COMPLEX-FORMING EQUILIBRIA IN ISOTACHOPHORESIS

VI. SIMULATION OF ISOTACHOPHORETIC EQUILIBRIA OF LANTHANOIDS AND DETERMINATION OF MOBILITIES AND STABILITY CONSTANTS OF ACETATE AND α-HYDROXYISOBUTYRATE COMPLEXES

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SUMMARY

     The isotachophoretic separation of fourteen lanthanoids (Ln) was studied using three different electrolyte systems, *viz.*, acetic acid (Ac), α-hydroxyisobutyric acid (HIB) and their mixture, as the complexing agent. A computational procedure based on the least-squares technique was used for the determination of the absolute mobilities of Ln–Ac, Ln–HIB and Ln(HIB)Ac complexes from the qualitative index R_E. The stability constants of Ln(HIB)Ac were also determined. Using the determined constants, the isotachophoretic separation of lanthanoids could be explained by the differences in the effective mobilities accompanied by the different abundances of multi-coordinated complexes.

INTRODUCTION

     For the chromatographic separation of lanthanoids (Ln), several complexing agents such as EDTA and its derivatives, lactic acid and α-hydroxyisobutyric acid have been used. It is well known that the separability depends on the stability constants of the complexes formed. However, the mechanism of the separation has not yet been described quantitatively. In addition to the complicated equilibria involved in complex formation, the essential reason may be the difficulty of quantification of adsorption–desorption phenomena between the samples and the column packings.
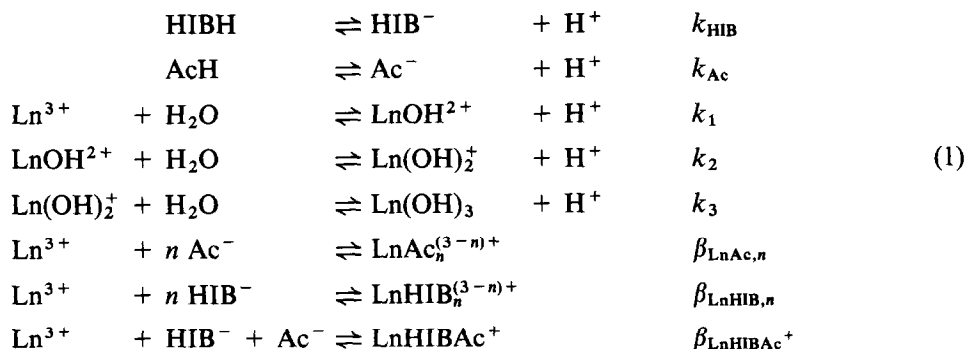
     Nukatsuka *et al.*[1] reported the isotachophoretic separation of Ln using α-hydroxyisobutyric acid (HIB) as the complexing agent, which was diluted with weakly interacting acetic acid (Ac). As no packings are utilized in isotachophoretic separations, the electrolyte system can be treated as a free solution and the separation behaviour can be explained quantitatively by the differences in the effective mobilities using a computational method as described previously[2,3].

     In this paper, complex-forming equilibria of isotachophoretically separated lanthanoids were simulated to clarify how the effective mobilities of lanthanoids differ

sufficiently for separation when HIB and Ac are used simultaneously as complexing agents. To simulate the isotachophoretic equilibria, absolute mobilities, acid dissociation constants and stability constants of lanthanoids and their complexes are necessary. Fortunately, some of these values have been reported by other workers: Spedding and co-workers[4,5] studied the absolute mobilities of Ln^{3+} extensively, Sonesson[6] determined the stability constants of multi-coordinated acetate complexes (1:1–1:4) and Powell[7], Devine[8] and Suzuki and Mikado[9] determined the stability constants of HIB complexes (1:1–1:4). However, the mobilities of complex ions are not available. To determine these mobilities, isotachophoretic qualitative indices, R_E, of Ln except for Pm were obtained using three different electrolyte systems, *viz.*, (1) acetic acid, (2) HIB and (3) their mixture, as the complexing agent. In electrolyte system (3), mixed ligand complexes such as $LnHIBAc^+$ may be formed among Ln, Ac and HIB. The stability constants of these complexes and the mobilities of $LnHIBAc^+$ could not be found in the literature. A computational procedure was applied to the observed R_E values in order to obtain the mobilities and stability constants. Using the values obtained and reported values, the isotachophoretic equilibria of Ln–Ac, Ln–HIB and the mixed ligand systems are discussed theoretically.

