Controlled changes in selectivity of cation separations by capillary electrophoresis using various crown-ether additives

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Abstract

This paper investigates how the concentration and type of crown ether affects the separation of cations and how one can optimize the concentration of the crown ether to achieve the best separation. An electrolyte consisting of 1.0 mM UV Cat-2, 3.0 mM tropolone, and 3.5 mM 18-crown-6 was found to provide the best separation for all cations investigated. Use of this optimized electrolyte was applied to the analysis of low levels of potassium in technical grade ammonium tungstate used in the electronics industry.

Keywords: Buffer composition; Selectivity; Crown ethers; Inorganic cations; Potassium; Ammonium tungstate

1. Introduction

In recent years the use of capillary electrophoresis (CE) for the analysis of ions has grown significantly. Applications of CE for the analysis of ions have included such matrices as drinking water [1–3], waste water [4–6], nerve agent degradation products [7], high purity water [8–11], and cleaning baths [8,12]. CE offers a selectivity that is complementary to existing techniques such as ion chromatography (IC).

Recently several papers [13–16] have investigated the effect of different complexing agents on the analysis of cations. Using these various complexing agents in the electrolyte and indirect UV detection, separations in under 7 min could be achieved, much faster than the 20+ min run times for cations by IC. In the case of separating potassium and ammonium (both of which have a similar ionic equivalent conductance), a crown ether was added to the electrolyte which interacts with potassium slowing its migration and allowing separation from ammonium [14,15]. The pH of the electrolyte can also be altered to achieve a separation [13]. This paper investigates how both the type and concentration of crown ether effects the separation of the common alkali and alkaline earth cations as well as ammonium. Using this data an optimal electrolyte for the separation of ammonium and potassium is used to analyze several solutions of technical grade ammonium tungstate, used in the electronics industry, for the presence of potassium (an impurity in the manufacturing of the tungstate)

2. Experimental

2.1. Instrumentation

The CE system employed was the Quanta 4000E CIA (Waters, Milford, MA, USA). A Hg lamp was used for indirect UV detection at 185 nm. AccuSep polyamide fused silica capillaries of dimension 60 cm×75 μm I.D. were used throughout. Data acquisi-

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tion and system control was carried out with a Waters Millennium 2010 Chromatography Manager with a SAT/IN module connecting the CE to the data station with the signal polarity inverted from the CE. Software data processing in the Millennium software for CE data was done using the CIA software option.

2.2. Preparation of electrolytes

High-purity water (Milli-Q) was used to prepare all solutions (Millipore, Bedford, MA, USA). The working electrolyte for cation analysis was a solution of 1.0 mM UV Cat-2 (Waters) and 3.0 mM tropolone (Aldrich Chemical, Milwaukee, WI, USA). 18-Crown-6, 15-crown-5, and 12-crown-4, (Aldrich) were added to the electrolytes as well in various

concentrations to evaluate the effect on migration times. All working electrolytes were prepared fresh daily and degassed prior to use. The capillary was purged with electrolyte for 2 min prior to each analysis.

2.3. Sample and standards information

Samples of various electronics-grade ammonium tungstate were obtained from a manufacturer of ammonium tungstate and used as received. Standards were prepared from their salts and were of ACS grade or better. Duplicate injections of standards at three different levels was done and a linear through zero calibration plot drawn with correlation coefficients (r^2) of 0.997 or better achieved. This calibration plot was used to quantify the amount of cations present in the ammonium tungstate sample analyzed.

