Journal of Chromatography, 523 (1990) 281–292
Elsevier Science Publishers B.V., Amsterdam

CHROM. 22 716

Use of crown ethers in the isotachophoretic determination of metal ions

KEIICHI FUKUSHI*
Kobe University of Mercantile Marine, Fukae, Higashinada, Kobe 658 (Japan)
and
KAZUO HIIRO
Department of Industrial Chemistry, Ube Technical College, Tokiwadai, Ube 755 (Japan)
(First received March 27th, 1990; revised manuscript received June 21st, 1990)

ABSTRACT

The effects of crown ethers on the effective mobilities of various metal ions in capillary isotachophoresis were studied. The effective mobilities of thallium, lead and silver ions decreased when the concentration of crown ethers in an ordinary leading electrolyte was increased up to 50 m*M*. Thus, by use of 18-crown-6, ammonium and thallium ions and thallium and lead ions were completely separated and could be determined. Similarly, by use of 15-crown-5, potassium and thallium ions and ammonium and silver ions were completely separated and could be determined.

INTRODUCTION

It is necessary to adjust the effective mobilities of analyte ions for the isotachophoretic separation of ions that have similar ionic mobilities. Use of cyclodextrins for this purpose was described in a previous paper [1].

Crown ethers have also been used for the same purpose. Alkali and alkaline earth metal ions have been separated or determined by use of 18-crown-6 in the leading electrolyte as a complexing agent for these ions [2–8]. However, there is no report concerning the isotachophoretic separation of heavy metal ions by use of crown ethers. It can be presumed that thallium, lead and silver ions also form inclusion complexes with crown ethers in the separating columns according to the formation constants of the metal–crown ether complexes [9] and that their effective mobilities decrease [1,2,10].

Isotachophoretic separations of ammonium and thallium ions and of potassium and thallium ions are difficult with ordinary leading electrolytes, because their ionic mobilities are very similar in aqueous solutions [11]. Further, there are slight differences between the ionic mobilities of thallium and lead ions and of ammonium and silver ions in aqueous solutions [11]. These ions can be determined accurately and precisely if large differences between their effective mobilities can be obtained.

We therefore studied the effects of 18-crown-6 and 15-crown-5 on the effective

0021-9673/90/$03.50

mobilities of ammonium, lead, potassium, thallium and silver cations. The results of these experiments were applied to subsequent simultaneous determinations by capillary isotachophoresis: ammonium and thallium ions and thallium and lead ions with ordinary leading electrolytes containing appropriate amounts of 18-crown-6 and potassium and thallium ions and ammonium and silver ions with leading electrolytes containing 15-crown-5.

EXPERIMENTAL

Apparatus

A Shimadzu Model IP-2A isotachophoretic analyser was used with a potential-gradient detector. The main column was a fluorinated ethylene–propylene (FEP) copolymer tube (12 cm × 0.5 mm I.D.) and the precolumn was a polytetrafluoroethylene (PTFE) tube (10 cm × 1.0 mm I.D.). A Hamilton Model 1701-N microsyringe was used for the injection of samples into the isotachophoretic analyser. Distilled, demineralized water was obtained from a Yamato-Kagaku Model WG-25 automatic still and a Nihon Millipore Milli-QII system.

Reagents

All reagents were of analytical-reagent grade and used without further purification. Distilled, demineralized water was used throughout. 18-Crown-6 and 15-crown-5 were obtained from Aldrich (Milwaukee, WI, U.S.A.). Standard solutions of various cations were prepared by dissolving their chlorides or nitrates in water; nitrates were used for the preparation of mixed solutions of ammonium and silver ions to prevent the precipitation of silver chloride.

Procedures

Inject 5-μl volumes of solutions containing 1.0 mM of each cation into the isotachophoretic analyser. As leading electrolyte use an aqueous solution containing 5 mM hydrochloric acid, 0.01 wt.-% Triton X-100 and an appropriate amount of crown ether (this leading electrolyte had already been found to be suitable for the isotachophoretic determination of cations [7]), and as terminating electrolyte 10 mM histidine adjusted to pH 4.0 with 0.5 M hydrochloric acid. For the determination of silver ion, use perchloric acid instead of hydrochloric acid to prevent the precipitation of silver chloride in the separating column. Maintain the migration current at 200 μA for the first 7 min in the former electrolyte system and 13 min in the latter, then reduce it to 100 μA. Increase the concentration of 18-crown-6 or 15-crown-5 in the leading electrolyte up to 50 mM.

