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# Simultaneous separation of yttrium and lanthanide ions by isotachopheresis

Takeshi Hirokawa\*, Yoshio Hashimoto

*Applied Physics and Chemistry, Faculty of Engineering, Hiroshima University, Kagamiyama 1, Higashi-hiroshima 739, Japan*

## Abstract

An operational electrolyte system was developed for the isotachopheretic separation of fifteen rare-earth elements (yttrium and lanthanides except for Pm) by adding a helping complexing agent to an  $\alpha$ -hydroxyisobutyric acid (HIBA) electrolyte system. As a result of testing several helping agents such as malonic acid, malic acid, tartronic acid and glycolic acid, the optimized leading electrolyte was a 20-mM ammonia solution containing 2 mM malonic acid and 7.5 mM HIBA (pH 4.8, 2-ethylbutyric acid buffer). The terminator was a 20-mM carnitine hydrochloride. According to the stability constants of rare-earth–malonate complexes evaluated by isotachopheretic method, the successful separation was due to the smaller stability constants of Y–malonate complexes compared with those of the medium lanthanide elements to be separated.

*Keywords:* Complexation; Buffer composition; Yttrium; Lanthanides; Rare earth ions

## 1. Introduction

Although capillary electrophoresis is a convenient analytical method even for complex mixtures such as rare-earth ore digested samples, no operational electrolyte system has been reported for the simultaneous separation of all rare-earth elements (REEs) [1,2]. Since electrophoretic separation of REE ions depends on the difference of the effective mobilities of the ions forming labile complexes with counter ions, choice of the complex-forming counter ions is decisively important. The most significant agent is  $\alpha$ -hydroxyisobutyric acid (HIBA), which is widely used for the electrophoretic separation of lanthanide [1,3–5]. However, there is a problem that if Y is added to lanthanide, no separation is obtained for Dy and Y. From the analytical viewpoint, the electrolyte

system which enables simultaneous separation of Y and Dy is practically important [6], since both elements are frequently contained in the real RE ore sample [7].

We have reported in our previous paper that the addition of tartaric acid to the leading electrolyte containing HIBA as a main complex-forming agent enabled isotachopheretic (ITP) separation of  $Y^{3+}$  and  $Dy^{3+}$ . However, instead, the separation of  $Eu^{3+}$  and  $Gd^{3+}$  became impossible [1].

The aim of this study is to develop a leading electrolyte for the simultaneous separation of fifteen rare-earth ions (yttrium and fourteen lanthanide). Malic acid, tartronic acid, glycolic acid, malonic acid and ethylene glycol were examined as a helping complexing agent taking a hint that the difference between  $Y^{3+}$  and  $Dy^{3+}$  could be recognized by tartaric acid [1]. Consequently, simultaneous separation of fifteen rare-earth elements was achieved by

\*Corresponding author.

using malonic acid as the helping agent. In this paper we describe the optimization process of the developed electrolyte system and the evaluation of stability constants of malonate complexes to clarify the cause of separation.

## 2. Experimental

### 2.1. Samples

An equimolar mixture containing fifteen RE ions ( $Y^{3+}$ ,  $La^{3+}$ ,  $Ce^{3+}$ ,  $Pr^{3+}$ ,  $Nd^{3+}$ ,  $Sm^{3+}$ ,  $Eu^{3+}$ ,  $Gd^{3+}$ ,  $Tb^{3+}$ ,  $Dy^{3+}$ ,  $Ho^{3+}$ ,  $Er^{3+}$ ,  $Tm^{3+}$ ,  $Yb^{3+}$  and  $Lu^{3+}$ ) was used to assess the separability of the electrolyte system developed. The concentration of each component was 0.33 mM. For the evaluation of stability constants, several solutions containing one to three REEs were used. These test mixtures were prepared from stock solutions of the chlorides (5 mM), which were prepared by dissolving them in purified water.

### 2.2. Operational electrolyte system

The operational electrolyte systems used for separation optimization are summarized in Table 1. The leading electrolytes containing different concentration of the helping complexing agents were prepared by mixing the following three leading electrolytes. The first was a 20-mM ammonia solution, the second was a 20-mM ammonia solution containing 15 mM HIBA and the last was a 20-mM ammonia solution

Table 1  
Operational electrolyte systems used for separation optimization

Leading electrolyte	20 mM Ammonia water
Main complexing agent	7.5 mM $\alpha$ -Hydroxyisobutyric acid (HIBA)
Helping complexing agent	(1) Tartaric acid, 0.1–0.8 mM (2) Malic acid, 0.1–0.8 mM (3) Tartronic acid, 0.1–0.8 mM (4) Glycolic acid, 0.5–1.5 mM (5) Ethylene glycol, 0.1–1.5 mM (6) Malonic acid, 0.1–2.5 mM
pH buffer	2-Ethylbutyric acid
pH	4.80
Additive	0.1% HPC
Terminating electrolyte	20 mM Carnitinehydrochloride
Additive	0.1% HPC

Table 2  
Operational electrolyte systems used for the evaluation of stability constants