THEORETICAL

The computational procedure for the analysis of the formation of multi-coordinated complexes has already been reported[3]. The complex-forming equilibria in the lanthanoid zone can be written as follows when the electrolyte systems contain Ac^- and HIB^- simultaneously forming multi-coordinate complexes (coordination number 1–4):

$$
\begin{array}{llll}
\text{HIBH} & \rightleftharpoons \text{HIB}^- & + \text{H}^+ & k_{\text{HIB}} \\
\text{AcH} & \rightleftharpoons \text{Ac}^- & + \text{H}^+ & k_{\text{Ac}} \\
\text{Ln}^{3+} + \text{H}_2\text{O} & \rightleftharpoons \text{LnOH}^{2+} & + \text{H}^+ & k_1 \\
\text{LnOH}^{2+} + \text{H}_2\text{O} & \rightleftharpoons \text{Ln(OH)}_2^+ & + \text{H}^+ & k_2 \\
\text{Ln(OH)}_2^+ + \text{H}_2\text{O} & \rightleftharpoons \text{Ln(OH)}_3 & + \text{H}^+ & k_3 \\
\text{Ln}^{3+} + n\,\text{Ac}^- & \rightleftharpoons \text{LnAc}_n^{(3-n)+} & & \beta_{\text{LnAc},n} \\
\text{Ln}^{3+} + n\,\text{HIB}^- & \rightleftharpoons \text{LnHIB}_n^{(3-n)+} & & \beta_{\text{LnHIB},n} \\
\text{Ln}^{3+} + \text{HIB}^- + \text{Ac}^- & \rightleftharpoons \text{LnHIBAc}^+ & & \beta_{\text{LnHIBAc}^+}
\end{array}
\tag{1}
$$

where k_{Ac} and k_{HIB} are the acid dissociation constants of Ac and HIB, k_1, k_2 and k_3 are those of Ln, $\beta_{\text{Ac},1}$–$\beta_{\text{Ac},4}$ are the overall stability constants of complexes of $LnAc^{2+}$–$LnAc_4^-$ and $\beta_{\text{HIB},1}$–$\beta_{\text{HIB},4}$ are those of $LnHIB^{2+}$–$LnHIB_4^-$. The formation of the mixed ligand complex of the form of $LnHIBAc^+$ was also considered. The other mixed ligand complexes such as $LnHIB_2Ac$ and $LnHIBAc_2$ were not taken into account, as their abundances under the electrolyte conditions used may be negligibly small, according to preliminary simulations. This will be discussed in a later section. The effective mobility of Ln^{3+} ($\bar{m}_{Ln}$) coexisting with Ac^- and HIB^- in the

steady state can be expressed using the mobilities, m, and the concentrations, C, of the lanthanoid species in the zone:

$$\bar{m}_{Ln} = \left(\sum_{i=0}^{2} m_{Ln^{3-i}} C_{Ln_i^{3-i}} + \sum_{j=1}^{n} m_{LnAc_j^{3-j}} C_{LnAc_j^{3-j}} + \sum_{j=1}^{n} m_{LnHIB_j^{3-j}} C_{LnHIB_j^{3-j}} + \right.$$

$$\left. + m_{LnHIBAc^+} C_{LnHIBAc^+} \right) \Big/ \left(C_{Ln}^t + C_{LnAc}^t + C_{LnHIB}^t + C_{LnHIBAc^+} \right) \qquad (2)$$

where C_{Ln}^t, C_{LnAc}^t, C_{LnHIB}^t and $C_{LnHIBAc^+}$ are the total concentrations of non-complexing Ln, $C_{Ln^{3+}} + C_{LnOH^{2+}} + C_{Ln(OH)_2^+} + C_{Ln(OH)_3}$, and the formed complexes, respectively. C_{LnAc}^t, C_{LnHIB}^t and $C_{LnHIBAc^+}$ can be expressed using overall stability constants of the complexes and the concentrations of Ln^{3+} and the ligands Ac^- and HIB^- as follows:

$$C_{LnAc}^t = \sum_{j=1}^{n} \beta_{LnAc,j} C_{Ln^{3+}} C_{Ac^-}^j \qquad (3)$$

$$C_{LnHIB}^t = \sum_{j=1}^{n} \beta_{LnHIB,j} C_{Ln^{3+}} C_{HIB^-}^j \qquad (4)$$

$$C_{LnHIBAc^+} = \beta_{LnHIBAc^+} C_{Ln^{3+}} C_{HIB^-} C_{Ac^-} \qquad (5)$$

Inserting eqn. 3 into eqn. 2, using dissociation constants to express concentrations of Ln species and eliminating $C_{Ln^{3+}}$ gives the following equation for $\bar{m}_{Ln}$:

$$\bar{m}_{Ln} = \frac{\left\{ \begin{array}{l} m_{Ln^{3+}} + k_1/C_H\, m_{LnOH^{2+}} + k_1 k_2/C_H^2 m_{Ln(OH)_2^+} + \\[2mm] + \sum_{j=1}^{n} m_{LnAc_j^{3-j}} \beta_{LnAc,j} C_{Ac^-}^j + \sum_{j=1}^{n} m_{LnHIB_j^{3-j}} \beta_{LnHIB,j} C_{HIB^-}^j + \\[2mm] + m_{LnHIBAc^+} \beta_{LnHIBAc^+} C_{Ac^-} C_{HIB^-} \end{array} \right\}}{\left\{ \begin{array}{l} 1 + k_1/C_H + k_1 k_2/C_H^2 + k_1 k_2 k_3/C_H^3 + \sum_{j=1}^{n} \beta_{LnAc,j} C_{Ac^-}^j + \\[2mm] + \sum_{j=1}^{n} \beta_{LnHIB,j} C_{HIB^-}^j + \beta_{LnHIBAc^+} C_{Ac^-} C_{HIB^-} \end{array} \right\}} \qquad (6)$$

Apparently from eqn. 6, the effective mobilities of Ln decrease with an increase in the stability constants and Ac^- and HIB^- concentrations or the total concentrations of HIB and Ac and the pH of the Ln zones. The total concentrations were controlled by the total concentrations of HIB and Ac in the leading zone and mass balance equations[2,3]. The effective mobility can be obtained after iterative calculation to fulfill the isotachophoretic conditions[2,3]. The qualitative index R_E can be expressed as follows:

$$R_E = \bar{m}_L/\bar{m}_{Ln} = \kappa_L/\kappa_{Ln} = E_{Ln}/E_L \tag{7}$$

where $\bar{m}_L$ and $\bar{m}_{Ln}$ are the effective mobilities of the leading and lanthanoid ions, κ_L and κ_{Ln} the specific conductivities of the zones and E_L and E_{Ln} the potential gradients. Analysis of the dependence of R_E on the total concentrations of Ac and HIB in the leading zone (practically the leading concentration at constant pH) gives the mobilities and stability constants of the complex ions.

EXPERIMENTAL

Stock solutions of Ln(III) ions were prepared by dissolving the chlorides (0.01 M) in deionized water. Lanthanoid chlorides were purchased from Mitzuwa Chemicals. Other chemicals used to prepare the leading and terminating electrolytes were purchased from Wako. All chemicals were of guaranteed grade.

The isotachopherograms were obtained by the use of a Shimadzu IP-1B isotachophoretic analyser equipped with a home-made potential gradient detector. The separating tube was 40 cm × 0.5 mm I.D. The driving currents applied were in the range 50–100 μA. All experiments were carried out at 25°C.

For precise measurement of R_E values, an internal standard such as Ba^{2+} or Na^+, and terminating ε-aminocaproic acid (ε-AMC) was used to correct the asymmetric potential of a potential gradient detector[10].

A Horiba F-7ss expanded-scale pH meter was used to measure the pH of the electrolytes.