Calculate the potential unit (PU) value [12], which is generally used as a parameter for the identification of the analyte ions, defined by

$$PU = (PG_A - PG_L)/(PG_T - PG_L) \qquad (1)$$

where PG is the potential gradient. The subscripts denote the analyte (A), leading (L) and terminating (T) ions, respectively. The relationship between the PU value and the effective mobility of the analyte ion ($\bar{m}_A$) [12] is given by

$$PU = (a-1)^{-1}\bar{m}_L/\bar{m}_A - (a-1)^{-1} \qquad (2)$$

where $\bar{m}$ is the effective mobility and $a = \bar{m}_L/\bar{m}_T$. Eqn. 2 indicates that the *PU* value becomes larger when the effective mobility of the analyte ion ($\bar{m}_A$) becomes smaller, and the former becomes smaller when the latter becomes larger. That is, the change in the effective mobility of the analyte ion can be obtained indirectly in terms of the *PU* value.

RESULTS AND DISCUSSION

Effective mobilities of analyte ions

When analyte ions (A^+ and B^+) form 1:1 complexes (AN^+ and BN^+) with an electrically neutral ligand N, their complex formation constants (K_{AN} and K_{BN}) are defined by

$$K_{AN} = [AN^+]_A/([A^+]_A[N]_A) \tag{3}$$

and

$$K_{BN} = [BN^+]_B/([B^+]_B[N]_B) \tag{4}$$

where the subscripts A and B denote the quantities related to each sample zone. Then the effective mobilities of A^+ and B^+ ($\bar{m}_A$ and $\bar{m}_B$) in their sample zones in the presence of ligand N are expressed as follows [10]:

$$\begin{aligned}\bar{m}_A &= (m_A[A^+]_A + m_{AN}[AN^+]_A)/([A^+]_A + [AN^+]_A)\\ &= (m_A + m_{AN}K_{AN}[N]_A)/(1 + K_{AN}[N]_A)\end{aligned} \tag{5}$$

$$\begin{aligned}\bar{m}_B &= (m_B[B^+]_B + m_{BN}[BN^+]_B)/([B^+]_B + [BN^+]_B)\\ &= (m_B + m_{BN}K_{BN}[N]_B)/(1 + K_{BN}[N]_B)\end{aligned} \tag{6}$$

where m_A, m_B, m_{AN} and m_{BN} are the ionic mobilities of the free analyte ions A^+, B^+ and the complexed analyte ions AN^+ and BN^+, respectively. Eqns. 5 and 6 indicate that cations A^+ and B^+ can be separated from each other even when they have the same ionic mobilities ($m_A = m_B$) if the complex formation constants with N are appreciably different ($K_{AN} \neq K_{BN}$): if $K_{AN} > K_{BN}$, $\bar{m}_A < \bar{m}_B$ and if $K_{AN} < K_{BN}$, $\bar{m}_A > \bar{m}_B$. In addition, $\bar{m}_A$ and $\bar{m}_B$ decrease with increasing $[N]_A$ and $[N]_B$, respectively.

In this study, N corresponds to crown ethers. The stabilities of inclusion complexes of analyte ions with crown ethers generally depend on (1) the kinds and location of the heteroatom in the crown ring, (2) the number of heteroatoms, (3) the relationship between the diameter of the cation and that of the cavity of the crown ether, (4) the charge of the cation, (5) the flexibility of the crown ring and (6) the intensity of interaction between the heteroatom and solvent, etc. [13].