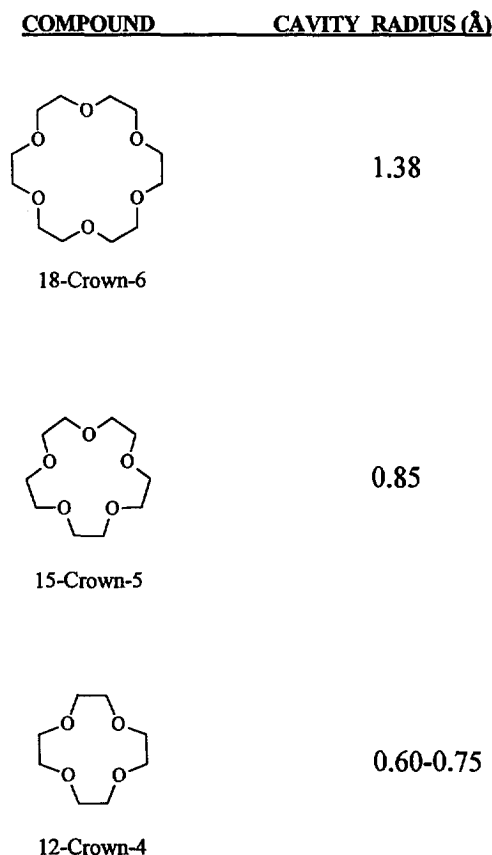| COMPOUND	CAVITY RADIUS (Å)
18-Crown-6	1.38
15-Crown-5	0.85
12-Crown-4	0.60-0.75

Fig. 1. Structure and cavity size of the crown ethers used as additives in the running buffer.

COMPOUND	RADIUS (Å)
Li$^+$	74
Mg$^+$	78
Ca^{2+}	1.00
Na$^+$	1.02
Ba^{2+}	1.36
K$^+$	1.38
NH$_4^+$	1.51

Fig. 2. Atomic radii of the common alkali and alkaline earth cations and ammonium investigated.

3. Results and discussion

The use of crown ethers offers the advantage of selectivity manipulation due to interactions between the crown ethers and the specific cation. This is typically based on the size of the cation and size of the crown ether cavity. Fig. 1 shows the structure and internal cavity size of the crown ethers investigated [17]. Fig. 2 shows the ionic radii of the common cations analyzed [17].
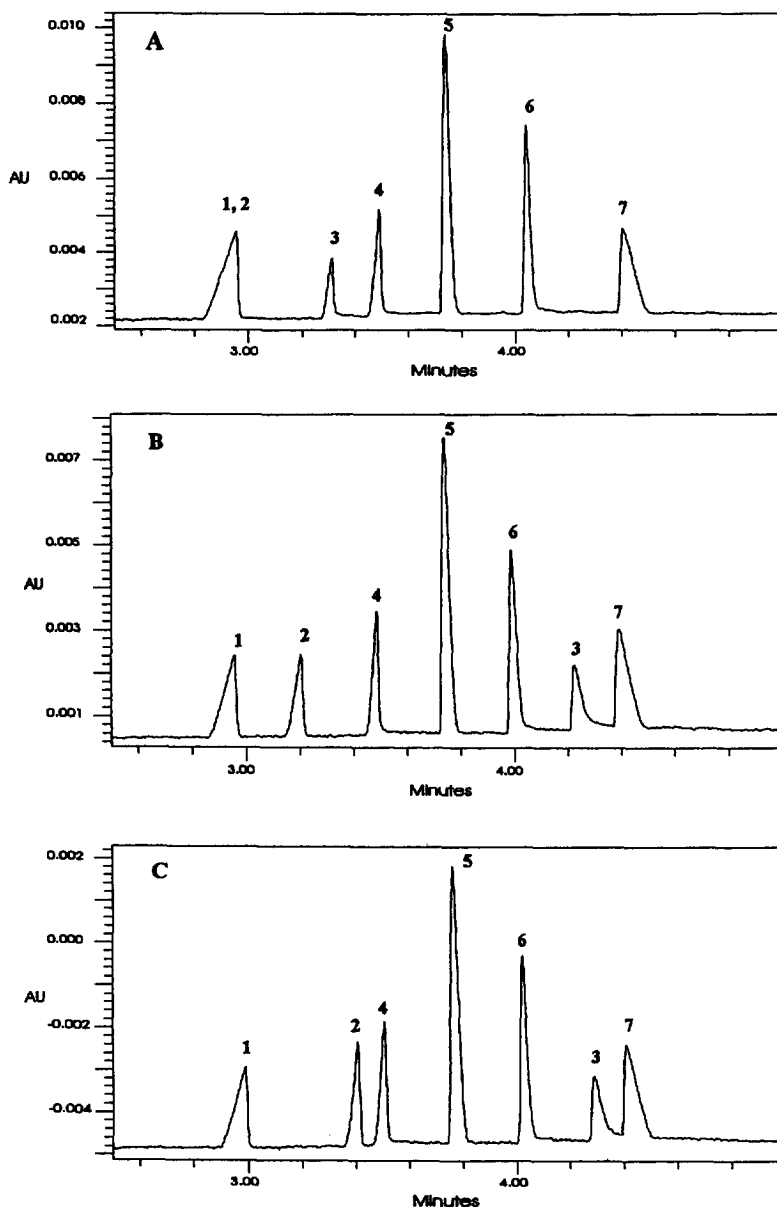