Leading electrolyte	(1) 5–25 mM Ammonia water (2) 20 mM Ammonia water
Complexing agent	(1) None (2) Malonic acid, 0–8.3 mM
pH buffer	2-Ethylbutyric acid
pH	4.80
Additive	0.1% HPC
Terminating electrolyte	20 mM Carnitinehydrochloride
Additive	0.1% HPC

containing 5 mM each helping complexing agent. The used agents were tartaric acid, malic acid, tartronic acid, glycolic acid, malonic acid and ethylene glycol. The pH of these solutions was adjusted to 4.80 by adding 2-ethyl-*n*-butyric acid. The terminating electrolyte was a 20-mM solution of carnitine hydrochloride. Table 2 summarizes the electrolyte systems used for the evaluation of stability constants of RE–2-ethylbutyrate complexes and RE–malonate complexes. All the electrolytes contained 0.1 % (w/w) hydroxypropylcellulose (HPC) to suppress electroendosmosis. A Horiba Model F7-AD expanded pH meter (Tokyo, Japan) was used for pH measurement.

### 2.3. Chemicals

The rare earth chlorides were of guaranteed grade (GR) obtained from Katayama Chemical (Osaka, Japan). A complexing agent HIBA (GR), and HPC (extra pure) were obtained from Tokyo Kasei (Tokyo, Japan). The viscosity of a 2% (w/w) HPC aqueous solution was 1000–4000 cP at 20°C according to the specification. Helping complexing agents tartaric acids (GR), malic acid (GR), tartronic acid (GR), ethyleneglycol (GR) and malonic acid (GR) were obtained from Katayama Kagaku (Tokyo, Japan). Tartronic acid (extra pure) was obtained from Nakarai Kagaku (Tokyo, Japan).

### 2.4. Isotachophoretic apparatus and $R_E$ measurement

The detector for ITP separation was a high frequency contactless conductivity detection

(HFCCD) system developed by Gas et al. [8]. The detection part was made of a fused-silica capillary (5 cm×0.32 mm I.D.), which was thermostatted to 25°C by a Peltier device. The detector was used in combination with the separation unit of a Labeco ZKI-001 isotachophoretic analyzer (Sp. Nova Ves, Slovakia). The separation column was a PTFE capillary (25 cm×0.32 mm I.D.). The amount of electric charge applied until the detection of terminating zone was 0.11 C in the blank run. The high voltage power supply was that for a Shimadzu IP-2A (Kyoto, Japan). The measurement was carried out at 25°C in a temperature controlled room.

The qualitative index used was  $R_E$ , which was defined as the ratio of the potential gradient ( $E/V$  cm<sup>-1</sup>) of the sample zones ( $E_S$ ) to that of the leading zone ( $E_L$ ) [9]. From isotachophoretic principles,  $R_E$  is equal to the ratio of the effective mobility of the leading ion ( $m_L$ ) to that of the sample ion ( $m_S$ ). When a conductivity detector is used, it is equal to the ratio of specific resistance of each zone. Since the HFCCD output signal showed a non-linear response to the specific resistance of the zones [8], the signal obtained was converted to the specific resistance using a fifth order polynomial expression of the output voltage. The expression was obtained using KCl solutions with known specific resistance. Li<sup>+</sup> was used as the internal standard to correct slight drift of the HFCCD signals. The simulated RE value was 2.008 when the concentration of the ammonia solution in the leading electrolyte was 20 mM. Reproducibility of thus obtained  $R_E$  values was very high and the error was less than 1%.

### 3. Results and discussion

#### 3.1. Simultaneous separation of fifteen lanthanide ions

As detailed in our previous paper [1], Y<sup>3+</sup> and Dy<sup>3+</sup> could not be separated to form a mixed zone when a leading electrolyte containing only HIBA as the complexing agent was used. The addition of tartaric acid as a helping complexing agent to the HIBA system enabled the separation of Y<sup>3+</sup> and Dy<sup>3+</sup>, however the separation of Eu<sup>3+</sup> and Gd<sup>3+</sup> deteriorated.

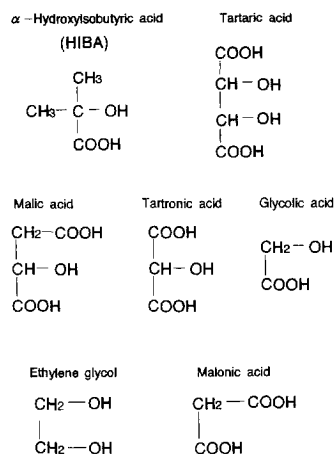


Fig. 1. Molecular structure of the complex-forming agents used.

Fig. 1 shows the molecular structures of HIBA and tartaric acid. The reason for the successful separation of lanthanides by HIBA is estimated to be that the bite distance of HIBA formed by two oxygen atoms from an OH group and a COOH group recognized the difference among lanthanide ions. In the case of tartaric acid, at least one of bite distances formed by several O–O pairs was probably effective for the separation of Y<sup>3+</sup> from Dy<sup>3+</sup>, but another bite distance might cause the deteriorated separation of Eu<sup>3+</sup> and Gd<sup>3+</sup>.

