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Selectivity enhancement on a poly(butadiene–maleic acid)-coated cation phase induced by ethylene oxide-based complexing agents

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Abstract

Crown ethers as well as acyclic compounds bearing ethylene oxide units are well-known as complexing agents for different cations. They are mainly used as ionophores in ion selective electrodes. In ion chromatography some studies have been preformed using crown ether stationary phases.

Using crown ethers as eluent components for the separation of alkali and alkaline earth metal cations on a poly(butadiene–maleic acid)-coated phase, it is possible to tune the selectivity to the special needs of the sample. An eluent with addition of 18-crown-6 elutes potassium after magnesium and calcium with an improved separation of sodium and ammonium compared to the same eluent without addition of 18-crown-6. In contrast, the addition of a polyethylene glycol improves the sodium ammonium separation without changing the elution order.

1. Introduction

The simultaneous and isocratic separation of alkali and alkaline earth metal cations with poly(butadiene–maleic acid)-coated silica has been introduced by Schomburg et al. [1]. The Metrosep Cation 1-2 (Metrohm, Herisau, Switzerland) is based on the same type of material, but with improved stability against organic solvents which especially allows also the determination of different amines [2]. The usage of dipicolinic acid as eluent additive enables the determination of the above-mentioned cations within 10 min [3].

Sodium and ammonium are separated to baseline on this type of material but selectivity is poor compared to e.g. strong acid silica-based materials. Particularly the determination of low amounts of ammonium in an excess of sodium is difficult. Ivask et al. [4] used polyethylene glycols (PEG) to improve this selectivity on methacrylate-based strong acid ion exchangers. We tested the addition of polyethylene glycols to the weak acid ion exchanger Metrosep Cation 1-2 and found the same effect, but the rather large contamination with sodium in commercially available products minimizes the use of these types of eluents.

Crown ethers are well-known as complexing agents for monovalent cations and are used in ion chromatography [5,6]. We tested the use of crown ethers as eluent additives on the Metrosep Cation 1-2 ion exchanger.

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2. Experimental

All measurements have been performed on an ion chromatograph consisting of a 709 IC-pump, 690 ion chromatograph (both from Metrohm, Herisau, Switzerland). Data acquisition was performed with a 714 IC-Metrodata integration system (Metrohm). All chemicals used were purchased from Fluka (Buchs, Switzerland) or Merck (Darmstadt, Germany) and were used without further purification.

Eluents were prepared with freshly deionized water. The composition of the eluents is given in the legends to the figures. Eluents were degassed for about 5 min under vacuum. The eluents were used without any further pH adjustments.

Sample solutions were prepared in 2 m*M* nitric acid [2].

3. Results and discussion

3.1. Polyethylene glycols

In preliminary tests on a Super-Sep cation column, which is the original material introduced by Schomburg et al. [1], three different polyethylene glycols have been tested (PEG 400, PEG 1000 and PEG 3000). Due to contamination with sodium and baseline disturbances in the chromatograms, PEG 1000 and PEG 3000 have not been used further.

With the standard eluent the new Metrosep Cation 1-2 [2] shows almost baseline separation between sodium and ammonium (Fig. 1).

The addition of 5% of PEG 400 to this eluent leads to shorter retention times and a better separation between ammonium and sodium. Fig.