Fig. 3. Electropherogram of a cation standard using a 1 mM UV Cat-2 and 3.0 mM tropolone electrolyte without any 18-crown-6 added (A), with 2.0 mM of 18-crown-6 added (B), and with 3.5 mM 18-crown-6 added (C). CE Conditions: fused-silica 60 cm×75 μm I.D. capillary, voltage: 20 kV (positive); hydrostatic injection (10 cm for 30 s); indirect UV detection at 185 nm. Solutes: 1=NH_4^+; 2=K^+; 3=Ba^{+2}; 4=Ca^{+2}; 5=Na^+; 6=Mg^+; 7=Li^+

3.1. 18-Crown-6 additive

As seen in Figs. 1 and 2 the ionic radius of potassium and cavity size of 18-crown-6 are very similar and therefore, the potassium ion fits inside the cavity of the 18-crown-6 ether slowing its migration. Fig. 3 demonstrates this by showing the separation of various cations without any crown ether (Fig. 3A), with 2 mM crown ether in solution (Fig. 3B) and with 3.5 mM crown ether in solution (Fig. 3C). As can be seen potassium slows down and is separated from ammonium. The migration time of barium also increases due to interactions with the crown ether since its ionic radius is similar to 18-crown-6. As the concentration of crown ether increases the interactions increase. Fig. 4 shows a plot of relative migration times, referenced to lithium, versus the concentration of 18-crown-6. Potassium is the most affected by the concentration increase and at a concentration of 20 mM 18-crown-6 it is co-migrating with lithium. One disadvantage of higher crown ether concentrations is an increase in run times. The time is about 1.3 min longer at 20 mM 18-crown-6 than at 2.0 mM. A slight decrease in sensitivity at the higher crown ether concentration is noted. This is more than likely due to an overall decrease in the effectiveness of the background, visualizing, electrolyte possibly due to interactions between the crown ether and electrolyte. Both of these problems can be overcome by increasing the run voltage and increasing the concentration of the
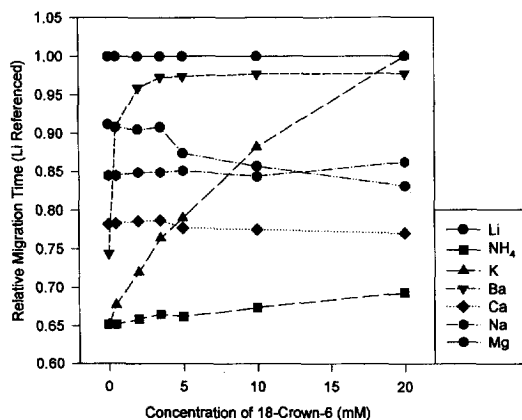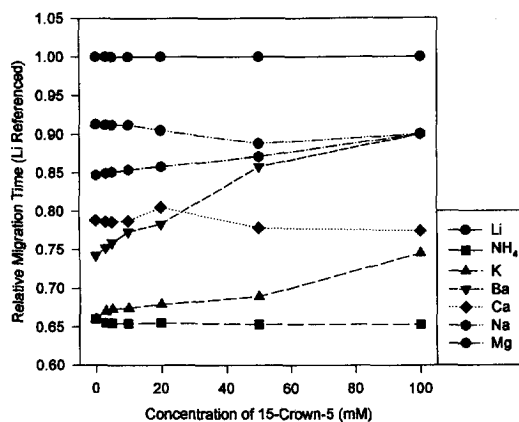

Fig. 5. Plot of relative migration times (referenced to lithium) versus amount of 15-crown-5 added.

background electrolyte (UV Cat-2) from 1.0 mM to 2.4 mM.