Moreover, when analyte ions (A^+ and B^+) also form 2:1 (crown ring:cation) complexes (AN_2^+ and BN_2^+) with electrically neutral ligand N, their complex formation constants (K_{AN_2} and K_{BN_2}) are defined by

$$\begin{aligned}K_{AN_2} &= [AN_2^+]_A/([AN^+]_A[N]_A)\\ &= [AN_2^+]_A/(K_{AN}[A^+]_A[N]_A^2)\end{aligned} \tag{7}$$

and

$$K_{BN_2} = [BN_2^+]_B/([BN^+]_B[N]_B)$$
$$= [BN_2^+]_B/(K_{BN}[B^+]_B[N]_B^2) \qquad (8)$$

Then the effective mobilities of A^+ and B^+ ($\bar{m}_A$ and $\bar{m}_B$) in their sample zones in the presence of ligand N are expressed as follows:

$$\bar{m}_A = (m_A[A^+]_A + m_{AN}[AN^+]_A + m_{AN_2}[AN_2^+]_A)/([A^+]_A + [AN^+]_A + [AN_2^+]_A)$$
$$= (m_A + m_{AN}K_{AN}[N]_A + m_{AN_2}K_{AN}K_{AN_2}[N]_A^2)/(1 + K_{AN}[N]_A + K_{AN}K_{AN_2}[N]_A^2) \qquad (9)$$

$$\bar{m}_B = (m_B[B^+]_B + m_{BN}[BN^+]_B + m_{BN_2}[BN_2^+]_B)/([B^+]_B + [BN^+]_B + [BN_2^+]_B)$$
$$= (m_B + m_{BN}K_{BN}[N]_B + m_{BN_2}K_{BN}K_{BN_2}[N]_B^2)/(1 + K_{BN}[N]_B + K_{BN}K_{BN_2}[N]_B^2) \qquad (10)$$

where m_{AN_2} and m_{BN_2} are the ionic mobilities of the complexed analyte ions AN_2^+ and BN_2^+, respectively. In this case, $\bar{m}_A$ and $\bar{m}_B$ depend on not only K_{AN} and K_{BN} but also K_{AN_2} and K_{BN_2} compared with the case previously described.

Determination of ammonium and thallium ions

The limiting molar conductivity of ammonium ion is approximately equal to that of thallium ion, *i.e.*, 73.5 and 74.7 S cm^2 mol^{-1}, respectively, at 25°C in aqueous solution [11]. Therefore, it is difficult to separate these ions from each other with ordinary leading electrolytes.

Fig. 1 shows the effect of 18-crown-6 concentration on the *PU* values of several cations (concentration 1.0 m*M*). The *PU* value of lead ion greatly increased with increasing 18-crown-6 concentration up to 1.0 m*M*, but then reached an almost constant value. The *PU* values of both potassium and thallium ions increased with increasing 18-crown-6 concentration up to 50 m*M*; the magnitude of the increase for potassium ion was the same as that for thallium ion. The magnitude of the increase in the *PU* value for ammonium ion was smaller than that for any other cation. When various cations form 1:1 complexes with crown ethers and their complex formation constants are given in Table I [9]. It is concluded that (1) the dependence of the increase in the *PU* value on the 18-crown-6 concentration, thallium ion ≈ potassium ion > ammonium ion, is in line with the order of magnitude of the complex formation constant with 18-crown-6 [1,2,10] and (2) at 18-crown-6 concentrations of 1.0 m*M* or above, lead is present mostly in the complexed form because of the large complex formation constant with 18-crown-6, so that the *PU* value of lead ion is almost constant [2,10].

Linear calibration graphs were obtained for ammonium and thallium ions up to 3.0 m*M* by using the leading electrolyte containing 20 m*M* 18-crown-6. The regression equations of these graphs for ammonium and thallium ions were $y = 9.6x$ and $y = 12.9x - 0.2$, respectively, where x is the concentration of the ion in m*M* and y the zone length in mm when the recording speed is adjusted to 40 mm/min, and the correlation coefficients were 0.998 and 1.000, respectively. The relative standard deviations were obtained by calculating the zone length per 1.0 m*M* at each point on the calibration graphs and were 0.036 and 0.028 ($n = 6$), respectively. The limits of

