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SEPARATION OF LANTHANIDES BY CAPILLARY TUBE ISOTACHOPHORESIS USING COMPLEX-FORMING EQUILIBRIA

ISOSHI NUKATSUKA, MITSUHIKO TAGA and HITOSHI YOSHIDA*

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060 (Japan)

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SUMMARY

Fourteen lanthanide ions have been separated and determined simultaneously by capillary tube isotachophoresis using complex-forming equilibria between 2-hydroxyisobutyric acid and the lanthanide ions. For simultaneous separation it is necessary for the sample ions to migrate at a higher leading ion concentration than usual (0.005 or 0.01 mol dm^{-3}). Only 20 min are required for an analysis and the relative standard deviation of the determination is 1.2–2.5% at the 5-nmol level.

INTRODUCTION

There are several papers describing separations by capillary tube isotachophoresis[1–3], and various methods have been used to improve the separability. These methods can be classified into two broad groups: one involves "chemical" operations, such as controlling the pH of the leading electrolyte or the use of complex-forming equilibria between the sample ion and the counter ion, and the other "mechanical" operations, such as the application of a counter flow or the use of a long capillary tube. The latter is based on the principle that the separability of a binary mixture depends on the amount of electricity which flows under electrophoretic migration[2,3]. However, even if a counter flow is applied, it takes a long time to achieve a satisfactory separation, and the use of a long capillary tube is also time consuming and sometimes causes the migration to be disturbed because a high voltage must be applied[4].

The separability seems to be improved by the use of a higher leading ion concentration, because the amounts of electricity are increased. The principal advantages of this method are that the time required for an analysis would be less, and that even on migration with a low buffer action the stability of sample zones would be improved owing to an increase in the amount of counter buffer ion. However, the detection limit in this instance increases with increasing leading ion concentration, as the concentration of the sample ion zones depends on that of the leading ion zone.

On the other hand, there are several papers relating to the use of complex-forming equilibria in capillary tube isotachophoresis[5–8]. This method makes the migration system very complicated and sometimes causes "enforced" isotachophoresis[2,3,8]. However, it is interesting to apply this method to the separation of metal ions.

In this work, we have attempted to separate lanthanides using complex-forming equilibria with 2-hydroxyisobutyric acid (HIBA), and to investigate the effect of the leading ion concentration on this system. The separability was evaluated by migrating solutions of equimolar mixtures of fourteen lanthanides and comparing the ranges in which complete separations between praseodymium(III) and neodymium(III) and/or europium(III) and gadolinium(III) are achieved. These pairs have the smallest differences in complexing ability with HIBA of the various pairs of lanthanides.

The separation of the lanthanides was also performed by zone electrophoresis. However, for their detection and determination by this means, intricate procedures were necessary and the accuracy of the determination was poor.

Recently, rapid separations of the lanthanides have been carried out by means of high-performance liquid chromatography[9,10]. Nevertheless, for detection, radio-activation or coloration in a special mixing cell was required and complicated gradient elution was also necessary. Further, it is difficult to make stable column beds with resins of small particle size. We have already shown the utility of capillary tube isotachophoresis using complex-forming equilibria for the separation of metal ions[8]. By using the method proposed in this paper, we performed the separation of lanthanides within 20 min.

EXPERIMENTAL

Apparatus

Isotachopherograms were recorded with a capillary tube isotachophoretic analyser Model IP-1B with PGD-1 potential gradient detector, (Shimadzu, Kyoto, Japan). The length of the capillary tube (PTFE, I.D. 0.5 mm) was 20 cm. Measurements of pH were made with expanded-scale pH meter (Model F-7ss, Horiba, Japan).

Materials

Stock solutions of lanthanides were prepared by dissolving the nitrate ignited or oxide in concentrated nitric acid, followed by evaporation of the nitric acid and dilution to 0.1 mol dm^{-3} with dilute nitric acid, except for cerium(III) solution, which was prepared by dissolving the nitrate in dilute nitric acid and titration with 1,2-cyclohexanediamine-N,N,N^1,N^1-tetraacetic acid (CyDTA).

