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Separation of alkali metals using isotachophoresis with cryptand 222 as a leading electrolyte additive

Jeff E. Prest*, Peter R. Fielden, Yanhua Qi

School of Chemical Engineering and Analytical Science, Manchester Institute of Biotechnology (MIB), The University of Manchester, 131 Princess Street, Manchester M1 7DN, UK

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ABSTRACT

This work shows how the inclusion of cryptand 222 as a leading electrolyte additive in isotachophoresis affects the electrophoretic mobilities of alkali metal cations. Using isotachophoresis the separation of alkali metals can be difficult due to the similar electrophoretic mobilities of three of the ions: caesium, rubidium and potassium. However, the presence of cryptand 222 in the leading electrolyte retards the mobilities of the caesium, rubidium and potassium to a different extent allowing separations to be made. A novel electrolyte system was formulated which consisted of a leading electrolyte of 10 mM caesium hydroxide, 0.75 mM cryptand 222 buffered to pH 9.4 with glycylglycine and a terminating electrolyte of 10 mM tetrabutylammonium hydroxide. The use of this electrolyte system allowed good separations of mixtures of rubidium, potassium, sodium and lithium to be achieved. The method was also applied to the analysis of edible salt samples.

1. Introduction

Isotachophoresis is a separation technique that is ideally suited to the analysis of small ions. The range of ions that can be separated can be considerably extended by manipulating the effective mobilities of the ions of interest. There are a wide range of strategies that can be employed for this purpose such as controlling the degree of ionisation using pH, ionic strength effects and complexation reactions. In particular this latter area has been the focus of much research and as such has been the subject of a number of review papers [1–4]. However, notable research has included the use of 2-hydroxyisobutyric acid to allow the separation of lanthanides using isotachophoresis [5]. However, the analysis of alkali metals in aqueous solutions using isotachophoresis can be difficult to achieve due to the similar, high, mobilities of three of the cations: potassium, rubidium and caesium. The separation of sodium and lithium from the other members of the group can be achieved readily as they have much lower mobilities. Unfortunately, there are few methods available for manipulating the mobilities of the alkali metals to facilitate separations. Two main approaches: the use of crown ethers and the use of polyethylene glycol (PEG), have been tried in isotachophoresis as methods of achieving such an effect. There are various crown ethers which can form complexes with alkali metals. Crown ethers that have different cavity diameters complex group I metal cations to a different degree. However, previous studies have shown that the most useful crown ether for application in isotachophoresis (and capillary zone electrophoresis) is 18-crown-6, the potassium selective crown ether. The use of 18-crown-6 in isotachophoresis was first proposed by Tazaki et al. [6] using an unbuffered electrolyte with H^+ as the leading ion. Subsequently, the use of more stable, buffered electrolyte systems incorporating 18-crown-6 has been used for the analysis of potassium [7] and rubidium [8] with leading ions of caesium and ammonium respectively. The use of PEG, proposed by Kaniansky et al. [9] has seen less widespread application. However, it was shown that through the incorporation of a 40–45% (v/v) concentration of PEG, a separation of the alkali metals lithium, sodium, potassium, rubidium and caesium could be achieved using a buffered leading electrolyte based on ammonium hydroxide. Isotachophoretic separations of alkali metals can be achieved more readily in organic solvents such as methanol [10]. However, the use of such solvents is impractical in many instruments.

Crown ethers are macrocyclic compounds. Another class of macrocycles is the group of compounds known as cryptands. Based on the effects observed with crown ethers it was thought that the use of this type of compound may also offer a potential method of manipulating the electrophoretic mobilities of alkali metal cations. However, to date there has been only a very limited use of cryptands in the field of electrophoretic separations. Previous work has tended to concentrate on the use of cryptands in the capillary zone electrophoretic (CZE) separation of small anions [11,12]. However, the work of Chiou and Shih [12] also reported the use of cryptand 222 for the CZE separation of small inorganic cations. In this work the effect of the cryptand on the separation

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* Corresponding author. Tel.: +44 161 3068900; fax: +44 161 3065201.
E-mail address: j.prest@manchester.ac.uk (J.E. Prest).

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of ammonium, potassium and sodium was investigated. The cryptand was shown to improve the separation a little, primarily by improving the resolution of sodium and ammonium, but a more significant effect was observed by incorporating 15% methanol in the background electrolyte.

This paper reports the first known investigation into the potential of using cryptand 222 as a method of manipulating the effective mobilities of alkali metal cations when performing isotachophoresis. The effect of the cryptand on the mobilities of alkali metal cations was investigated. This enabled a novel electrolyte system to be devised that allowed for the separation of rubidium, potassium, sodium and lithium to be achieved.

2. Materials and methods

Separations were performed using an ItaChrom EA202M electrophoretic analyser (JH-Analytik, Aalen, Germany). This instrument was fitted with two columns; a 100 mm long, 0.8 mm internal diameter (ID) fluorinated ethylene–propylene copolymer preseparation column and a 140 mm long, 0.3 mm ID silica analytical column. Contactless conductivity detectors were fitted to both columns and the analytical column was also equipped with an on-column UV detector. Control of the instrument and data processing were carried out with a personal computer using ITPPro32 software version 1.0 (Kas Comp, Bratislava, Slovakia). All of the separations performed in this study were carried out using only the preseparation column. To perform runs, samples were injected using the standard internal 30 μL sample loop and then analysed using a two-step control program. In this program the first step involved the application of a current of 350 μA for 210 s and then a lower current of 150 μA was applied in the second step. Detection took place during the second of these steps.