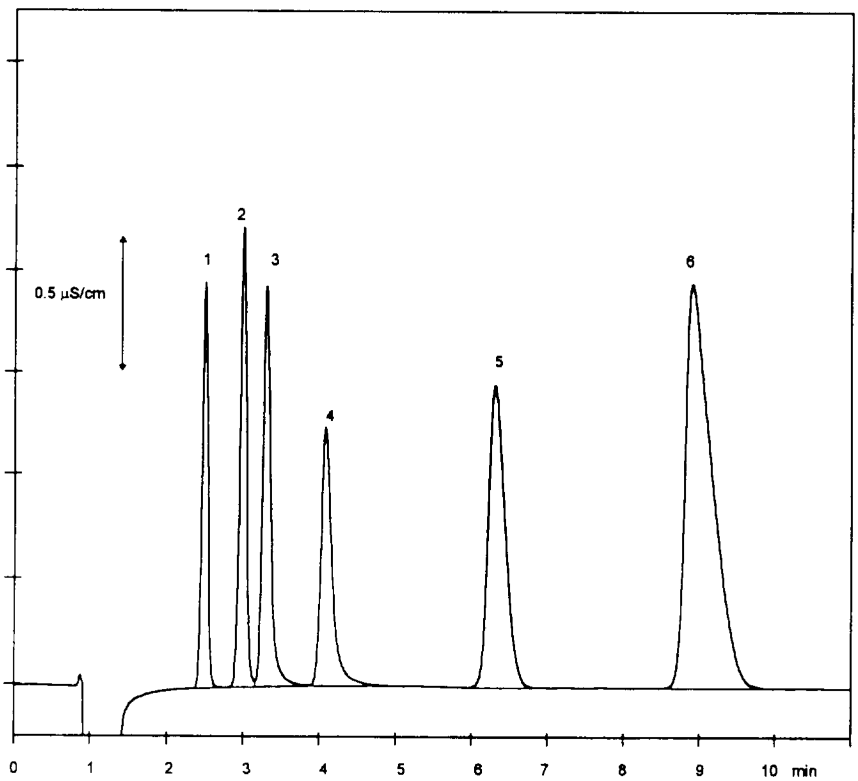

Fig. 1. Separation of Li^+ (1 = 1 mg/l), Na^+ (2 = 5 mg/l), NH_4^+ (3 = 5 mg/l), K^+ (4 = 10 mg/l), Ca^{2+} (5 = 10 mg/l) and Mg^{2+} (6 = 10 mg/l) on Metrosep Cation 1-2. Eluent: 4 mmol/l tartaric acid, 1 mmol/l dipicolinic acid. Flow-rate 1 ml/min. Injection volume 10 µl.

2a shows a standard chromatogram with this eluent. The separation of the peak apexes is now 0.4 min compared to 0.3 min without PEG (Fig. 2b).

The eluent contains about 0.2 mg/l sodium as well as traces of ammonium due to contamination of the PEG 400. The fairly small improvement in selectivity and the contamination of the eluent limits the use of such an eluent.

3.2. Crown ethers

Three crown ethers (15-crown-5, 18-crown-6 and dibenzo-18-crown-6) have been used in the present study. 15-Crown-5 contains five oxygen atoms which may act as coordination sites. The cavity built by this compound is small and only lithium can be complexed. The two other compounds contain six oxygen atoms and their cavity fits well to potassium.

The influence of these crown ethers is analyzed by adding different amounts of the respective compound to the standard eluent. Table 1 summarizes the results for the six cations lithium, sodium, ammonium, potassium, calcium and magnesium.

There is virtually no influence of 15-crown-5 on the retention times. Both 18-crown-6 and dibenzo-18-crown-6 show a large influence on potassium elution. With increasing concentrations of this crown ether potassium elutes later. At ca. 0.5 mmol/l potassium elutes at the same time as magnesium. With 1 mmol/l potassium elutes well separated after magnesium. Here it is very important to use dipicolinic acid in the eluent to avoid coelution of potassium and calcium. Dibenzo-18-crown-6 is even more powerful in changing the elution of potassium.

