analysis. Standards and samples consisted of excess of copper compared the amount of chelating agents in the sample; this is reasonable because it is impossible to know the amounts of chelating agents in an unknown sample. When the solutions stood overnight a blue precipitation formed on the bottom of the volumetric flask. To be sure that the chelating agents did not participate in the precipitation, the blue precipitation was analyzed by X-ray powder diffractometry [35], which proved that the chelating agents were not involved in the precipitation. The most matching phase analysis entries from ICDD powder diffraction database [36] were slightly varying polymorphs of copper hydrogen phosphate hydrates (PDF2 entries 31–458, 12–520 and 22–548).

3. Results and discussion

3.1. Optimization of the phosphate BGE

Optimization of the phosphate run buffer started on the basis of our previous study [1] which concerned the determination of DTPA, EDTA and NTA. First the optimized method with 75 μm i.d. capillary [1] was tested for CDTA, DTPA, EDTA, HEDTA, IDA, NTA, PDTA and TTHA after complexation with copper. After the initial measurements it was clear that the method for three chelating agents [1] needed further development to separate all the eight chelating agents properly. The composition of the buffer had to be optimized, and the increment of the buffer used previously was not very good choice with 75 μm i.d. capillary, as it would have increased the current too much. Hence experiments with a narrower capillary were done. The current was clearly lower using 80 mmol L^{-1} phosphate buffer and a 50 μm i.d. capillary (−95 μA) compared to 75 μm i.d. capillary (−250 μA). The detection wavelength of 210 nm was added to our previous method [1]. Comparison between 210 and 254 nm was done and 254 nm was chosen for the calculations, due to the higher absorbance values. The wavelength of 191 nm was used to ensure that all the chelating agents were fully complexed. In this study all chelating agents are considered as copper complexes, hence this is not mentioned every time these agents appear in the text.

The concentration of BGE was at first held at 80 mmol L^{-1} and pH varied 6.6–7.6. When pH was lowered to 6.6 the peaks were wider and smaller, and separation was worse. At pH 7.6 the peaks were sharper than at pH 6.6 and separation was slightly better, but IDA gave a very broad and short peak. The separation of all the chelating agents was worse at pH 7.6 than at pH 7.1. The current at pH 6.6 and 7.6 was −85 and −103 μA, respectively. The change in the concentration of TTAB in the range 0.5–1.0 mmol L^{-1} in the BGE was also tested when the pH was changed, but the change in the concentration of TTAB did not improve the separation of the peaks at any pH value, and thus it was kept at 0.5 mmol L^{-1}.

Next, the concentration of BGE was increased slowly from 80 mmol L^{-1}, the best separation being obtained with 95 mmol L^{-1} phosphate buffer +0.5 mmol L^{-1} TTAB, pH 7.1, current −120 μA. The decrease in BGE concentration

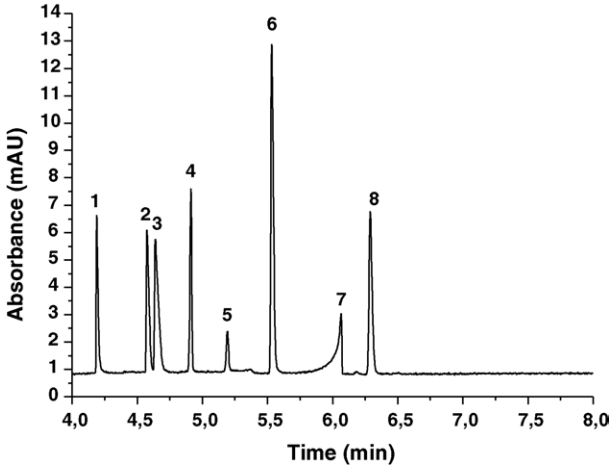


Fig. 1. Electropherogram of the sample containing 1.0 mmol L^{-1} of each complexing agent and 33 mmol L^{-1} of copper. Peaks: (1) CuDTPA, (2) CuEDTA, (3) CuPDTA, (4) CuCDTA, (5) CuNTA, (6) CuTTHA, (7) CuIDA and (8) CuHEDTA. Conditions: 95 mmol L^{-1} phosphate buffer, pH 7.1, c(TTAB) 0.5 mmol L^{-1}, temperature 25 °C, applied voltage −20 kV, before sample injection hydrodynamic injection of 5 mmol L^{-1} NaCl 1 s 50 mbar, hydrodynamic sample injection for 2 s 50 mbar, detection at 254 nm.

was not attempted, as our previous study [1] had shown that lowering the concentration made for worse separation of the chelating agents.