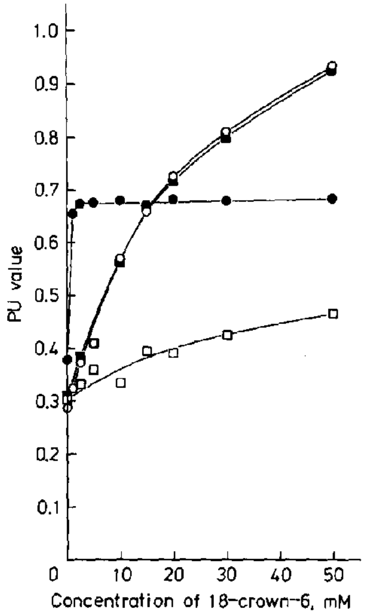

Fig. 1. Effect of 18-crown-6 concentration on the *PU* values of ammonium, lead, potassium and thallium ions. □ = NH_4^+; ● = Pb^{2+}; ■ = K^+; ○ = Tl^+.

determination for ammonium and thallium ions were $1.0 \cdot 10^{-2}$ and $7.8 \cdot 10^{-3}$ m*M*, respectively, corresponding to a 0.1-mm zone length. When 5-μl volumes of mixed solutions containing various concentrations of ammonium and thallium ions were injected and analysed by use of the calibration graphs, the error in the determination of these ions was less than ±20%, as shown in Table II. The isotachopherogram of mixture 2 in Table II is shown in Fig. 2. Completely separated zones with sharp boundaries for the ammonium and thallium ions were obtained with the leading electrolyte containing 20 m*M* 18-crown-6, while the mixed zone of these ions was formed without 18-crown-6.

Determination of thallium and lead ions

There is a slight difference between the limiting molar conductivities of thallium and lead (69.5 S cm^2 mol^{-1}) ions [11]. If the difference between the effective mobilities of these ions increases further, these ions can be determined accurately.

As the *PU* value of lead ion greatly increased with increasing 18-crown-6

TABLE I

COMPLEX FORMATION CONSTANTS (LOG *K*) OF VARIOUS CATIONS WITH CROWN ETHERS IN AQUEOUS SOLUTION (25°C)

Crown ether	NH_4^+	Pb^{2+}	K^+	Tl^+	Ag^+
18-Crown-6	1.23	4.27	2.03	2.27	1.50
15-Crown-5	1.71	1.85	0.74	1.23	0.94

TABLE II

ANALYTICAL RESULTS FOR AMMONIUM AND THALLIUM IONS

Mixture No.	Added (m*M*)		Found (m*M*)		Error (%)	
	NH_4^+	Tl^+	NH_4^+	Tl^+	NH_4^+	Tl^+
1	0.50	3.0	0.51	3.2	+2.0	+6.7
2	1.0	1.0	0.97	1.0	−3.0	0.0
3	1.0	2.5	0.80	2.5	−20	0.0
4	1.5	2.0	1.5	2.1	0.0	+5.0
5	2.0	1.5	2.0	1.5	0.0	0.0
6	2.5	1.0	2.4	1.0	−4.0	0.0
7	3.0	0.50	3.0	0.53	0.0	+6.0

concentration up to 1.0 m*M*, as mentioned above, the variations of the *PU* values of thallium and lead ions were investigated when the 18-crown-6 concentration was increased up to 1.0 m*M* in 0.1 m*M* steps. The *PU* value of thallium ion increased slightly with increasing 18-crown-6 concentration up to 0.5 m*M*, but then almost levelled off, as shown in Fig. 3. On the other hand, the *PU* value of lead ion increased with increasing 18-crown-6 concentration, but only slightly when the concentration was >0.4 m*M*.