The leading electrolyte systems used are summarized in Table I together with the calculated concentrations and effective mobilities of the leading zone constituents. The leading electrolytes Nos. 1–8 in Table I were 5.2–25.9 mM KOH solutions buffered by adding acetic acid at $pH_L \approx 4.8$ (pH_L = pH of leading electrolyte). Triton X-100 (reagent grade) surfactant was added to the leading electrolytes at a level of 0.2%. pH_L was determined taking into account the buffering ability of acetic acid ($pK_a = 4.756$).

The R_E values of fourteen lanthanoids were measured under the electrolyte conditions. Two examples of the isotachopherograms of Ba, La, Ce, Pr, Nd and Sm are shown in Fig. 1. It can be seen that the light lanthanoids could be separated by complex formation with acetic acid, but the mixture containing heavier lanthanoids could not be separated. Such a separation behaviour can be understood from Fig. 2, which summarizes the observed R_E values. Apparently even at the high concentrations of K^+ or Ac^-, the R_E values of Sm–Lu were similar, suggesting the difficulty of separation.

The leading electrolytes Nos. 9–13 in Table I were 6.4–10.6 mM KOH solu-

TABLE I

LEADING ELECTROLYTE CONDITIONS AND CALCULATED CONCENTRATIONS AND EFFECTIVE MOBILITIES OF CONSTITUENTS

PH_L = pH of leading electrolyte. C_L^t = Total concentration (mM) of leading ion (K$^+$). $\bar{m}_L$ = Effective mobility (cm^2 V^{-1} sec^{-1}) of leading ion × 10^5. $C_{B,L}^t$ = Total concentration (mM) of buffer ion. The buffer ions are acetate for systems 1–8 and 14–17 and α-hydroxyisobutyrate (HIB) for systems 9–13. $\bar{m}_{B,L}$ = Effective mobility (cm^2 V^{-1} sec^{-1}) of buffer ion × 10^5. $C_{A,L}^t$ = Total concentration (mM) of additive ion (HIB). $\bar{m}_{A,L}$ = Effective mobility (cm^2 V^{-1} sec^{-1}) of additive ion × 10^5. Negative signs of mobilities indicate counter direction of sample migration.

System	pH_L	C_L^t	$\bar{m}_L$	$C_{B,L}^t$	$\bar{m}_{B,L}$	$C_{A,L}^t$	$\bar{m}_{A,L}$
1	4.80	5.18	72.5	9.54	−21.6		
2	4.80	8.32	71.7	15.2	−21.4		
3	4.80	9.85	71.4	17.9	−21.4		
4	4.80	12.42	71.0	22.5	−21.3		
5	4.80	14.98	70.6	27.0	−21.2		
6	4.79	17.60	70.2	31.9	−20.9		
7	4.79	20.70	69.8	37.3	−20.8		
8	4.80	25.88	69.2	45.9	−20.8		
9	4.65	6.35	72.7	7.60	−18.1		
10	4.69	7.41	72.6	8.73	−19.0		
11	4.70	8.47	72.4	9.93	−19.2		
12	4.68	9.53	72.2	11.2	−18.7		
13	4.73	10.59	72.1	12.3	−19.8		
14	4.77	9.85	72.2	16.8	−20.7	1.00	−26.3
15	4.80	9.85	72.3	14.7	−21.4	2.00	−26.5
16	4.78	9.85	72.3	13.1	−21.4	3.00	−26.5
17	4.78	9.85	72.2	11.8	−20.9	4.00	−26.4

tions. pH$_L$ was adjusted to *ca.* 4.7 by adding HIB. At this pH a good buffering ability cannot be obtained (pK_a of HIB = 3.971). However, this pH$_L$ was preferable in comparison with the electrolyte systems using acetic acid. The electrolyte systems were used for the separation of La, Ce, Pr, Nd, Sm, Eu and Gd. The heavier lanthanoids could not be detected when ε-AMC was used as the terminator. Fig. 3 shows
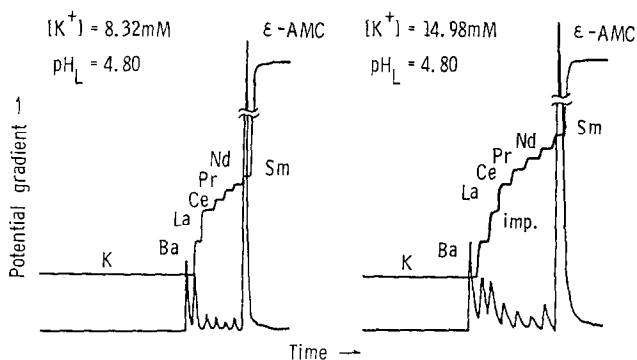