After the buffer composition had been optimized, the amount of sample injected to the capillary in one measurement was optimized. In all the experiments 50 mbar pressure was used; only the duration was changed. Times of 2–4 s were tested. With 3 and 4 s injection time the amount of sample was too high, resulting broadened and shorter peaks, thus clearly worsening the separation. The best injection time was 2 s.

Finally, improvement in separation and attaining of even narrower peaks, was tested with salt injection before sample injection by using 5 mmol L^{-1} sodium chloride with injection times of 1–3 s at 50 mbar pressure. With times of 2 and 3 s it was noted that when amount of salt introduced prior to the sample increased above the optimum, the peaks became broader. The best separation and narrowest peaks were obtained with 1 s and 50 mbar salt injections. The migration time increased slightly (+0.5 min) compared to measurements without salt injection, but better peaks to electropherograms were obtained, and thus salt injection was added to the method. The salt injection did not increase the electric current during analysis. The electropherogram of eight chelating agents in the optimized conditions can be seen in Fig. 1.

3.2. A new ionic liquid as a flow modifier

The separation of CDTA, DTPA, EDTA, HEDTA, IDA, NTA, PDTA and TTHA as copper complexes with

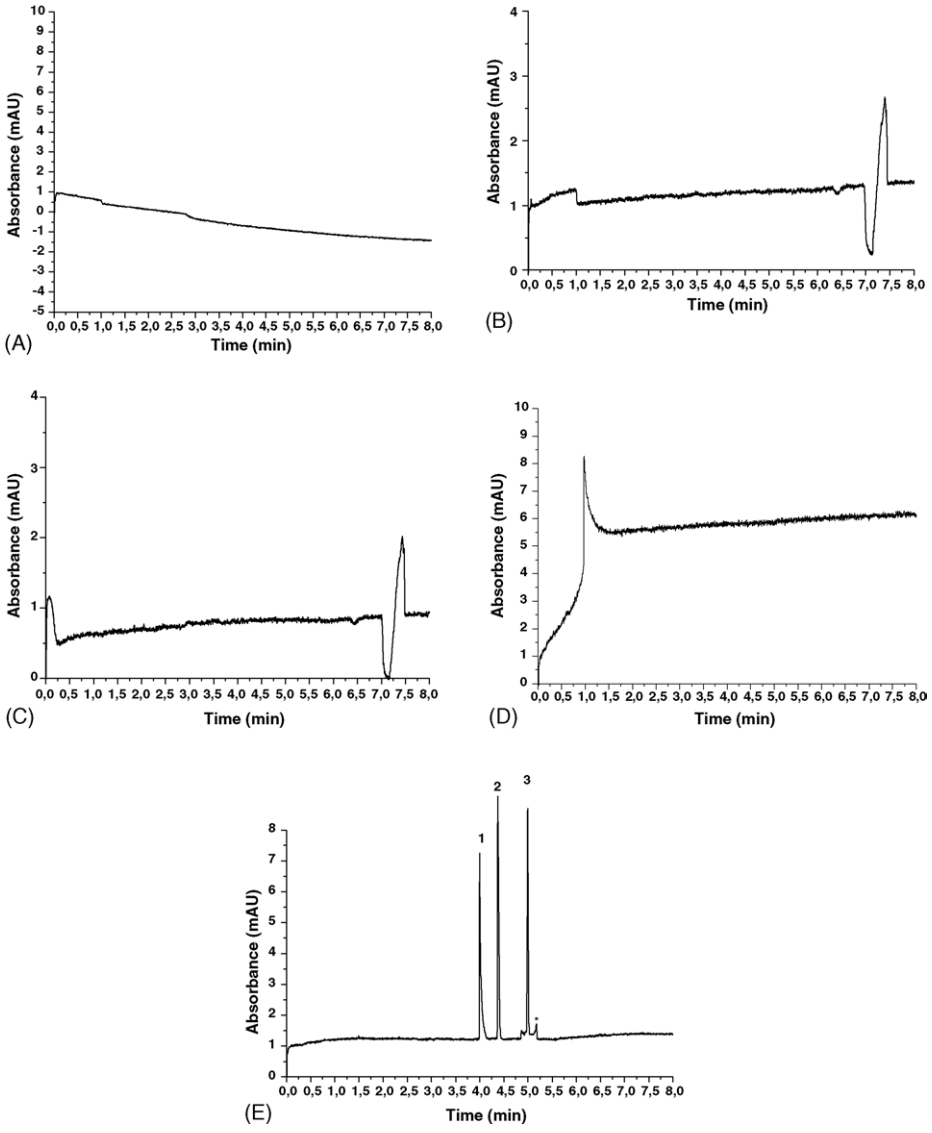


Fig. 2. Five ionic liquids tested as flow modifiers. (A) DEDHAB, (B) DMDPeAI, (C) DEDHAI, (D) DMDOAB and (E) DMDNAB. Sample contained 1.0 mmol L^{-1} of DTPA, EDTA, NTA and 12 mmol L^{-1} of copper. Peaks: (1) CuDTPA, (2) CuEDTA and (3) CuNTA (*) impurity. Conditions: 95 mmol L^{-1} phosphate buffer, pH 7.1, c(flow modifier) 0.5 mmol L^{-1}, temperature 25 °C, applied voltage −20 kV, hydrodynamic sample injection for 2 s 50 mbar, detection at 254 nm.