Linear calibration graphs were obtained for thallium and lead ions with the leading electrolyte containing 0.8 m*M* 18-crown-6. The regression equations for thallium and lead ions were $y = 8.6x - 0.5$ and $y = 22.5x - 0.5$, respectively, and the correlation coefficients were 0.999 and 1.000, respectively. The relative standard deviations were 0.048 and 0.028, respectively. The limits of determination for thallium and lead ions were $1.2 \cdot 10^{-2}$ and $4.4 \cdot 10^{-3}$ m*M*, respectively. The error in the simultaneous determination of these ions was less than ±20%, as shown in Table III. The isotachopherogram of mixture 2 in Table III is shown in Fig. 4. The difference

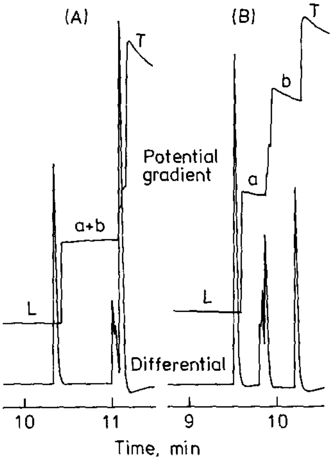

Fig. 2. Isotachopherograms for the separation of ammonium and thallium ions. (A) Without 18-crown-6; (B) 20 m*M* 18-crown-6. L = Leading ion; a = NH_4^+; b = Tl^+; T = terminating ion.

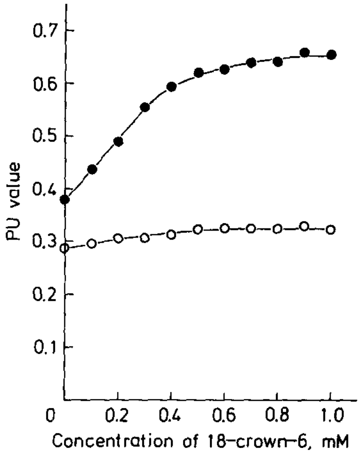

Fig. 3. Effect of 18-crown-6 concentration on the *PU* values of thallium and lead ions. ○ = Tl^+; ● = Pb^{2+}.

between the step heights of thallium and lead ions increased further by use of the leading electrolyte containing 0.8 m*M* 18-crown-6.

The volume of sample (mixed solution containing 1.0 m*M* of thallium and lead ions) injected into the isotachophoretic analyser was increased up to 50 μl. When the leading electrolyte containing 0.8 m*M* 18-crown-6 was used, the zone lengths for both thallium and lead ions increased in proportion to the volume up to 40 μl. On the other hand, when the leading electrolyte without 18-crown-6 was used, both zone lengths increased in proportion to the volume up to 15 μl. That is, by using the former leading electrolyte, the amounts of those ions which could be determined were increased about 2.7 times compared with the use of the latter.

The solubilities of thallium monochloride at 20°C and lead dichloride at 25°C in water are 0.325 and 1.08 g per 100 g, respectively [14]. In this study, the concentrations of the analyte ions were less than 3.0 m*M*. Therefore, thallium monochloride and lead dichloride are not precipitated in the separation column.

TABLE III

ANALYTICAL RESULTS FOR THALLIUM AND LEAD IONS

Mixture No.	Added (m*M*)		Found (m*M*)		Error (%)	
	Tl^+	Pb^{2+}	Tl^+	Pb^{2+}	Tl^+	Pb^{2+}
1	0.50	3.0	0.48	2.9	−4.0	−3.3
2	1.0	1.0	1.2	1.0	+20	0.0
3	1.0	2.5	1.0	2.5	0.0	0.0
4	1.5	2.0	1.7	2.0	+13	0.0
5	2.0	1.5	2.2	1.5	+10	0.0
6	2.5	1.0	2.9	1.0	+16	0.0
7	3.0	0.50	3.4	0.53	+13	+6.0

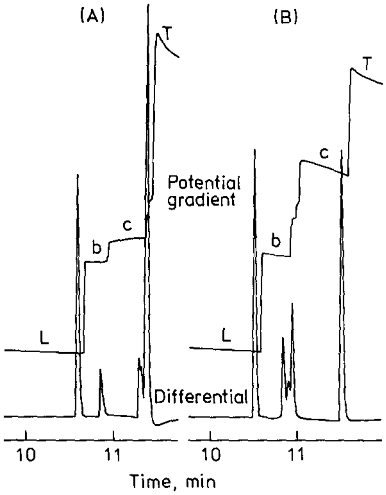

Fig. 4. Isotachopherograms for the separation of thallium and lead ions. (A) Without 18-crown-6; (B) 0.8 m*M* 18-crown-6. L = Leading ion; b = Tl^+; c = Pb^{2+}; T = terminating ion.