Another important difference between the two 18-crown-6 types is primarily seen in the be-

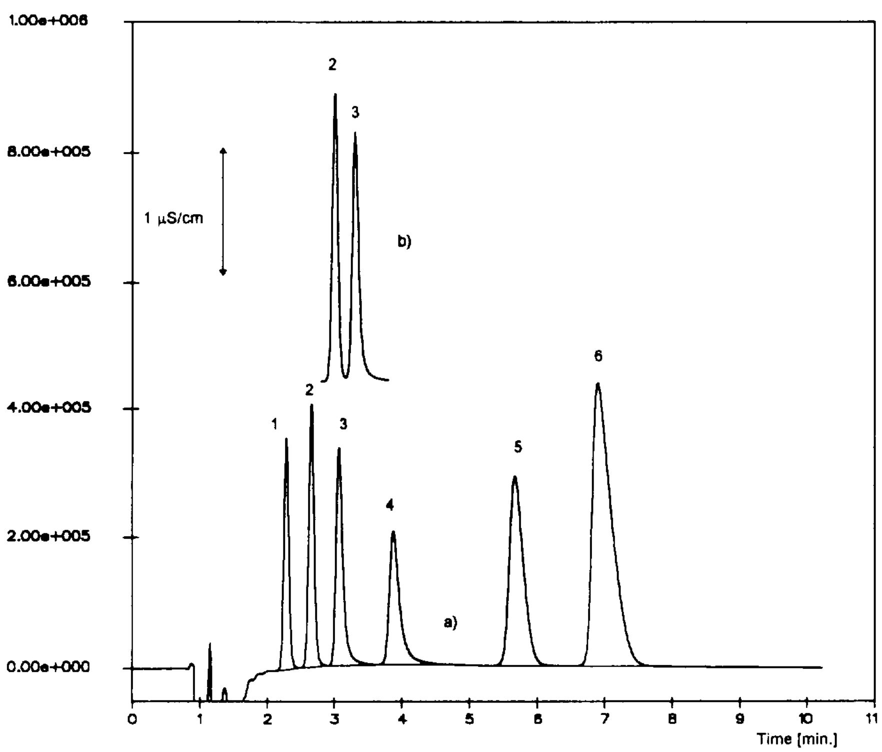

Fig. 2. Standard cations with addition of 5% PEG 400 to the eluent (same conditions and numbering as in Fig. 1): (a) chromatogram with PEG 400; (b) sodium and ammonium part of chromatogram without PEG 400.

Table 1
Influence of crown ethers on the selectivity of Metrosep Cation 1-2[a]

Crown ether (mmol/l)	Retention time (min)					
	Lithium	Sodium	Ammonium	Potassium	Calcium	Magnesium
15-Crown-5						
0.00	2.52	3.02	3.33	4.18	6.40	9.09
0.50	2.52	3.09	3.35	4.26	6.45	9.10
1.00	2.50	3.09	3.31	4.26	6.33	8.86
1.50	2.50	3.12	3.32	4.31	6.36	8.84
18-Crown-6						
0.00	2.50	2.99	3.29	4.08	6.30	8.89
0.10	2.51	3.08	3.49	5.68	6.47	9.09
0.25	2.51	3.13	3.64	7.09	6.51	9.01
0.50	2.48	3.19	3.82	9.25	6.56	8.77
1.00	2.49	3.32	4.17	12.0	6.87	8.84
Benzo-18-Crown-6						
0.00	2.52	3.02	3.32	4.11	6.42	9.06
0.10	2.50	3.19	3.43	5.83	6.45	8.99
0.25	2.50	3.39	3.57	7.82	6.59	8.98
0.50	2.49	3.67	3.67	10.2	6.71	8.81
1.00	2.47	4.08	4.08	15.5	6.93	8.62

[a] Reproducibility is about 1% of the respective retention time. Eluent: 4 mmol/l tartaric acid; 1 mmol/l dipicolinic acid; x mmol/l of the respective crown ether.

haviour of ammonium and sodium. While the influence on ammonium is the same for both compounds, dibenzo-18-crown-6 leads to a higher retention of sodium. Thus the separation of ammonium from sodium with 18-crown-6 increases with increasing concentration in the eluent. With dibenzo-18-crown-6 the peaks of these cations tend to coelute.