The electrolyte system developed incorporated a leading electrolyte composed of 10 mM caesium hydroxide (99.5%, Acros, Loughborough, UK) with cryptand 222 (Kryptofix® 222, Merck purchased from VWR, Lutterworth, UK) added. The terminating electrolyte was 10 mM tetrabutylammonium hydroxide (TBAOH) (40% solution, BDH, Poole, UK). 1 g L^{-1} hydroxyethyl cellulose (HEC) (molecular weight *ca.* 250,000; Aldrich, Gillingham, UK) was added to the leading electrolyte to suppress electroosmotic flow and the pH of the electrolyte was adjusted to 9.4 using glycylglycine (99+%, Acros). Cation stock solutions (1000 mg L^{-1}) were produced using the following salts lithium bromide (Aldrich), sodium chloride (Aldrich), potassium chloride (Fluka, Gillingham, UK), rubidium bromide (Acros), ammonium nitrate (BDH), magnesium chloride (Aldrich) and calcium chloride (Fluka). All salts had a purity of 99% or higher. Stock solutions were diluted as required to produce cation samples. All solutions were prepared using reverse osmosis (RO) deionised water.

Salt samples were produced using sachets of edible salt obtained from local cafeterias. 1000 mg L^{-1} stock solutions were obtained by dissolving the appropriate mass of salt in RO deionised water.

3. Results and discussion

One of the problems with analysing alkali metals using isotachophoresis is the high mobilities of three of the species, namely potassium, rubidium and caesium. These cations have absolute mobilities of 76.2×10^{-9} m^2 V^{-1} s^{-1}, 80.6×10^{-9} m^2 V^{-1} s^{-1} and 80.0×10^{-9} m^2 V^{-1} s^{-1} [13] respectively. These mobilities cause difficulties in two ways. Firstly, the high mobility means that it is a problem to find a suitable leading ion for use in isotachophoresis and secondly, the very similar magnitudes mean that they are difficult to separate from one another using electrophoretic methods. For many species mobilities can be easily manipulated by, for example, changing the pH of the leading ion or adding complexing agents to the electrolyte systems. Unfortunately in the case of the alkali metal cations the first of these approaches offers no benefit as the species are all strong bases. The second approach is also more difficult to realise with the alkali metals than other species, for example the alkaline earth metals, as few substances form complexes with them. There are however, two approaches which have shown some success; the addition of 18-crown-6 ether and the addition of PEG to leading electrolytes as complexing agents.

Another possible way of improving separations of alkali metals was thought to be the use of cryptands, another type of macrocyclic compound. Studies involving the use of crown ethers revealed that the ‘potassium selective’ 18-crown-6 was most useful in manipulating the electrophoretic mobilities of the alkali metals [6]. Therefore, it was thought the ‘potassium selective’ cryptand 222 may be the most useful of the cryptands to use as a leading electrolyte additive in isotachophoresis. To investigate the use of cryptand 222 as a complexing agent in isotachophoresis, a series of experiments was carried out. This involved performing separations using leading electrolytes containing different concentrations of cryptand 222. A complication in the use of cryptand 222 for this purpose, compared to 18-crown-6 ether, is that whereas the crown ether is a neutral species the cryptand contains ionisable groups and has pK_a values of 7.3 and 9.6 [14]. Therefore, to promote complexation and to avoid problems arising from the migration of uncomplexed cryptand through the separation it was necessary to perform the separations under alkaline conditions. Cryptand 222 should interact less strongly with caesium than with rubidium or potassium so a buffered leading ion of caesium was selected for these experiments. The pH of the leading ion was set at pH 9.4. At this pH cryptand 222 is only partially protonated and has a lower electrophoretic mobility than the tetrabutylammonium terminating ion, therefore no interference from the migration of the cryptand is observed.

To investigate whether cryptand 222 would have an effect on the behaviour of the alkali metal cations a series of experiments was carried out with a number of different electrolyte systems. The electrolyte systems tested contained cryptand 222 concentrations of between 0 and 3.0 mM. With each electrolyte system, runs were carried out in triplicate with samples of lithium, sodium, potassium and rubidium and the relative step heights (RSHs) recorded. In this work the RSH was taken as the height of the sample step from the leading ion divided by the height of the terminating ion step from the leading ion. In isotachophoresis, step heights are related to the conductivities of the ions that are detected and therefore are related to the mobility of a particular species. The RSH, which is a more reliable measure than actual step height, can thus be used as an indicator of the electrophoretic mobility of an ion. Therefore, the RSHs observed with the cations under the different conditions were recorded and the results obtained are shown in Fig. 1. It is apparent from Fig. 1 that the presence of the cryptand had a significant effect on the mobility of the potassium, as this species yielded no visible step and was thus slower than the terminating ion, when cryptand 222 concentrations of greater than 1.0 mM were used. The results also show that the presence of the cryptand had an identifiable effect on the mobilities of both sodium and rubidium but little effect on the mobility of lithium. These results fit with the complexation behaviour of cryptand 222 that has been observed previously by Lehn and Sauvage [15] who determined the stability constants (log K) of the alkali metal–cryptand complexes to be 5.4 for potassium, 4.35 for rubidium, 3.9 for sodium and <2 for lithium and caesium. Cryptand 222 is regarded as the potassium selective cryptand as it has a cavity radius of 1.4 Å [11], which is close to the ionic radius of potassium, at 1.38 Å [16]. Thus, it tends to form stronger complexes with potassium than with the other alkali metals. It was thought that the small rise in RSH for lithium