Determination of potassium and thallium ions

The limiting molar conductivity of potassium ion (73.5 S cm^2 mol^{-1}) is approximately equal to that of thallium ion [11], so it is difficult to separate these ions with ordinary leading electrolytes.

Fig. 5 shows the effect of 15-crown-5 concentration on the *PU* values of several cations. The *PU* values of both potassium and thallium ions increased almost linearly with increasing 15-crown-5 concentration up to 50 m*M*; the magnitude of the increase for thallium ion was larger than that for potassium ion. The *PU* value of lead ion also increased with increasing 15-crown-5 concentration, but only slightly when the latter was >30 m*M*. The *PU* value of ammonium ion increased slightly with increasing

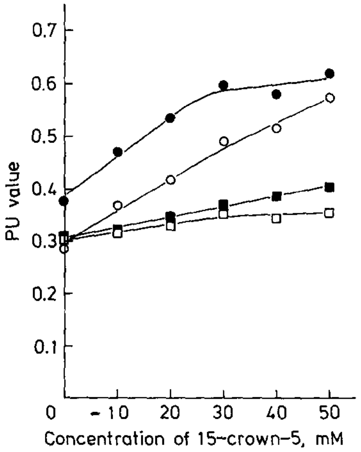

Fig. 5. Effect of 15-crown-5 concentration on the *PU* values of ammonium, potassium, thallium and lead ions. □ = NH_4^+; ■ = K^+; ○ = Tl^+; ● = Pb^{2+}.

TABLE IV

CAVITY DIAMETERS OF CROWN ETHERS AND IONIC RADII OF VARIOUS CATIONS

Crown ether	Cavity diameter (Å)	Cation	Ionic radius (Å)
18-Crown-6	2.6–3.2	NH_4^+	1.45
15-Crown-5	1.7–2.2	Pb^{2+}	1.18
		K^+	1.33
		Tl^+	1.49
		Ag^+	1.13

15-crown-5 concentration up to 30 m*M*, but then almost levelled off. In this instance, the dependence of the increase in the *PU* value on the 15-crown-5 concentration is not necessarily in line with the order of magnitude of the complex formation constant with 15-crown-5 shown in Table I. Cations with diameters larger than those of crown rings also form 2:1 (crown ring:cation) complexes [*e.g.*, K^+(benzo-15-crown-5)$_2$ complex] [13]. Cavity diameters of crown ethers [13] and ionic radii of various cations [15,16] are shown in Table IV. Because the ionic radii of both thallium and ammonium ions are larger than that of potassium ions, it can be presumed that these cations also form 2:1 complexes with 15-crown-5. Therefore, the dependences of the increases in the *PU* value on the 15-crown-5 concentration cannot be compared with one another on the basis of only the order of magnitude of the complex formation constants given in Table I.

Linear calibration graphs were obtained for potassium and thallium ions by using the leading electrolyte containing 50 m*M* 15-crown-5. The regression equations for potassium and thallium ions were $y = 10.5x - 0.1$ and $y = 12.0x - 0.3$, respectively, both correlation coefficients being 1.000. The relative standard deviations were 0.0072 and 0.031, respectively. The limits of determination for potassium and thallium ions were $9.5 \cdot 10^{-3}$ and $8.3 \cdot 10^{-3}$ m*M*, respectively. The error in the simultaneous determination of these ions was less than ±16%, as shown in Table V. The isotachopherogram of mixture 2 in Table V is shown in Fig. 6. Completely separated zones with sharp boundaries for the potassium and thallium ions were obtained with

TABLE V

ANALYTICAL RESULTS FOR POTASSIUM AND THALLIUM IONS

Mixture No.	Added (m*M*)		Found (m*M*)		Error (%)	
	K^+	Tl^+	K^+	Tl^+	K^+	Tl^+
1	0.50	3.0	0.48	3.1	−4.0	+ 3.3
2	1.0	1.0	0.98	0.98	−2.0	− 2.0
3	1.0	2.5	0.97	2.5	−3.0	0.0
4	1.5	2.0	1.5	2.1	0.0	+ 5.0
5	2.0	1.5	2.0	1.6	0.0	+ 6.7
6	2.5	1.0	2.5	1.1	0.0	+10
7	3.0	0.50	2.9	0.58	−3.3	+16