95 mmol L^{-1} phosphate BGE pH 7.1 with TTAB as flow modifier was clear but the suitability of the new ionic liquids synthesized in our laboratory as flow modifiers for separation of the eight chelating agents was tested. The synthesis and characterization of new quaternary alkylammonium bromide and iodide compounds are given in ref. [34] by Busi et al. The compounds tested as flow modifiers were DEDHAB, DEDHAI, DMDPeAI, DMDOAB and DMDNAB [34].

The first measurements with the new flow modifiers were carried out with a sample containing only DTPA, EDTA and NTA as copper complexes. Concentrations of the new potential flow modifiers varied over the range 0.2–1.0 mmol L^{-1}, and it was observed that in concentration of 0.2 mmol L^{-1} no baseline separation was achieved. At concentrations of 0.5 and 1.0 mmol L^{-1} of flow modifiers only DMDNAB worked and the best peaks were obtained at the concentration of 0.5 mmol L^{-1}. The electropherograms are shown in Fig. 2. As a result only DMDNAB reversed the electroosmotic flow. The rest of the ammonium bromide and iodide compounds tested were not able to separate the chelating agents and reverse the flow in the capillary.

For phosphate BGE, with DMDNAB as a flow modifier, a higher voltage (−25 kV) was tested. Increasing the voltage shortened the analysis time, compressed the peaks and worsened the separation. The current increased up to −170 μA at the higher voltage, and hence it was lowered to −20 kV after summation of the positive and negative effects for the analysis. The separation of CDTA, DTPA, EDTA, HEDTA, IDA, NTA, PDTA and TTHA, using DMDNAB as an additive in optimized conditions, can be seen in Fig. 3.

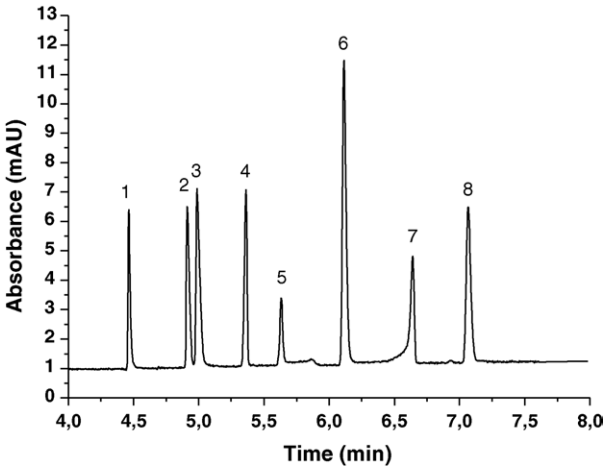
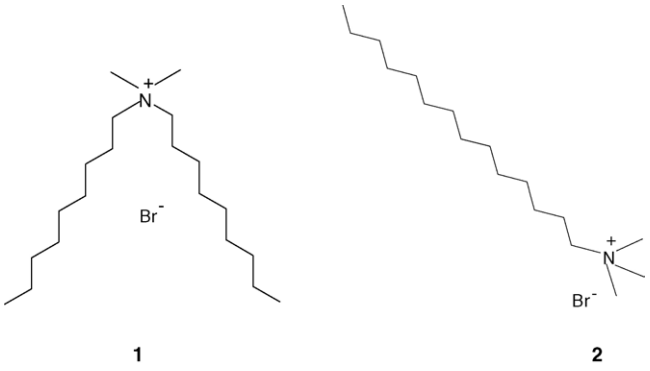