Fig. 1. Observed isotachopherograms of Ba^{2+}, Na$^+$, La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+} coexisting with acetic acid at different leading ion concentrations. The leading ion is K$^+$ and the terminating ion is ε-aminocaproate (ε-AMC). imp = Impurity in the electrolyte system.
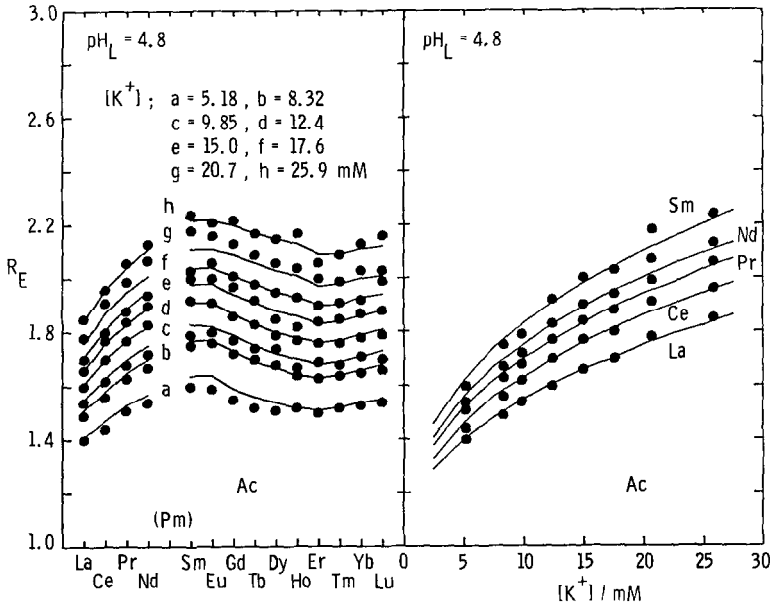
Fig. 2. Observed R_E values (●) of fourteen lanthanoids coexisting with acetic acid at $pH_L \approx 4.8$. The curves show the dependence on K^+ concentration of simulated R_E values using best-fitted mobility.

Fig. 3. Observed isotachopherograms of Ba^{2+}, Na^+, La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+} coexisting with α-hydroxyisobutyric acid at different leading ion concentrations. The leading ion is K^+ and the terminating ion is ε-aminocaproate (ε-AMC).
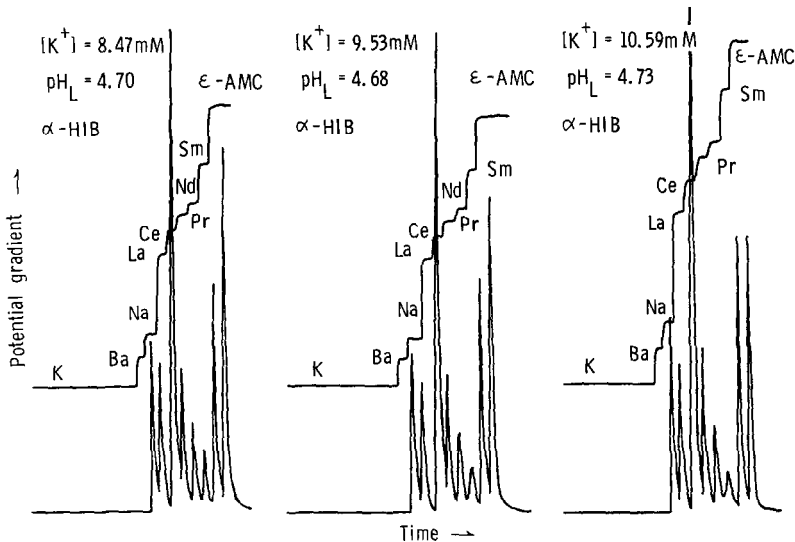
three examples of the isotachopherograms observed for Ba, Na, La, Ce, Pr, Nd and Sm. Fig. 4 shows the dependence of K^+ concentration on the observed R_E values. On comparing Fig. 4 with Fig. 2, it is apparent that the step heights of the lanthanoids increased significantly, suggesting a stronger interaction of HIB with lanthanoids.