The leading electrolytes were prepared by mixing potassium hydroxide solution standardized by gravimetry with sodium tetraphenylborate (TPB), 2-hydroxy-isobutyric acid (HIBA) solution standardized by acid–base titration and Triton X-100 or poly(vinyl alcohol) (PVA), followed by dilution to the desired concentration and adjusting the pH with acetic acid.

The terminating electrolyte was prepared by dissolving β-alanine in water and adjusting the pH to 4.00 with acetic acid.

The chemicals used were of the highest grade commercially available, and deionized water was used.

RESULTS AND DISCUSSION

Effect of leading ion concentration

Effect of leading ion and HIBA concentrations on the mobility of the terminating ion. A terminating ion that has a sufficiently low mobility is essential for isotacho-

phoresis and much attention should be paid when complex-forming equilibria are applied[8]. The terminating ion must be free from mutual interaction with the complexing agent and must have a mobility lower than that of any sample ions which interact with the complexing agent. Of the various terminating ions examined, β-alanine was the most suitable. However, as the effective mobility of β-alanine depends on pH, it cannot be used as a terminating ion when the pH of the leading electrolyte is low or the buffering action of the counter ion is weak.

HIBA was used as the complexing agent. As the stability constants of the lanthanide complexes with HIBA are not very large [La(III)–Lu(III), log K = 4–10][11], the desirable HIBA concentration was above ca. 0.01 mol dm^{-3} in the leading electrolyte. The pH of the leading electrolyte required was over 5. The amount of buffering agent (acetate) in the leading electrolyte decreased with increasing concentration of HIBA owing to its low pK_a value (3.971)[12], and the buffering ability of the leading electrolyte was therefore low. Hence there was a decrease in the pH in the terminating zone, and the effective mobility of β-alanine became so large that it could not be used as a terminating ion (see Fig. 2).

This problem was solved by enhancing the buffering ability of the leading electrolyte increasing the leading ion and the buffering counter ion concentrations. As shown in Fig. 1, when the concentration of the leading ion (K$^+$) was 0.011 mol dm^{-3}, the effective mobility of β-alanine was larger than that of some heavy rare earths and "enforced" isotachophoretic migration occurred. However, at a higher leading ion concentration the effective mobility of β-alanine was small and the usual migration occurred. These effects are the result of an increase in the acetate ion concentration in the leading electrolyte and an improvement of the buffering ability of the leading electrolyte.

Generally the pH of the terminating electrolyte should be adjusted to that of leading electrolyte, but in this work the pH of the terminating electrolyte was adjusted to 4.00, because at higher pH values the initial voltage was so high that the migration was sometimes impossible. On the other hand, at lower pH, the initial voltage was low and the time required for the analysis decreased because a large current could be used.

Effect of leading ion concentration on the mobilities and separabilities of lanthanides. Fig. 1 also shows the effect of the leading ion concentration on the effective mobilities of lanthanides. The effective mobilities of light elements tend to decrease and those of heavy elements tend to increase with increasing leading ion concentration. The differences between the mobilities of the various lanthanides become decrease with increasing leading ion concentration, apparently owing to an increasing interaction between acetate and lanthanides and a decreasing interaction between HIBA and lanthanides with increasing leading ion concentration.

Europium(III) and gadolinium(III) could not be separated from each other at a leading ion concentration of 0.037 mol dm^{-3}. However, the separabilities of the lanthanides were greatly improved, as shown in Table I. The separable range of praseodymium(III)–neodymiun(III) at a leading ion concentration of 0.037 mol dm^{-3} is 4.5 times greater than at 0.011 mol dm^{-3}.