3.2. Effect of other additives

In addition to 18-crown-6, two other crown ethers (15-crown-5 and 12-crown-4) were investigated. Based on the information in Figs. 1 and 2 it was expected that very little selectivity changes, especially for ammonium and potassium, would be found. Surprisingly there is selectivity changes of the cations with the crown ethers but at much higher levels than with 18-crown-6. This is shown in Figs. 5 and 6 which are plots of relative migration times

Fig. 4. Plot of relative migration times of cations (referenced to lithium) versus amount of 18-crown-6 added.
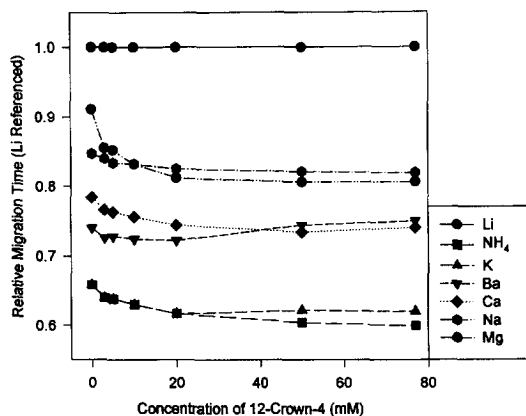

Fig. 6. Plot of relative migration times (referenced to lithium) versus amount of 12-crown-4 added.

(referenced to lithium) versus the crown ether concentration. As can be seen, at concentrations above 20 mM crown ether noticeable selectivity changes are evident. This may be due not only to size interactions but also steric and bulk interactions of the cations with the crown ethers. Overall, 18-crown-6 ether was found to provide the most significant selectivity changes over a narrower concentration range.

3.3. Analysis of ammonium tungstate samples

Using this data on the selectivity changes of 18-crown-6 an optimized separation electrolyte was used to analyze for potassium in an aqueous extract of a technical grade, ammonium tungstate sample used in the electronics industry. Based on the selectivity chart in Fig. 4, a concentration less than 5.0 mM was chosen, since this provides the best
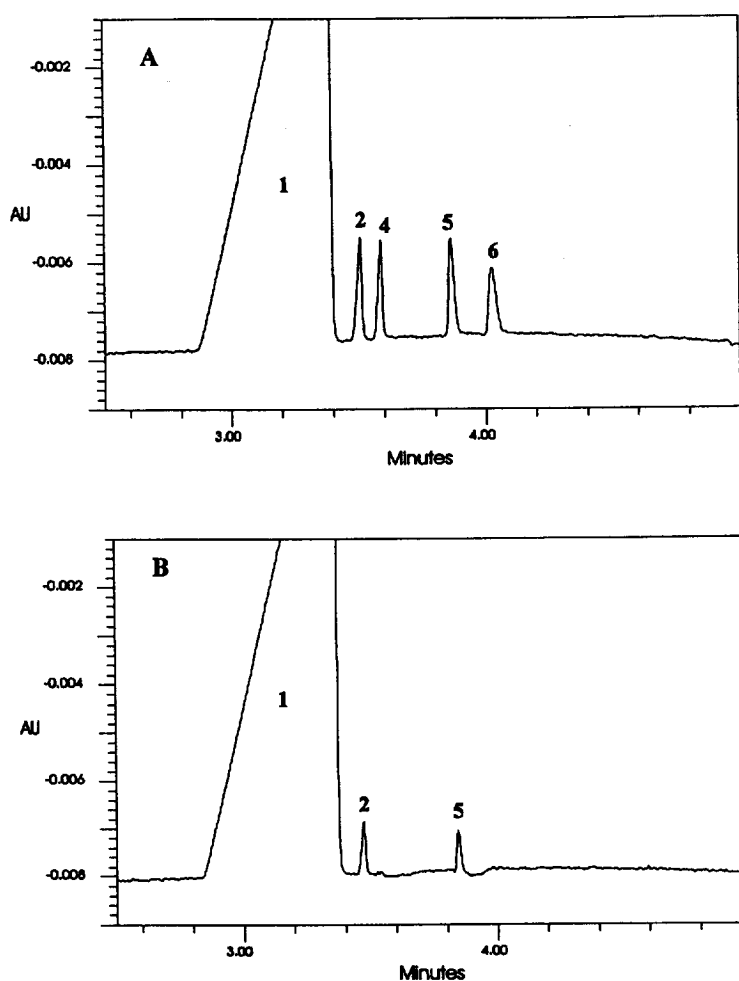