Several organic acids having a similar but simpler structure in comparison with tartaric acid were selected as the helping agents. They were malic acid, tartronic acid, glycolic acid, ethyleneglycol and malonic acid. Several leading electrolytes were prepared by adding these agents to the HIBA system and the separation behavior of Y<sup>3+</sup>–Dy<sup>3+</sup> pair and Eu<sup>3+</sup>–Gd<sup>3+</sup> pair was studied by using them.

Besides complexing agents, a pH buffer contained in a leading electrolyte also form complexes with lanthanide ions and may affect separation depending on the mobilities and the abundances of the formed complexes. Although acetic acid has been used as the pH buffer in our previous studies [1,4], 2-ethylbutyric acid was used in this study. The reason for the change was that the low separability of Eu<sup>3+</sup> and Gd<sup>3+</sup> might be caused partly by the fact that the stability constants of Eu(AcO)<sub>n</sub><sup>3-n</sup> complexes are larger than those of Gd(AcO)<sub>n</sub><sup>3-n</sup> complexes [10], contrary to the HIBA case [11]. In the present

system the main complexing agent HIBA will work better according to this estimation, since the stability constants of 2-ethylbutyrate complexes are probably smaller than those of acetate complexes due to large steric hindrance, as confirmed in the later section.

Fig. 2 shows the effective mobility difference between  $Y^{3+}$  and  $Dy^{3+}$  and between  $Eu^{3+}$  and  $Gd^{3+}$  ( $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ), which were observed varying the concentrations of the helping-complexing agents (tartaric acid, malic acid, ethyleneglycol and malonic acid). The differences were evaluated from the effective mobilities of the ions obtained from the observed RE values. Although the mobility difference between  $Y^{3+}$  and  $Dy^{3+}$  was not zero ( $0.15 \cdot 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) in the HIBA system, such degree of difference was not enough for the mutual separation. By adding tartaric acid and malonic acid to the HIBA system respectively, the mobility differ-

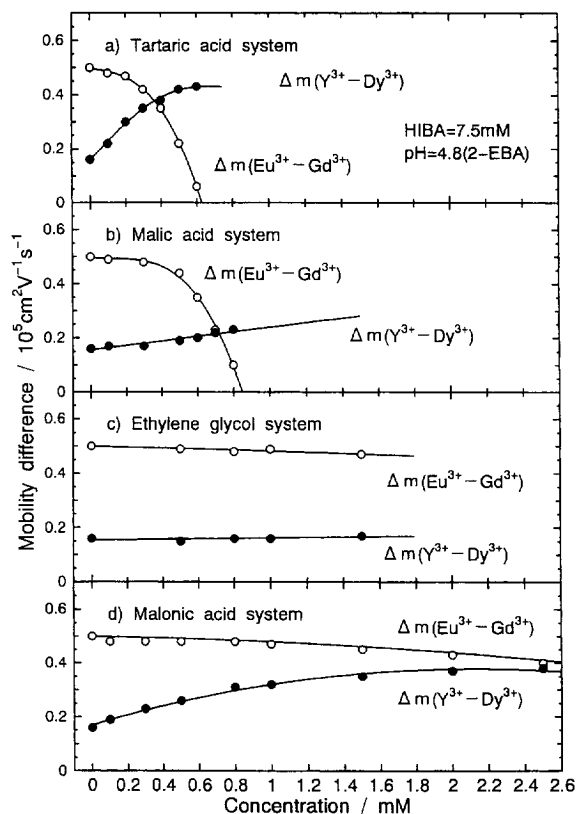


Fig. 2. Mobility difference between the  $Eu^{3+}$  and  $Gd^{3+}$  pair and  $Y^{3+}$  and  $Dy^{3+}$  vs. concentration of helping complexing agents. Electrolyte system is as shown in Table 1.

ence of  $Y^{3+}$  and  $Dy^{3+}$  was successfully increased to  $0.4 \cdot 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

On the other hand, the effective mobility differences between  $Eu^{3+}$  and  $Gd^{3+}$  decreased with increase in the concentration of added tartaric acid and malic acid. Although the zero mobility difference at the ITP steady state does not always mean that no separation occurs,  $Eu^{3+}$  and  $Gd^{3+}$  were forming a genuine mixed zone at least in the tartaric acid system according to our particle-induced X-ray emission (PIXE) investigation of the fractions [1]. Consequently, malonic acid was the most suitable helping complexing agent, since its addition to the HIBA system increased the mobility difference between  $Y^{3+}$  and  $Dy^{3+}$  without decreasing the difference between  $Eu^{3+}$  and  $Gd^{3+}$ .

The concentration of added malonic acid was optimized for the simultaneous separation of fifteen RE ions. Fig. 3 shows the effective mobilities of yttrium ion and medium and heavy lanthanide ions, when the concentration of HIBA was fixed at 7.5 mM and that of the added malonic acid was varied in the range 0–2.5 mM. In this range all RE ions migrated before the terminating zone. When the malonic acid concentration was 2 mM, the effective mobility differences of all neighboring RE ions were optimum for the separation.

Fig. 4 shows the isotachopherogram of fifteen RE ions obtained using the optimized operational electrolyte system. Obviously, they could be simultaneously separated. The injected amount was 1.65 nmol each.