Table I also shows that the lower limit of the separable range become slightly greater at higher leading ion concentrations.
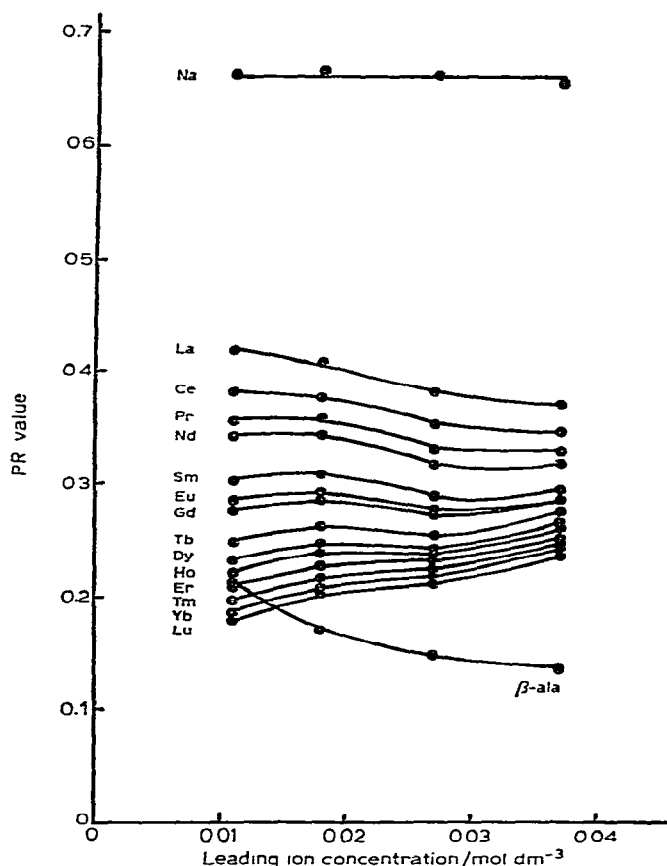
Fig. 1. Effect of leading ion concentration. Leading electrolyte: $0.011-0.037$ mol dm^{-3} KOH, 0.010 mol dm^{-3} HIBA, CH$_3$COOH, 0.0025% PVA, pH 5.70. The PR value (potential gradient ratio value) represents the ratio of the potential gradient of the leading ion to that of the sample ion (PG_L/PG_S), which corresponds to the ratio of the mobility of sample ion to that of the leading ion $(m_S/m_L)^7$.

TABLE I

EFFECT OF LEADING ION CONCENTRATION ON SEPARABLE RANGE (nmol)

Conditions as in Fig. 1.

Lanthanides	Leading ion concentration (mol dm^{-3})			
	0.011	0.018	0.027	0.037
Pr–Nd	1–3	1–6	2–8	3–12
Eu–Gd	1–4	1–5	2–6	—

Separation of lanthanides

Effect of HIBA concentration and pH of the leading electrolyte. The effective mobilities of lanthanides decreased and that of β-alanine increased with increasing HIBA concentration in the leading electrolyte, as shown in Fig. 2. As a result, ytter-
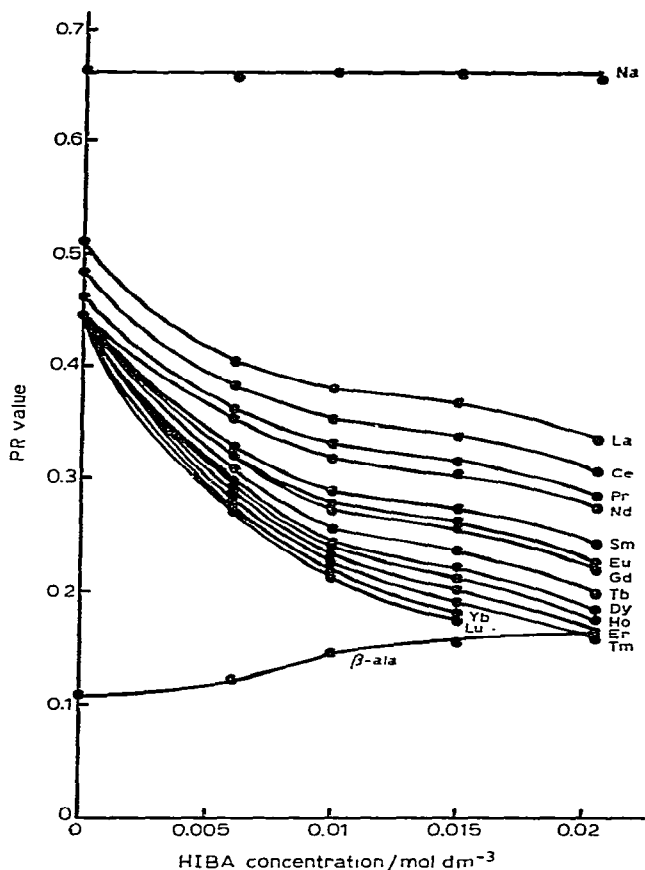
Fig. 2. Effect of HIBA concentration in the leading electrolyte. Leading electrolyte: 0.027 mol dm^{-3} KOH, 0–0.021 mol dm^{-3} HIBA, CH_3COOH, 0.0025% PVA, pH 5.70.