Fig. 3. Electropherogram of the sample containing 1.0 mmol L^{-1} of each complexing agent and 33 mmol L^{-1} of copper. Peaks: (1) CuDTPA, (2) CuEDTA, (3) CuPDTA, (4) CuCDTA, (5) CuNTA, (6) CuTTHA, (7) CuIDA and (8) CuHEDTA. Conditions: 95 mmol L^{-1} phosphate buffer, pH 7.1, c(DMDNAB) 0.5 mmol L^{-1}, temperature 25 °C, applied voltage −20 kV, before sample injection hydrodynamic injection of 5 mmol L^{-1} NaCl 1 s 50 mbar, hydrodynamic sample injection for 2 s 50 mbar, detection at 254 nm.

3.3. Comparison of the two flow modifiers

When the structures of the TTAB and DMDNAB are compared, it is noticeable that they differ clearly from each other (Scheme 1). TTAB has only one alkyl chain, containing 14 carbons, and it has three methyls attached to the nitrogen. DMDNAB consists of two alkyl chains containing nine carbons and two methyls attached to nitrogen. The



Scheme 1. Molecular structures of the two compared flow modifiers. (1) DMDNAB and (2) TTAB.

Table 1
Comparison of migration times of the peaks, correlation coefficients of calibration, limits of detections and efficiencies of the eight chelating agents as copper complexes with 95 mM phosphate buffer, pH 7.1 using TTAB or DMDNAB as a flow modifier

Chelating agent	Time[a] (min)	Time[b] (min)	R^2 [a]	R^2 [b]	LOD[a] (mmol L^{-1})	LOD[b] (mmol L^{-1})	Efficiency[a] plates	Efficiency[b] plates
DTPA	4.3 (2.0)	4.5 (1.6)	0.999	0.999	0.04	0.06	916,344	736,758
EDTA	4.7 (2.2)	4.9 (1.9)	0.998	0.998	0.05	0.05	583,045	545,865
PDTA	4.7 (2.2)	5.0 (1.9)	0.997	0.997	0.06	0.06	168,728	278,739
CDTA	5.0 (2.7)	5.4 (1.8)	0.997	0.997	0.03	0.05	1,303,541	775,728
NTA	5.3 (2.6)	5.6 (2.2)	0.997	0.998	0.08	0.14	781,574	565,023
TTHA	5.7 (2.9)	6.1 (2.3)	0.997	0.997	0.02	0.03	937,024	500,577
IDA	6.2 (2.9)	6.7 (2.9)	0.997	0.997	0.06	0.10	237,746	334,808
HEDTA	6.5 (3.3)	7.1 (3.0)	0.997	0.997	0.03	0.06	839,420	450,489

Migration times reported in the table are means of the migration times ($n = 5$), values in parenthesis are relative standard deviations. LOD is calculated by using the equation LOD = 3 × noise × (c/peak_height). Efficiency is calculated by using the equation $N = 16(t_m/w)^2$.

[a] 0.5 mM TTAB as a flow modifier.

[b] 0.5 mM DMDNAB as a flow modifier.

structures of the additives added in the BGE are not alike, but both of them work properly. Melanson et al. [37] considered the behavior of single- and double-chained surfactants in capillary electrophoresis. Single-chained surfactants form spherical aggregates at the silica surfaces and double-chained surfactants form a bilayer inside the capillary [37]. This difference markedly affects the stability of the measurement and separation of analytes inside the capillary. According to Melanson et al. [37] as a double-chained ionic liquid, DMDNAB may form a stable bilayer inside the capillary and may allow a more stable environment for the separation of analytes than the common single-chained flow modifier TTAB.