### 3.2. Evaluation of stability constants for RE–2-ethylbutyrate complexes and RE–malonate complexes

The stability constants of RE–malonate complexes were obtained by using the isotachophoretic method [12] in order to clarify why the RE ions were successfully separated by using malonic acid as the helping complexing agent. For this purpose, the  $R_E$  values of the RE ions were measured varying the concentration of malonic acid in the leading electrolyte. Since 2-ethylbutyric acid was used as the pH buffer of the malonic acid system, the stability constants of 2-ethylbutyrate complexes were obtained at first.

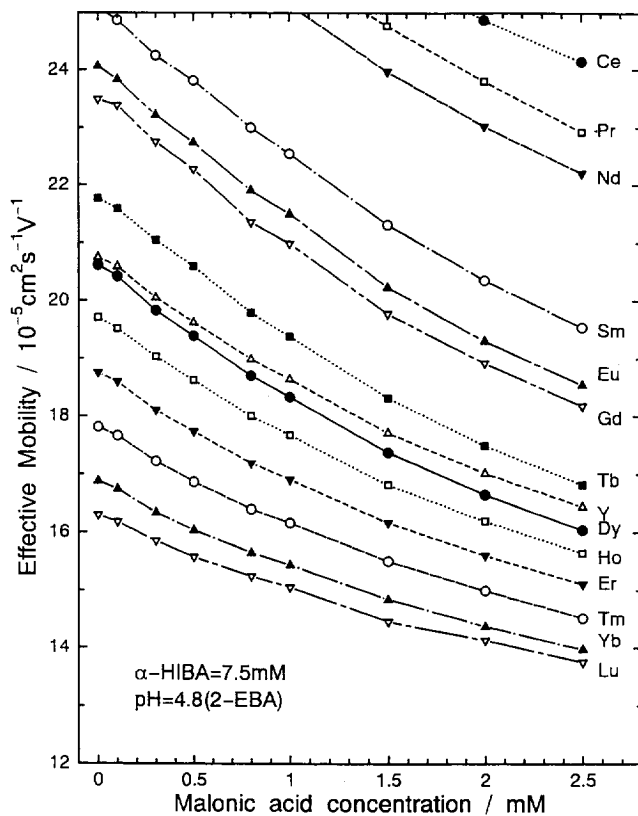


Fig. 3. Effective mobility of medium and heavy lanthanide and yttrium vs. concentration of malonic acid added to the HIBA system. Electrolyte system is as shown in Table 1.

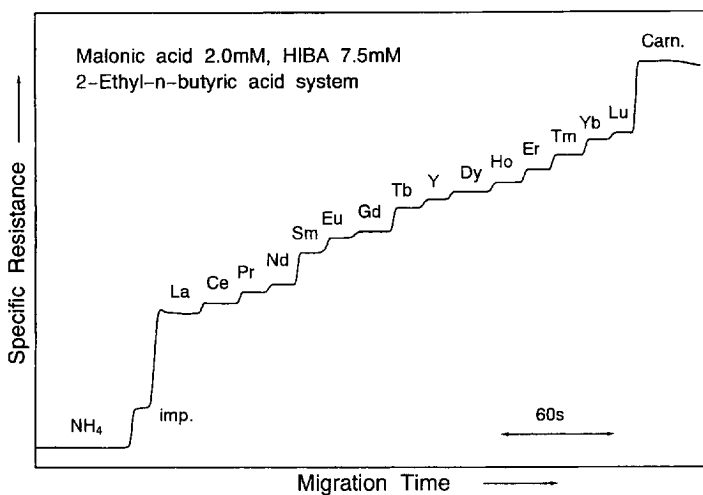


Fig. 4. Isotachopherogram of fifteen rare earth ions obtained by using the optimized electrolyte system. The sample amount was 5  $\mu$ l (0.33 mM). Migration current=40  $\mu$ A. See Table 1 for the details of the electrolyte system.

The operational electrolyte systems used are summarized in Table 2. For the 2-ethylbutyrate complexes, the concentration of the leading ammonium ion was varied in the range 5–25 mM, and 2-ethylbutyric acid was added to adjust the pH of the leading electrolyte to 4.8 (the 2-ethylbutyric acid system). The concentration of 2-ethylbutyric acid was in the range of 10–50 mM. On the other hand, for the malonate complexes, the concentration of the leading ion was kept constant as 20 mM, and the concentration of malonic acid was varied up to 8.3 mM. The pH of the leading electrolyte was adjusted to 4.8 by adding 2-ethylbutyric acid (the malonic acid system).

Fig. 5 shows the concentration dependence on the  $R_E$  values observed for  $\text{La}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Dy}^{3+}$  and  $\text{Lu}^{3+}$ . It should be noted that the large  $R_E$  value means small effective mobility. Obviously from Fig. 5, the concentration dependence on the  $R_E$  values was much greater for malonic acid, suggesting that the stability constants were much larger than those of the 2-ethylbutyrate complexes.