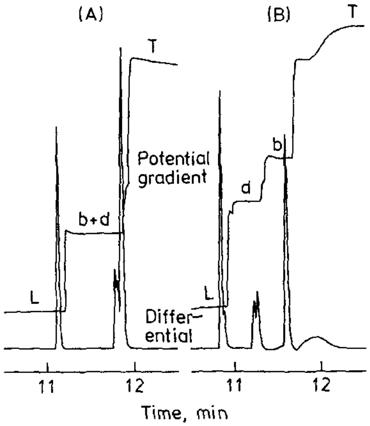

Fig. 6. Isotachopherograms for the separation of potassium and thallium ions. (A) Without 15-crown-5; (B) 50 m*M* 15-crown-5. L = Leading ion; b = Tl^+; d = K^+; T = terminating ion.

the leading electrolyte containing 50 m*M* 15-crown-5, whereas a mixed zone of these ions was formed without 15-crown-5.

Determination of ammonium and silver ions

There is a small difference between the limiting molar conductivities of ammonium and silver (61.9 S cm^2 mol^{-1}) ions [11]. If the difference between the effective mobilities of these ions increases further, greater amounts of these ions can be determined accurately.

Fig. 7 shows the effects of 18-crown-6 and 15-crown-5 concentrations on the *PU* values of ammonium and silver ions. The *PU* value of silver ion increased to similar extents with increasing 18-crown-6 and 15-crown-5 concentrations up to 50 m*M*. In contrast, the *PU* value of ammonium ion increased with increasing 18-crown-6

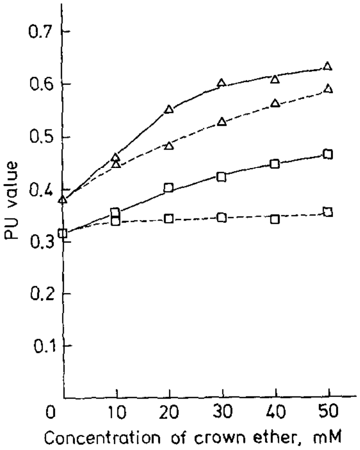

Fig. 7. Effect of crown ether concentration on the *PU* values of ammonium and silver ions. □ = NH_4^+; △ = Ag^+; solid lines, 18-crown-6; dashed lines, 15-crown-5.

TABLE VI

ANALYTICAL RESULTS FOR AMMONIUM AND SILVER IONS

Mixture No.	Added (m*M*)		Found (m*M*)		Error (%)	
	NH_4^+	Ag^+	NH_4^+	Ag^+	NH_4^+	Ag^+
1	0.50	3.0	0.53	3.1	+6.0	+3.3
2	1.0	1.0	0.86	0.97	−14	−3.0
3	1.0	2.5	0.91	2.5	−9.0	0.0
4	1.5	2.0	1.6	2.0	+6.7	0.0
5	2.0	1.5	2.2	1.6	+10	+6.7
6	2.5	1.0	2.7	1.1	+8.0	+10
7	3.0	0.50	3.2	0.50	+6.7	0.0

concentration up to 50 m*M*, whereas it remained almost constant with increasing 15-crown-5 concentration. Therefore, the leading electrolyte containing 50 m*M* 15-crown-5 was adopted for the simultaneous determination of ammonium and silver ions. It is concluded that the dependence of the increase in the *PU* value for ammonium ion on the 18-crown-6 concentration is almost identical with that for silver ion, as are the magnitudes of their complex formation constants with 18-crown-6 [1,2,10]. On the other hand, the dependences of increase in the *PU* value on the 15-crown-5 concentration cannot be compared with each other on the basis of only the order of magnitude of the complex formation constant shown in Table I, as described in the previous section.