The length of the alkyl chain of the additive has a significant influence on the separation process inside the capillary, this was clearly seen in our study when shorter analytes than DMDNAB were tested; the shorter ones did not work at all (Fig. 2). This behavior was expected, as shorter alkyl chains are less hydrophobic than longer ones and they form a less stable bilayer inside the capillary. The other reason for the unworkability of shorter ammonium bromides is due to the size of the compounds. Shorter and smaller ammonium bromides can roll over, and they do not form a balanced layer to assist the flow reversal and separation of anionic analytes.

From Figs. 1 and 3 one can clearly see that the separation of eight chelating agents was better in BGE with DMDNAB, although the total analysis time is a little longer. The total time, however, is still quite short, less than 7.5 min, compared to other analytical methods. In addition the shape of the sixth peak (IDA) is better when using the BGE with DMDNAB.

In Table 1, the migration times, correlation coefficients, limits of detections (LOD) and efficiencies are introduced for both methods. Migration times are calculated as averages ($n = 5$) and they are given with relative standard errors. DMDNAB gives smaller or similar relative standard errors for migration times than TTAB. When the correlations are

Table 2
Comparison of the resolution of eight chelating agents as copper complexes using TTAB or DMDNAB as a flow modifier

Adjacent peaks	Resolution[a]	Resolution[b]
DTPA–EDTA	18.9	19.0
EDTA–PDTA	1.9	2.4
PDTA–CDTA	9.4	12.3
CDTA–NTA	13.5	9.7
NTA–TTHA	15.1	14.9
TTHA–IDA	14.9	13.3
IDA–HEDTA	6.1	9.7

Buffer used is 95 mmol L^{-1} phosphate buffer pH 7.1 and c(flow modifier) = 0.5 mmol L^{-1} ($n = 5$). Resolutions were calculated by using equation $R_s = 2(t_2 - t_1)/(w_1 + w_2)$.
[a] TTAB as a flow modifier.
[b] DMDNAB as a flow modifier.

Table 3
Results from standard addition studies of two natural waters and one paper mill water

Sample	Chelating agent added	Added (mmol L^{-1})	Result (mmol L^{-1})[a]	Result (mmol L^{-1})[b]
Jyväsjärvi	DTPA	0.8	0.79 ± 0.03	0.76 ± 0.05
	EDTA	0.8	0.77 ± 0.05	0.80 ± 0.03
	PDTA	0.8	0.77 ± 0.04	0.75 ± 0.06
	CDTA	0.8	0.77 ± 0.04	0.77 ± 0.06
	NTA	0.8	0.85 ± 0.03	0.84 ± 0.03
	TTHA	0.8	0.76 ± 0.03	0.78 ± 0.03
	IDA	0.8	0.80 ± 0.02	0.81 ± 0.03
	HEDTA	0.8	0.76 ± 0.03	0.78 ± 0.03
Kotalampi	DTPA	0.8	0.78 ± 0.03	0.79 ± 0.05
	EDTA	0.8	0.82 ± 0.02	0.75 ± 0.05
	PDTA	0.8	0.81 ± 0.02	0.76 ± 0.05
	CDTA	0.8	0.82 ± 0.04	0.76 ± 0.05
	NTA	0.8	0.84 ± 0.05	0.83 ± 0.04
	TTHA	0.8	0.84 ± 0.03	0.75 ± 0.05
	IDA	0.8	0.75 ± 0.05	0.76 ± 0.04
	HEDTA	0.8	0.83 ± 0.04	0.75 ± 0.05
Cleaned waste water	DTPA	0.7	0.68 ± 0.04	0.73 ± 0.02
	EDTA	0.7	0.70 ± 0.04	0.68 ± 0.02
	PDTA	0.7	0.71 ± 0.03	0.68 ± 0.02
	CDTA	0.7	0.70 ± 0.04	0.70 ± 0.01
	NTA	0.7	0.70 ± 0.05	0.73 ± 0.05
	TTHA	0.7	0.72 ± 0.03	0.69 ± 0.02
	IDA	0.7	0.66 ± 0.04	0.70 ± 0.03
	HEDTA	0.7	0.70 ± 0.02	0.69 ± 0.03