To analyze such dependence, the following

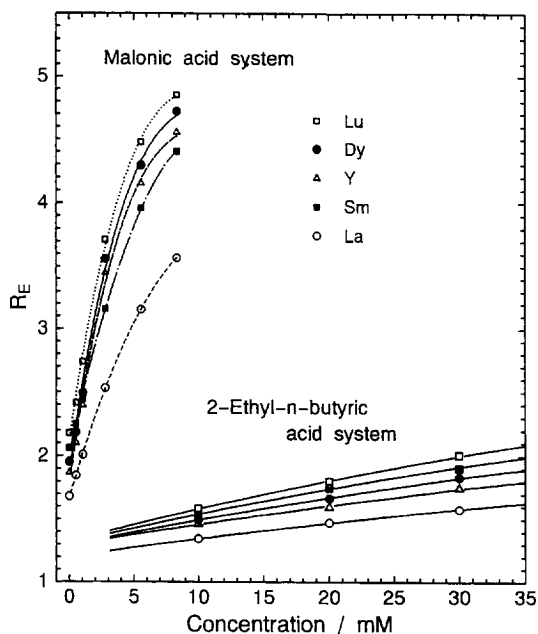
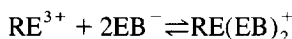
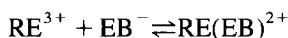


Fig. 5.  $R_E$  values of  $\text{La}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Dy}^{3+}$  and  $\text{Lu}^{3+}$  vs. concentration of 2-ethylbutyric acid and malonic acid.

equilibrium was assumed for the ITP steady state zone formed in 2-ethylbutyric acid system:



where EBH stands for 2-ethylbutyric acid. Although the maximum coordination number of the acetate complexes has been reported as four [10], that of the 2-ethylbutyrate complexes was assumed to be two. This was because the 2-ethylbutyrate complexes were more labile than those of acetate complexes as shown later and the abundance of the complexes with more than three ligands were negligibly small according to our preliminary calculations. The effective mobility of the rare-earth ions ( $m_{\text{RE}}$ ) coexisting with 2-ethylbutyrate counter ions can be expressed as follows:

$$\begin{aligned} m_{\text{RE}} &= \frac{m_{\text{RE}}[\text{RE}^{3+}] + m_{\text{REEB}}[\text{REEB}^{2+}] + m_{\text{RE}(\text{EB})_2}[\text{RE}(\text{EB})_2^+]}{[\text{RE}^{3+}] + [\text{REEB}^{2+}] + [\text{RE}(\text{EB})_2^+]} \\ &= \frac{m_{\text{RE}} + m_{\text{REEB}}\beta_1[\text{EB}^-] + m_{\text{RE}(\text{EB})_2}\beta_2[\text{EB}^-]^2}{1 + \beta_1[\text{EB}^-] + \beta_2[\text{EB}^-]^2} \end{aligned} \quad (1)$$

where the brackets show the concentration of the chemical species in them,  $m$  shows the mobility of the subscripted species and  $\beta$  the overall stability constants.

For the malonate complexes, the coordination number is known to be up to two both for a monoanion and a dianion [13–15]. In the present model, only the 1:1 complex of  $\text{RE}^{3+}$  and dianion was considered, since the abundance of the other complexes was estimated to be very small. Concerning the complexes with the monoanion, in addition to the fact that the stability constant was smaller than that of the dianion complex [13–15], the abundance of the monoanion itself was small under the operational condition of pH 4.8 (malonic acid,  $\text{p}K_1=2.847$  and  $\text{p}K_2=5.696$ ). Then, the equilibrium reaction in the steady state zone can be written as follows:

Table 3  
Observed and best-fitted  $R_E$  values in the 2-ethylbutyric acid system