Linear calibration graphs were obtained for ammonium and silver ions by use of the leading electrolyte containing 50 m*M* 15-crown-5. The regression equations for

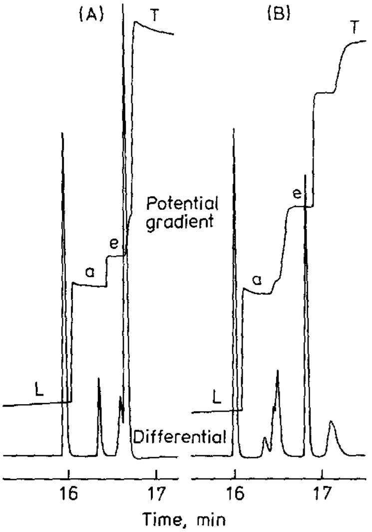

Fig. 8. Isotachopherograms for the separation of ammonium and silver ions. (A) Without 15-crown-5; (B) 50 m*M* 15-crown-5. L = Leading ion; a = NH_4^+; e = Ag^+; T = terminating ion.

ammonium and silver ions were $y = 9.0x + 0.1$ and $y = 11.2x - 0.3$, respectively, both correlation coefficients being 0.999. The relative standard deviations were 0.046 and 0.051, respectively. The limits of determination for ammonium and silver ions were $1.1 \cdot 10^{-2}$ and $8.9 \cdot 10^{-3}$ m*M*, respectively. The error in the simultaneous determination of these ions was less than ±14%, as shown in Table VI. The isotachopherogram of mixture 2 in Table VI is shown in Fig. 8. The difference between the step heights of ammonium and silver ions increased further by using the leading electrolyte containing 50 m*M* 15-crown-5.

REFERENCES

1 K. Fukushi and K. Hiiro, *J. Chromatogr.*, 518 (1990) 189.
2 M. Tazaki, M. Takagi and K. Ueno, *Chem. Lett.*, (1982) 639.
3 F. S. Stover, *J. Chromatogr.*, 298 (1984) 203.
4 F. S. Stover, *J. Chromatogr.*, 368 (1986) 476.
5 K. Fukushi and K. Hiiro, *Talanta*, 35 (1988) 55.
6 K. Fukushi and K. Hiiro, *Fresenius' Z. Anal. Chem.*, 332 (1988) 125.
7 K. Fukushi and K. Hiiro, *Talanta*, 35 (1988) 799.
8 A. A. G. Lemmens, F. M. Everaerts, J. W. Venema and H. D. Jonker, *J. Chromatogr.*, 439 (1988) 423.
9 R. Oda, in R. Oda, T. Shono and I. Tabushi (Editors), *Crown Ether no Kagaku* (*Crown Ether Chemistry*), Kagaku-Dojin, Kyoto, 1978, p. 9.
10 M. Tazaki, T. Hayashita, Y. Fujino and M. Takagi, *Bull. Chem. Soc. Jpn.*, 59 (1986) 3459.
11 Chemical Society of Japan, *Kagaku Binran*, Maruzen, Tokyo, 3rd ed., 1984, p. II-460.
12 H. Miyazaki and K. Kato, *Tosoku-Denki-Eido-Ho* (*Isotachophoresis*), Kodansha Scientific, Tokyo, 1980, p. 30.
13 K. Takemoto, M. Miyata and K. Kimura, *Hosetsu-Kagobutsu* (*Inclusion Compounds*), Tokyo-Kagaku-Dojin, Tokyo, 1989, p. 18.
14 M. Oki, T. Osawa, M. Tanaka and H. Chihara (Editors), *Kagaku-Dai-Jiten* (*Encyclopedic Dictionary of Chemistry*), Tokyo-Kagaku-Dojin, Tokyo, 1st ed., 1989, pp. 319 and 321.
15 T. Shono, in R. Oda, T. Shono and I. Tabushi (Editors), *Crown Ether no Kagaku* (*Crown Ether Chemistry*), Kagaku-Dojin, Kyoto, 1978, p. 112.
16 R. Kiriyama and H. Kiriyama, *Kozo-Muki-Kagaku* (*Structural Inorganic Chemistry*), Kyoritsu-Shuppan, Tokyo, 1985, p. 237.