Fig. 7. Electropherogram of an aqueous sample of high purity ammonium tungstate (B) as compared to a standard (A). CE Conditions: 1 mM UV Cat-2, 3.0 mM tropolone, and 3.5 mM 18-crown-6; fused-silica 60 cm×75 μm I.D. capillary; voltage: 20 kV (positive); hydrostatic injection (10 cm for 30 s); indirect UV detection at 185 nm. Solutes and amounts found in sample: 1=NH_4^+ (858 mg/l); 2=K^+ (7.4 mg/l); 4=Ca^{+2} (none detected); 5=Na^+ (7.0 mg/l); 6=Mg^+ (none detected).

separation of all of the cations as well as potassium. Fig. 7 shows the separation of a technical-grade ammonium tungstate sample with 3.5 m*M* 18-crown-6 added (Fig. 7B) as compared to a standard (Fig. 7A). As can be seen the concentration of 3.5 m*M* 18-crown-6 offers the best separation of potassium from ammonium.

4. Conclusions

The use of crown ethers in the separation of cations provides an easy way to separate ammonium and potassium as well as effect the overall resolution of the cations. 18-crown-6 ether shows the highest degree of selectivity change for ammonium and potassium. Using this selectivity information one can optimize the separation based on the sample matrix expected thus allowing for optimal resolution between cations of interest.

Further work will continue investigating other crown ether additives to see how they interact and effect the selectivity of cations. One other potential class of compounds for interactions with cations are cryptands which are large cage-like crown ethers with larger cavity sizes.

Acknowledgments

References

[1] J.P. Romano and J.A. Krol, J. Chromatogr., 640 (1993) 403.

[2] S.A. Oehrle, J. Chromatogr., in press.

[3] J.P. Romano, J.A. Krol, S.A. Oehrle and G.J. Fallick, Capillary Ion Analysis: An Effective Technique for Analyzing Inorganic and Small Organic Ions in Environmental Matrices; Presented at EnviroACS, Washington, DC, July, 1995.

[4] P.E. Jackson and P.R. Haddad, J. Chromatogr., 640 (1993) 481.

[5] S.A. Oehrle, R.D. Blanchard, C.L. Stumpf and D.L. Wulfeck, J. Chromatogr. A, 680 (1994) 645.

[6] J.P. Romano, Am. Lab., May 1993, 48.

[7] S.A. Oehrle and P.C. Bossle, J. Chromatogr. A, 692, (1995) 247.

[8] P. Gupta and S.H. Tan, Ultrapure Water, May/June (1994) 54.

[9] G. Bondoux and T. Jones, LC·GC, 13 (1995) 144.

[10] G. Bondoux, P. Jandik and W.R. Jones, J. Chromatogr., 602 (1992) 79.

[11] J.A. Krol, Trace Anion and Cation Analysis in High Purity DI Water Using Capillary Ion Analysis; Presented at the International IC Symposium, Baltimore, MD, 1993.

[12] S.A. Oehrle, LC·GC, 14 (1996) 226.

[13] A. Weston, P.R. Brown, P. Jandik, Heckenberg and W.R. Jones, J. Chromatogr., 593 (1992) 289.

[14] E. Simunicova, D. Kaniansky and K. Loksikova, J. Chromatogr. A, 665 (1994) 203.

[15] Y. Shi and J.S. Fritz, J. Chromatogr. A, 671 (1994) 429.

[16] Y.H. Lee and T.I. Lin, J. Chromatogr., 575 (1994) 227.

[17] R.M. Izatt, J.S. Bradshaw, Nielson, J.D. Lamb and J.J. Christensen, Chem. Rev., 85 (1985) 271.