Conc. (mM) <sup>a</sup>	Obsd. <sup>b</sup>	Calcd. <sup>c</sup>	Error <sup>d</sup>	Obsd.	Calcd.	Error	Obsd.	Calcd.	Error
	<b>La</b>			<b>Ce</b>			<b>Pr</b>		
10	1.344	1.339	0.37	1.407	1.400	0.50	1.462	1.444	1.23
20	1.475	1.478	-0.20	1.554	1.569	-0.97	1.613	1.629	-0.99
30	1.578	1.586	-0.51	1.701	1.696	0.29	1.757	1.767	-0.57
40	1.683	1.678	0.30	1.805	1.801	0.22	1.884	1.880	0.21
50	1.758	1.758	0.00	1.889	1.891	-0.11	1.983	1.976	0.35
	M.e. = 0.28%			M.e. = 0.42%			M.e. = 0.67%		
Conc. (mM)	<b>Nd</b>			<b>Sm</b>			<b>Eu</b>		
10	1.514	1.488	1.72	1.537	1.529	0.52	1.518	1.512	0.40
20	1.663	1.686	-1.38	1.748	1.752	-0.23	1.727	1.731	-0.23
30	1.816	1.831	-0.83	1.906	1.918	-0.63	1.892	1.898	-0.32
40	1.957	1.947	0.51	2.061	2.054	0.34	2.040	2.036	0.20
50	2.051	2.045	0.29	2.172	2.169	0.14	2.157	2.156	0.05
	M.e. = 0.95%			M.e. = 0.37%			M.e. = 0.24%		
Conc. (mM)	<b>Gd</b>			<b>Tb</b>			<b>Dy</b>		
10	1.505	1.491	0.93	1.483	1.467	1.08	1.494	1.486	0.54
20	1.682	1.699	-1.01	1.654	1.667	-0.79	1.667	1.678	-0.66
30	1.853	1.860	-0.38	1.821	1.828	-0.38	1.834	1.829	0.27
40	2.006	1.994	0.60	1.970	1.965	0.25	1.954	1.957	-0.15
50	2.109	2.111	-0.09	2.087	2.086	0.05	2.072	2.069	0.14
	M.e. = 0.60%			M.e. = 0.51%			M.e. = 0.35%		
Conc. (mM)	<b>Ho</b>			<b>Er</b>			<b>Tm</b>		
10	1.489	1.470	1.28	1.510	1.498	0.79	1.523	1.512	0.72
20	1.650	1.668	-1.09	1.689	1.703	-0.83	1.722	1.728	-0.35
30	1.821	1.828	-0.38	1.863	1.866	-0.16	1.893	1.901	-0.42
40	1.969	1.964	0.25	2.012	2.003	0.45	2.048	2.048	0.00
50	2.088	2.084	0.20	2.123	2.123	0.00	2.182	2.177	0.23
	M.e. = 0.64%			M.e. = 0.45%			M.e. = 0.34%		
Conc. (mM)	<b>Yb</b>			<b>Lu</b>			<b>Y</b>		
10	1.570	1.554	1.02	1.585	1.575	0.63	1.464	1.456	0.55
20	1.773	1.787	-0.79	1.803	1.818	-0.83	1.597	1.612	-0.94
30	1.964	1.972	-0.41	2.009	2.008	0.05	1.749	1.746	0.17
40	2.135	2.127	0.37	2.176	2.169	0.32	1.871	1.864	0.37
50	2.263	2.262	0.04	2.305	2.308	-0.13	1.968	1.970	-0.10
	M.e. = 0.53%			M.e. = 0.39%			M.e. = 0.43%		

<sup>a</sup> Concentration of 2-ethylbutyric acid in the leading electrolytes.

<sup>b</sup> Observed  $R_E$  values.

<sup>c</sup> Best-fitted  $R_E$  values.

<sup>d</sup> Percent error (obsd. - calcd.)/obsd. × 100.

Table 4  
Observed and best-fitted  $R_E$  values in the malonic acid system

Conc. (mM) <sup>a</sup>	Obsd. <sup>b</sup>	Calcd. <sup>c</sup>	Error <sup>d</sup>	Obsd.	Calcd.	Error	Obsd.	Calcd.	Error
	<u>La</u>			<u>Ce</u>			<u>Pr</u>		
0	1.683	1.678	0.30	1.805	1.801	0.22	1.884	1.880	0.21
0.52	1.846	1.752	5.09	1.981	1.887	4.75	2.054	1.975	3.85
1.04	2.009	1.924	4.23	2.168	2.070	4.52	2.225	2.167	2.61
2.78	2.529	2.556	-1.07	2.727	2.740	-0.48	2.806	2.847	-1.46
5.56	3.154	3.179	-0.79	3.360	3.418	-1.73	3.533	3.514	0.54
8.35	3.569	3.549	0.56	3.874	3.835	1.00	3.917	3.924	-0.18
	M.e. = 2.01%			M.e. = 2.12%			M.e. = 1.48%		
Conc. (mM)	<u>Nd</u>			<u>Sm</u>			<u>Eu</u>		
0	1.957	1.947	0.51	2.061	2.054	0.34	2.040	2.036	0.20
0.52	2.135	2.041	4.40	2.248	2.180	3.02	2.254	2.184	3.11
1.04	2.329	2.226	4.42	2.444	2.406	1.55	2.508	2.449	2.35
2.78	2.874	2.892	-0.63	3.159	3.195	-1.14	3.316	3.355	-1.18
5.56	3.565	3.602	-1.04	3.960	3.940	0.50	4.100	4.095	0.12
8.35	4.080	4.059	0.51	4.400	4.406	-0.14	4.546	4.537	0.20
	M.e. = 1.92%			M.e. = 1.12%			M.e. = 1.19%		
Conc. (mM)	<u>Gd</u>			<u>Tb</u>			<u>Dy</u>		
0	2.006	1.994	0.60	1.970	1.965	0.25	1.954	1.957	-0.15
0.52	2.226	2.141	3.82	2.194	2.134	2.73	2.186	2.125	2.79
1.04	2.477	2.411	2.66	2.480	2.458	0.89	2.492	2.460	1.28
2.78	3.286	3.337	-1.55	3.515	3.529	-0.40	3.561	3.581	-0.56
5.56	4.070	4.068	0.05	4.234	4.243	-0.21	4.292	4.301	-0.21
8.35	4.510	4.499	0.24	4.661	4.648	0.28	4.720	4.707	0.28
	M.e. = 1.49%			M.e. = 0.79%			M.e. = 0.88%		
Conc. (mM)	<u>Ho</u>			<u>Er</u>			<u>Tm</u>		
0	1.969	1.964	0.25	2.012	2.003	0.45	2.048	2.048	0.00
0.52	2.195	2.140	2.51	2.239	2.184	2.46	2.283	2.238	1.97
1.04	2.496	2.485	0.44	2.535	2.534	0.04	2.574	2.597	-0.89
2.78	3.572	3.591	-0.53	3.613	3.632	-0.53	3.671	3.682	-0.30
5.56	4.301	4.286	0.35	4.342	4.321	0.48	4.418	4.367	1.15
8.35	4.672	4.675	-0.06	4.698	4.708	-0.21	4.718	4.754	-0.76
	M.e. = 0.69%			M.e. = 0.70%			M.e. = 0.85%		
Conc. (mM)	<u>Yb</u>			<u>Lu</u>			<u>Y</u>		
0	2.135	2.127	0.37	2.176	2.169	0.32	1.871	1.864	0.37
0.52	2.370	2.321	2.07	2.413	2.366	1.95	2.101	2.022	3.76
1.04	2.674	2.670	0.15	2.739	2.715	0.88	2.396	2.351	1.88
2.78	3.700	3.722	-0.59	3.712	3.745	-0.89	3.449	3.473	-0.70
5.56	4.460	4.429	0.70	4.474	4.450	0.54	4.151	4.159	-0.19
8.35	4.821	4.837	-0.33	4.850	4.858	-0.16	4.553	4.537	0.35
	M.e. = 0.70%			M.e. = 0.79%			M.e. = 1.21%		