bium(III) and lutetium(III) were not detected and "enforced" isotachophoretic migration was observed with thulium(III).

A decrease in the pH of the leading electrolyte increased the effective mobilities of lanthanides and β-alanine. Thulium(III), ytterbium(III) and lutetium(III) were not detected at pH 4.10, and dysprosium(III), holmium(III) and erbium(III) were not detected at pH 3.57, as shown in Fig. 3. The effective mobilities of lanthanides did not change above pH 5 as the pK_a value of HIBA was 3.971.

Tables II and III show that the separabilities of lanthanides increase with increasing HIBA concentration and increasing pH of the leading electrolyte.

Surface-active agents. Surface-active agents can be utilized to suppress electrode reactions and to increase the viscosity of the leading electrolyte, and Triton X-100 and PVA are the most effective[13]. However, when Triton X-100 was added to the leading electrolyte an effect of electrode reactions between the detection electrode and lanthanides was observed on the isotachopherograms. Also, the isotachopherograms of lanthanides became more indistinct with increasing atomic number.
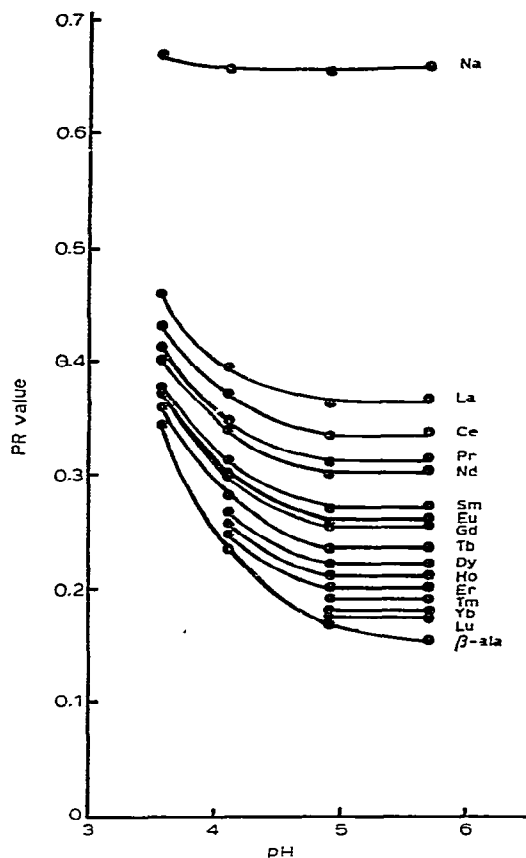
Fig. 3. Effect of pH of the leading electrolyte. Leading electrolyte: 0.027 mol dm^{-3} KOH, 0.015 mol dm^{-3} HIBA, CH$_3$COOH, 0.0025% PVA, pH 3.57–5.70.

TABLE II

EFFECT OF HIBA CONCENTRATION IN THE LEADING ELECTROLYTE ON SEPARABLE RANGE (nmol)

Conditions as in Fig. 2.