The leading electrolytes Nos. 14–17 in Table I were 9.85 mM KOH solutions containing HIB in the range 1–4 mM, and the pH$_L$ was adjusted to ca. 4.8 by adding acetic acid. Four different electrolytes (Nos. 14–17) were used and the R_E values of fourteen lanthanoids were measured. Fig. 5 shows two examples of isotachopherograms of Na and fourteen lanthanoids. When the leading electrolyte containing 1 mM HIB was used, the separation behaviour of Ln was strongly effected by the formation of Ln–Ac complexes and the separation was not improved, except that heavy lathanoids were separated from the mixed zone of Gd, Eu, Tb, Dy and Ho. The mixed zone could be dissolved by increasing the HIB concentration. When the electrolyte containing 4 mM HIB was used, the fourteen lanthanoids could be completely separated. Fig. 6 summarizes the observed R_E values varying HIB concentration in the range of 0–4 mM. It is apparent that the separation of Eu and Gd was the most difficult.

It should be noted that the K^+ and HIB concentrations under the present conditions were low in comparison with the earlier reported conditions[1], K^+ = 27 mM, total HIB = 15 mM and pH$_L$ = 4.92. Under these conditions the mixed ligand complexes LnHIB$_2$Ac or LnHIBAc$_2$ could not be neglected.
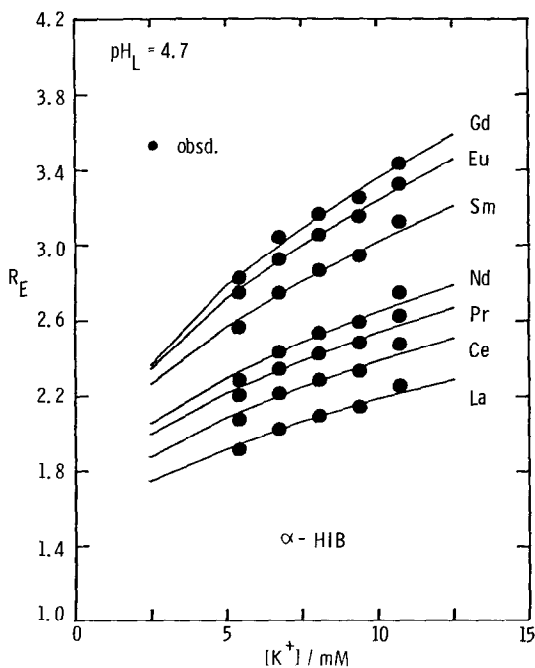
Fig. 4. Observed R_E values ($\bullet$) of La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+} and Gd^{3+} coexisting with α-hydroxyisobutyric acid at pH$_L$ $\approx$ 4.7. The curves show the dependence on K^+ concentration of simulated R_E values using best-fitted mobility.
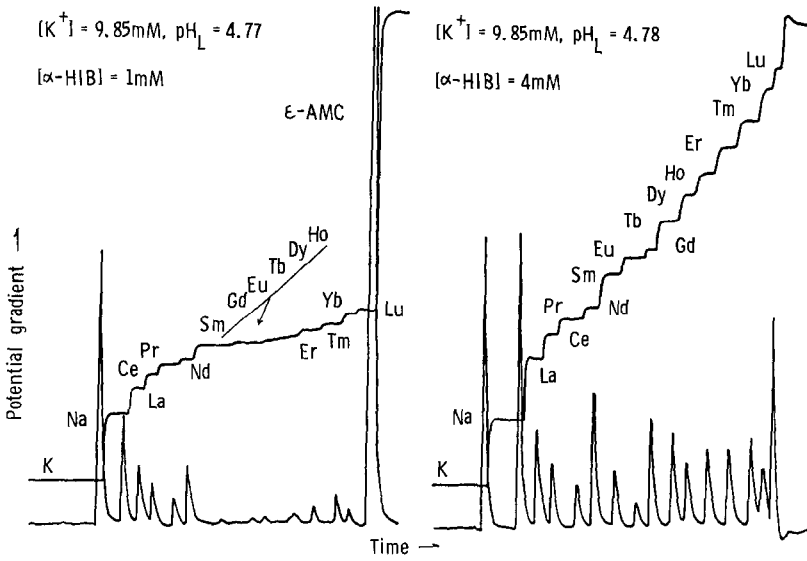
Fig. 5. Observed isotachopherograms of Na$^+$ and fourteen lanthanoids coexisting with acetic acid and α-hydroxyisobutyric acid (1 and 4 mM). The leading ion is K$^+$ and the terminating ion is ε-aminocaproate (ε-AMC).
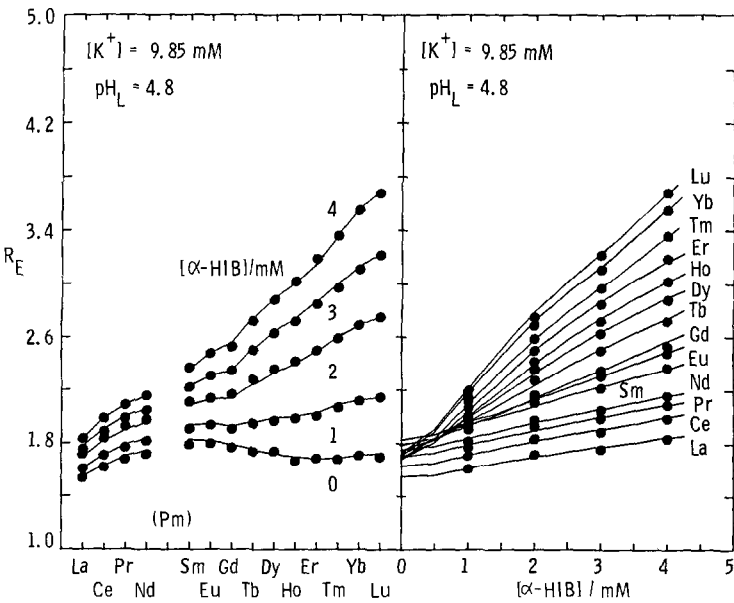
Fig. 6. Observed R_E values (●) of fourteen lanthanoids coexisting with acetic acid and α-hydroxyisobutyric acid at pH$_L$ = 4.8. The concentrations of HIB are in the range 0–4 mM. The curves show the dependence on K$^+$ concentration of simulated R_E values using best-fitted mobility.