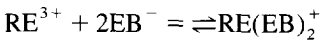
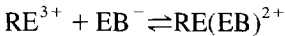
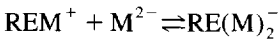
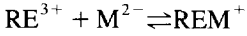
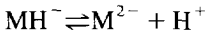
<sup>a</sup> Concentration of malonic acid in the leading electrolytes.

<sup>b</sup> Observed  $R_E$  values.

<sup>c</sup> Best-fitted  $R_E$  values.

<sup>d</sup> Percent error (obsd. - calcd.) / obsd. × 100.





where  $\text{MH}_2$  stands for malonic acid. The above equilibrium contained the 2-ethylbutyrate complexes, because 2-ethylbutyric acid was used as the pH buffer in the malonic acid system and it co-migrated with malonic acid.

The effective mobility of RE ions under the above equilibrium can be expressed by the following equation:

$$\begin{aligned} \bar{m}_{\text{RE}} &= \frac{m_{\text{RE}}[\text{RE}^{3+}] + m_{\text{REEB}}[\text{REEB}^{2-}] + m_{\text{RE}(\text{EB})_2}[\text{RE}(\text{EB})_2^+] + m_{\text{REM}}[\text{REM}^+]}{[\text{RE}^{3+}] + [\text{REEB}^{2-}] + [\text{RE}(\text{EB})_2^+] + [\text{REM}^+]} \\ &= \frac{m_{\text{RE}} + m_{\text{REEB}}\beta_1[\text{EB}^-] + m_{\text{RE}(\text{EB})_2}\beta_2[\text{EB}^-]^2 + m_{\text{REM}}\beta_{\text{REM}}[\text{M}^{2-}]}{1 + \beta_1[\text{EB}^-] + \beta_2[\text{EB}^-]^2 + \beta_{\text{REM}}[\text{M}^{2-}]} \quad (2) \end{aligned}$$

The mobilities appearing in Eqs. (1) and (2) ( $m$ ) are necessary in the evaluation of the stability constants. In case of the 2-ethylbutyrate complexes, estimated values using formula mass of the complex ions were used as reported for the acetate complexes [4].

The stability constants were determined iteratively by the least-squares method which minimizes the following quantity:

$$\begin{aligned} S &= \sum (R_{\text{E,obs}} - R_{\text{E,cal}})^2 \\ &= \sum (R_{\text{E,obs}} - \bar{m}_{\text{L,cal}} / \bar{m}_{\text{RE,cal}})^2 \end{aligned}$$

where  $m_{\text{L,cal}}$  is equal to the effective mobility calculated for the leading ion. Its typical value was  $70.7 \cdot 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  depending on the ionic strength of the leading electrolyte.

Table 3 shows the  $R_{\text{E}}$  values of the rare-earth ions observed for the 2-ethylbutyric acid system and the best-fitted RE values. Table 4 shows those for the

malonic acid system. In both cases, good agreement was obtained between the observed and best-fitted values confirming validity of the used assumptions. The evaluated stability constants and the mobilities (25°C, ionic strength=0) are summarized in Table 5. The stability constants are also shown in Fig. 6 together with those of acetate complexes [4,10]. Simultaneous determination of the stability constants and the mobilities for the 2-ethylbutyrate complexes was impossible because the dispersions of the evaluated constants were too large due to small abundance of the complexes. On the other hand, in case of the malonate complexes, both mobilities and stability constants could be determined simultaneously. This was because the complexes were sufficiently abundant, when the concentration of malonic acid is large.