Fig. 3 shows chromatograms of six cations with the standard eluent (tartaric acid–dipicolinic acid) as well as with 1 mmol/l 18-crown-6 added to the same eluent.

In contrast to dipicolinic acid the cation complexed with crown ether elutes later than the uncomplexed cation. Since the complexes of dipicolinic acid with e.g. calcium are neutral (or even negatively charged for 1:2 complexes), they are not retarded on the cation column. The crown ether complexes on the other hand have the same charge as the cation itself, but they are much larger. Thus the potassium complex shows a larger retention on the stationary phase than free potassium. The net retention is higher as long as the crown ether is present in the eluent.

We also tested whether it would be possible to analyze the 18-crown-6–potassium complex directly. The sample contained 10 mg/l potassium in 1 mmol/l 18-crown-6. On a Metrosep Cation 1-2 column with the tartaric acid–dipicolinic acid eluent the sample peak eluted at the retention time expected for uncomplexed potassium. This proves that the complex is not stable on column. Thus, addition of crown ether to the eluent is necessary to produce this type of change in selectivity.

4. Conclusions

Ethylene oxide-based compounds may be used to change the selectivity of the poly(butadiene–maleic acid)-based ion exchangers. Of the used crown ethers addition of 18-crown-6 to the eluent is the most promising since it moves

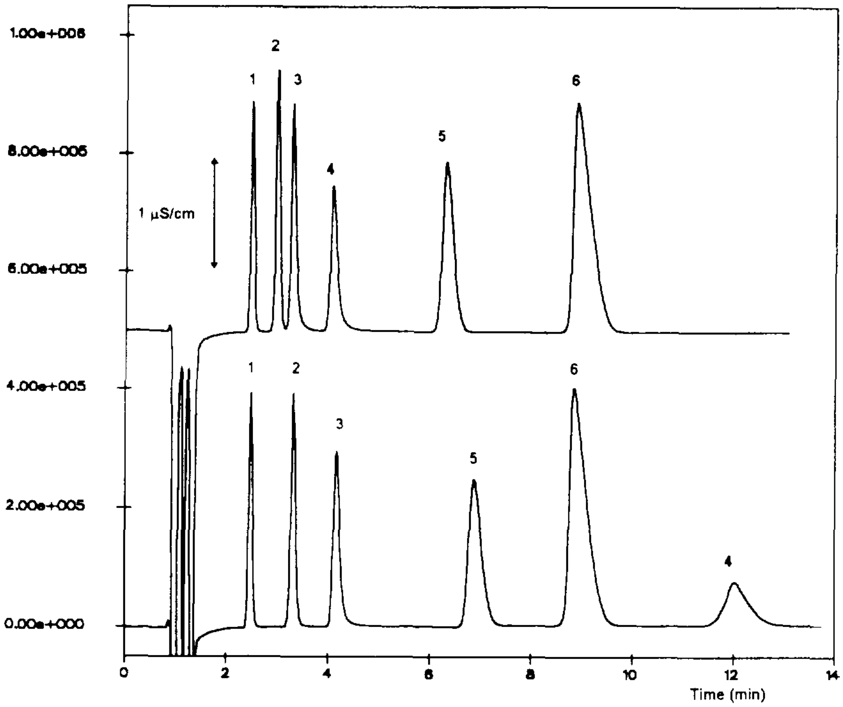

Fig. 3. Standard cations (same peak numbering as in Fig. 1). (a) Eluent: 4 mmol/l tartaric acid, 1 mmol/l dipicolinic acid. (b) Eluent: 4 mmol/l tartaric acid, 1 mmol/l dipicolinic acid, 1 mmol/l 18-crown-6.

potassium to longer retention times and improves the sodium–ammonium separation. Addition of polyethylene glycols to the eluent improves this separation without changing the selectivity for potassium. Overall, eluents with 18-crown-6 are preferred for use in routine work because they give the best separation between ammonium and sodium and because of their high purity.

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