The buffer used in these measurements was 95 mmol L^{-1} phosphate buffer pH 7.1 with 0.5 mmol L^{-1} TTAB or DMDNAB. The amount of copper in the sample was 33 mmol L^{-1} in every sample ($n = 5$). Errors were calculated by using the equation $x \pm (ts/\sqrt{n})$, t-value 2.78 ($p = 0.05$).
[a] 0.5 mM TTAB as a flow modifier.
[b] 0.5 mM DMDNAB as a flow modifier.

compared, DMDNAB also gives better or similar correlation coefficients than TTAB. The LOD values presented in Table 1 are calculated using the equation based on 3× noise. The literature offer another way of calculating LOD values [38] which use the standard deviation of the noise instead of noise in the equation. Furthermore this kind of calculations certainly gives smaller values, which are not comparable to the noise-based LOD values.

Quite similar LODs are obtained using either TTAB or DMDNAB method with two notable exceptions, NTA and IDA. The LODs for these two analytes are much higher with DMDNAB as a flow modifier than with TTAB. In both methods all other analytes have nearly similar LOD values. It can be seen in Table 1 that both methods achieved very high efficiencies, shown by separated, sharply defined peaks. The TTAB method gave higher efficiencies for all the chelating agents except PDTA and IDA, to which DMDNAB was better. Separation differences can be seen also in Table 2, which gives the calculated resolution values. DMDNAB gives better resolutions for the adjacent peaks of DTPA–EDTA, EDTA–PDTA, PDTA–CDTA and IDA–HEDTA. TTAB gives better resolutions for CDTA–NTA, NTA–TTHA and TTHA–IDA, but it is noticeable that the difference in the resolutions of NTA–TTHA and TTHA–IDA is not very big compared to those for DMDNAB.

Finally the performances of the two methods were tested with two natural water samples and one paper mill sample. These samples did not contain measurable concentrations of CDTA, DTPA, EDTA, HEDTA, IDA, NTA, PDTA and TTHA and so standard addition tests were made. The results obtained are shown in Table 3 and they were found to be accurate and precise. Both methods were suitable for the analysis of real water samples.

4. Conclusions

Capillary electrophoresis is a powerful technique in analytical chemistry. Nowadays, new methods are being developed very rapidly. Ionic liquids are useful additives for separation science and especially for capillary electrophoretic separations. These kinds of compounds might soon supplant the common flow modifiers, as they may be able to separate analytes better than the former ones.

In this study a new ionic liquid DMDNAB was used successfully as a flow modifier for the determination of CDTA, DTPA, EDTA, HEDTA, IDA, NTA, PDTA and TTHA as copper complexes by CE. The separation efficiencies were very high with DMDNAB and TTAB. The resolution of eight chelating agents was better when the new ionic liquid was used as an additive. Separation and the resolution were analyzed on the basis of values calculated from the electropherograms. The calibration plots gave good correlation coefficients and the LOD's for all the analytes were acceptable. The eight chelating agents were detected in less than 7 min and in less that 7.5 min, with TTAB and DMDNAB as the flow modifier, respectively. Both methods proved to be usable for water samples.

In the near future the suitability of the ionic liquids synthesized in our laboratory will also be tested in nonaqueous capillary electrophoresis.