Obviously from Fig. 6, the stability constants for the rare-earth–2-ethylbutyrate complexes (1:1) were smaller than those of acetate complexes. This was as expected from the fact that 2-ethylbutyric acid was

Table 5  
Mobilities and stability constants of RE–2-ethyl-*n*-butyrate complexes and RE–malonate complexes (25°C, ionic strength=0)

	2-Ethyl- <i>n</i> -butyric acid				Malonic acid		Lit.: log $\beta$ [15]
	$m_1^a$	$m_2^b$	log $\beta_1^c$	log $\beta_2^d$	$m_1^e$	log $\beta_1^f$	
La	39.3	17.0	2.07	3.43	16.1	4.52	4.01
Ce	39.2	17.0	2.27	3.65	14.9	4.62	4.21
Pr	39.2	17.0	2.36	3.79	15.0	4.70	4.30
Nd	39.0	16.9	2.45	3.87	14.1	4.72	4.33
Sm	38.6	16.8	2.47	4.09	13.6	4.85	4.63
Eu	38.5	16.8	2.39	4.07	13.7	4.91	4.72
Gd	38.2	16.7	2.32	3.99	13.9	4.88	4.81
Tb	38.1	16.7	2.19	3.97	13.9	4.94	4.84
Y	42.8	18.0	1.90	3.86	14.3	4.87	–
Dy	38.0	16.6	2.22	3.88	13.8	4.97	4.97
Ho	37.8	16.6	2.19	3.95	14.1	4.98	–
Er	37.7	16.6	2.24	3.97	14.1	5.01	4.89
Tm	37.6	16.5	2.23	4.05	14.0	5.02	4.91
Yb	37.4	16.5	2.31	4.14	13.6	5.03	4.91
Lu	37.3	16.4	2.33	4.19	13.6	5.04	4.84

<sup>a</sup> Mobility of 1:1 complex.

<sup>b</sup> Mobility of 1:2 complex.

<sup>c</sup> Log  $\beta$  of 1:1 complex.

<sup>d</sup> Log  $\beta$  of 1:2 complex.

<sup>e</sup> Mobility of 1:1 complex.

<sup>f</sup> log  $\beta$  of 1:1 complex.

<sup>a</sup> and <sup>b</sup> are estimated values. <sup>c</sup>–<sup>e</sup> are evaluated values.

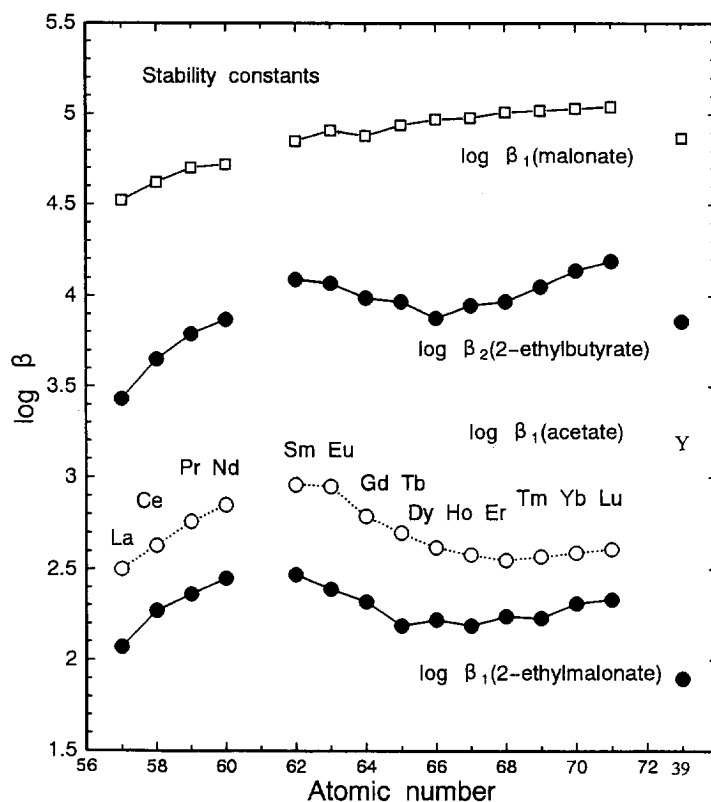


Fig. 6. Stability constants evaluated for RE–2-ethylmalonate complexes (1:1 and 1:2) and malonate complexes (1:1) and stability constants reported for acetate complexes (1:1) [10].

more bulky than acetic acid. The stability constants of malonate complexes were much greater than those of acetate complexes and 2-ethylbutyrate complexes. The values increased gradually with the increase of the atomic number as shown in Fig. 6. This observation agreed well with the values shown in Table 3 reported by Degischer et al. [15], although they were obtained at different ionic strength.

Although the stability constants of the malonate complexes were similar among medium lanthanide, they were significantly smaller than that of the Y–malonate complex. That is, decrement of the effective mobility of both  $\text{Dy}^{3+}$  and  $\text{Tb}^{3+}$  was larger than that of  $\text{Y}^{3+}$  when malonic acid was added to the HIBA system. This is the cause of successful separation of  $\text{Y}^{3+}$  from  $\text{Dy}^{3+}$  and  $\text{Tb}^{3+}$ .

Some RE ore samples were isotachophoretically analyzed by using the operational electrolyte system

developed in the present work. It was confirmed that ITP was very convenient analytical method for the RE ore sample. Its cost performance is probably the greatest among many analytical methods. However, as discussed in [6], it should be noted that separation of minor components from major components depends on the sample amount and the electric charge given in the ITP process, even if the developed electrolyte system is used. The analytical results will be published elsewhere in due course.

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