Lanthanides	HIBA concentration (mol dm^{-3})				
	0	0.0062	0.010	0.015	0.021
Pr–Nd	—	2–7	2–8	2–10	2–13
Eu–Gd	—	—	2–6	2–9	2–13

These problems could be overcome by using PVA. The most favourable PVA concentration in the leading electrolyte is 0.0025%. Higher concentrations of PVA (even 0.05%) sometimes prevent clear separations.

Separation of lanthanides. The relative standard deviations of simultaneous determinations of 5 nmol of lanthanides were 1.2–2.5%, as shown in Table IV. Those

TABLE III

EFFECT OF pH OF THE LEADING ELECTROLYTE ON SEPARABLE RANGE (nmol)

Conditions as in Fig. 3.

Lanthanides	pH of leading electrolyte			
	3.57	4.10	4.92	5.70
Pr–Nd	2–7	2–8	2–10	2–10
Eu–Gd	—	2–5	2–8	2–9

TABLE IV

SEPARATION OF LANTHANIDES

Conditions as in Fig. 4.

Cation	Sample size (nmol)	Average zone length*(mm)	R.S.D.(%)*
La(III)	4.98	6.6	1.4
Ce(III)	5.00	6.6	1.6
Pr(III)	5.00	6.4	1.8
Nd(III)	4.53	5.8	2.4
Sm(III)	4.94	5.7	1.3
Eu(III)	5.02	6.2	1.4
Gd(III)	4.53	6.1	2.3
Tb(III)	5.00	6.2	1.2
Dy(III)	5.00	6.0	1.6
Ho(III)	5.00	6.0	1.4
Er(III)	5.00	6.0	2.2
Tm(III)	5.00	5.9	1.4
Yb(III)	5.00	5.8	2.1
Lu(III)	5.00	5.0	2.5

* Six determinations.

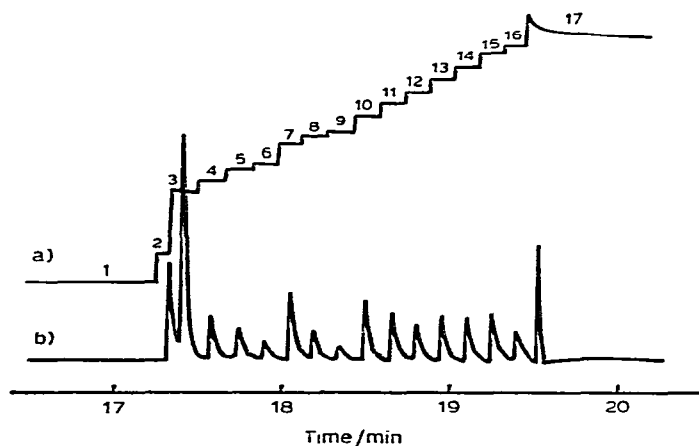Fig. 4. Isotachopherogram for the simultaneous separation of lanthanides. Leading electrolyte: 0.027 mol dm^{-3} KOH, 0.015 mol dm^{-3} HIBA, CH$_3$COOH, 0.0025% PVA, pH 4.92. Migration current, 225 μA; chart speed, 40 mm min^{-1}; sample, 5.0 μl of a mixed solution of 10^{-3} mol dm^{-3} lanthanides. (a) Potential gradient; (b) differential potential gradient. 1, K$^+$; 2, Na$^+$; 3, La^{3+}; 4, Ce^{3+}; 5, Pr^{3+}; 6, Nd^{3+}; 7, Sm^{3+}; 8, Eu^{3+}; 9, Gd^{3+}; 10, Tb^{3+}; 11, Dy^{3+}; 12, Ho^{3+}; 13, Er^{3+}; 14, Tm^{3+}; 15, Yb^{3+}; 16, Lu^{3+}; 17, β-Ala.

of neodymium(III) and gadolinium(III), which migrated after praseodymium(III) and europium(III), respectively, were not as good. These pairs have only slight differences in the stability constants of their HIBA complexes and in their effective mobilities.

Fig. 4 shows an isotachopherogram of the separation of lanthanides. The time required for an analysis was about 20 min.

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