References

[1] P.-L. Laamanen, A. Mali, R. Matilainen, Anal. Bioanal. Chem. 381 (2005) 1264.
[2] T.-F. Jiang, Y.-L. Gu, B. Liang, J.-B. Li, Y.-P. Shi, Q.-Y. Ou, Anal. Chim. Acta 479 (2003) 249.
[3] W. Qin, S.F.Y. Li, J. Chromatogr. A 1048 (2004) 253.
[4] W. Qin, H. Wei, S.F.Y. Li, J. Chromatogr. A 985 (2003) 447.
[5] T. Soga, Y. Ueno, H. Naraoka, Y. Ohashi, M. Tomita, T. Nishioka, Anal. Chem. 74 (2002) 2233.
[6] D. Baker, Capillary Electrophoresis, Techniques in Analytical Chemistry, first ed., John Wiley, New York, NY, 1995, p. 35.
[7] S. Qi, S. Cui, X. Chen, Z. Hu, J. Chromatogr. A 1059 (2004) 191.
[8] S.M. Mwonggela, A. Numan, N.L. Gill, R.A. Agbaria, I.M. Warner, Anal. Chem. 75 (2003) 6089.
[9] E.G. Yanes, S.R. Gratz, M.J. Baldwin, S.E. Robinson, A.M. Stalcul, Anal. Chem. 73 (2001) 3838.
[10] J. Peng, J. Liu, G. Jiang, C. Tai, M. Huang, J. Chromatogr. A 1072 (2005) 3.
[11] J. Liu, J. Peng, Y. Chi, G. Jiang, Talanta 65 (2005) 705.
[12] N. Hirayama, M. Deguchi, H. Kawasumi, T. Honjo, Talanta 65 (2005) 255.
[13] K.S. Khachatryan, S.V. Smirnova, I.I. Torocheshnikova, N.V. Shvedene, A.A. Formanovsky, I.V. Pletnev, Anal. Bioanal. Chem. 381 (2005) 464.
[14] S.V. Smirnova, I.I. Torocheshnikova, A.A. Formanovsky, I.V. Pletnev, Anal. Bioanal. Chem. 378 (2004) 1369.
[15] R. Sridhar, P.T. Perumal, Tetrahedron 61 (2005) 2465.
[16] M.J. Earle, P.B. McCormac, K.R. Seddon, Chem. Commun. 20 (1998) 2245.
[17] N.E. Leadbeater, H.M. Torenius, J. Org. Chem. 67 (2002) 3145.
[18] S.J. Nara, J.R. Harjani, M.M. Salunkhe, Tetrahedron Lett. 43 (2002) 2979.
[19] P.-Y. Chen, C.L. Hussey, Electrochim. Acta 50 (2005) 2533.
[20] C. Villagrán, C.E. Banks, C. Hardacre, R.G. Compton, Anal. Chem. 76 (2004) 1998.
[21] M. Holzapfel, C. Jost, A. Prodi-Schwab, F. Krumeich, A. Würsig, H. Buqa, P. Novák, Carbon 43 (2005) 1488.
[22] C.P. Mehnert, R.A. Cook, N.C. Dispenziere, M. Afework, J. Am. Chem. Soc. 124 (2002) 12932.
[23] C.P. Mehnert, E.J. Mozeleski, R.A. Cook, Chem. Commun. 24 (2002) 3010.
[24] D.W. Armstrong, L. Zhang, L. He, M.L. Gross, Anal. Chem. 73 (2001) 3679.
[25] X. Xiaohua, Z. Liang, L. Xia, J. Shengxiang, Anal. Chim. Acta 519 (2004) 207.
[26] W. Zhang, L. He, Y. Gu, X. Liu, S. Jiang, Anal. Lett. 36 (2003) 827.
[27] M. Vaher, M. Koel, M. Kaljurand, J. Chromatogr. A 979 (2002) 27.
[28] M. Vaher, M. Koel, M. Kaljurand, Electrophoresis 23 (2002) 426.
[29] A.M. Stalcup, B. Capovska, J. Liq. Chromatorgr. R T 27 (2004) 1443.
[30] P. Stepnowski, Anal. Bioanal. Chem. 381 (2005) 189.
[31] T.P. Knepper, Trends Anal. Chem. 22 (2003) 708.
[32] C. Schmidt, H.-J. Brauch, Environ. Toxicol. 19 (2004) 620.
[33] M. Bucheli-Witschel, T. Egli, FEMS Microbiol. Rev. 25 (2001) 69.
[34] S. Busi, H. Mansikkamäki, M. Lahtinen, J. Valkonen, K. Rissanen, J. Solid State Chem. 178 (2005) 1722.

[35] X-ray powder diffraction data were obtained at room temperature by Huber imaging-plate Guinier camera 670. Conditions were: 45 kV, 25 mA, Cu $K\alpha_1$ radiation ($\lambda = 1.5406$ Å) and a germanium monochromator was used. The diffracted X-ray photons with angular range 4–100° (2θ) were captured on the curved imaging plate detector and the diffraction data was recorded with a step resolution of 0.005 (2θ) over 120 min.
[36] International Centre for Diffraction Data, Powder Diffraction File Sets 1–51, Newton Square, Pennsylvania, 2001.
[37] J.E. Melanson, N.E. Baryla, C.A. Lucy, Anal. Chem. 72 (2000) 4110.
[38] S.P. Porras, E. Kenndler, Electrophoresis 25 (2004) 2946.