RESULTS AND DISCUSSION

The evaluation of the mobilities and stability constants of Ln complexes and the data processing were carried out with a SORD M223 microcomputer and an NEC MS-120 minicomputer.

Table II shows the physico-chemical constants of the electrolyte systems. They were taken from the literature[11], except for the mobilities of HIB and AMC, which were determined by the isotachophoretic method.

Table III shows the absolute mobilities of Ln and the stability constants of Ln–Ac and Ln–HIB complexes at an ionic strength of zero.

The stability constants of $LnAc_4^-$ are not shown, as the abundances of the complex ions were negligibly small according to preliminary simulations under the

TABLE II

MOBILITIES AND ACID DISSOCIATION CONSTANTS OF CONSTITUENTS[11] OF LEADING AND TERMINATING ELECTROLYTES (25°C).

m_0 = Absolute mobilities (cm^2 V^{-1} sec^{-1}) $\times$ 10^5. pK_a = Thermodynamic acid dissociation constant.

Cation	m_0	pK_a	Anion	m_0	pK_a
K$^+$	76.2	—	α-Hydroxyisobutyric acid	33.5*	3.971
ε-Aminocaproic acid	28.8*	4.373	Acetic acid	42.4	4.756

* Determined by our isotachophoretic method.

TABLE III

ABSOLUTE MOBILITIES OF LANTHANOIDS (Ln)[4,5] AND THERMODYNAMIC STABILITY CONSTANTS OF Ln–ACETATE (Ac)[6] AND Ln–α-HYDROXYISOBUTYRATE (HIB) COMPLEXES[8]

m_0 = Absolute mobilities (cm^2 V^{-1} sec^{-1}) of Ln^{3+} $\times$ 10^5. Log β_n = Overall stability constants of n-coordinated complexes.

Ln^{3+}	m_0	Ln–Ac complexes			Ln–HIB complexes			
		Logβ_1	Logβ_2	Logβ_3	Logβ_1	Logβ_2	Logβ_3	Logβ_4
La^{3+}	72.3	2.50	3.96	4.99	2.99	5.15	6.20	—
Ce^{3+}	72.4	2.63	4.26	5.14	3.09	5.44	6.36	—
Pr^{3+}	72.2	2.76	4.47	5.28	3.24	5.56	6.79	—
Nd^{3+}	72.0	2.85	4.61	5.46	3.29	5.66	7.08	—
Sm^{3+}	71.1	2.96	4.79	5.86	3.42	6.00	7.64	8.83*
Eu^{3+}	70.3	2.95	4.77	5.86	3.51	6.19	8.11	8.56*
Gd^{3+}	69.8	2.79	4.65	5.72	3.53	6.25	8.21	9.34
Tb^{3+}	69.0	2.70	4.50	5.76	3.62	6.47	8.51	9.69
Dy^{3+}	68.0	2.62	4.34	5.80	3.66	6.55	8.60	9.82*
Ho^{3+}	68.7	2.58	4.31	5.76	3.73	6.71	8.84	9.37
Er^{3+}	68.3	2.55	4.26	5.66	3.78	6.87	9.06	10.49
Tm^{3+}	67.8	2.57	4.29	5.60	3.83	6.94	9.20	10.40
Yb^{3+}	67.5	2.59	4.37	5.55	3.89	7.07	9.35	10.49
Lu^{3+}	67.0	2.61	4.41	5.56	3.94	7.17	9.56	11.06

* Ref. 9.

present electrolyte conditions. In the following simulations, therefore, the formation of $LnAc_4^-$ was not considered. The stability constants in Table III were evaluated by applying activity coefficients calculated by applying the Debeye–Hückel equation to the reported stability constants at a constant ionic strength of 0.1 or 1.0 M[6,8,9]. In isotachophoresis the ionic strength differs among the separated zones and the value is usually less than 0.01 M. Therefore, the reported stability constants, as such, could not be used in simulation. In simulation the values in Table III were again corrected taking into account the ionic strength of the separated zones.

The pK_a values of the Ln used were $pK_1 = 6$, $pK_2 = 7$ and $pK_3 = 8$, considering the reported values of pK_1 of Ln^{3+} in the range 5.6–9.0 (ref. 12). The precise values are preferable but are not necessary for the present purpose, as almost all of the non-complexing lanthanoids may exist as trivalent ions under the present experimental conditions of $pH_L = 4.6$–4.8, considering that the pH of the sample zone is lower than pH_L. The suitability of the assumed pK_a values was confirmed by measuring the R_E values of Ln at $pH_L = 5.3$ ($[K^+] = 15$ mM) using acetic acid as the complexing agent. The R_E values agreed well with those obtained at $pH_L = 4.8$ (Fig. 2), except for Dy and Ho. The observed R_E values of Dy and Ho at $pH_L = 5.3$ were higher than those at $pH_L = 4.8$ by $ca.$ 0.08, suggesting the formation of small amounts of hydroxy complexes. However, at $pH_L = 4.8$ the abundance may be negligibly small. As a precaution we did not consider the R_E values at $pH_L = 5.3$ in the following mobility determination.

The mobilities of the three-coordinate complexes were zero, but those of $LnAc^{2+}$, $LnAc_2^+$, $LnHIB^{2+}$, $LnHIB_2^+$ and $LnHIB_4^-$ were not known. In addition to these ions, the mobilities of mixed ligand complexes of $LnHIBAc^+$ should be determined; there may be formed by the use of the electrolyte systems containing complexing agents of both Ac and HIB (Nos. 14–17). The mobilities of monovalent ions of $LnAc_2^+$, $LnHIB_2^+$ and $LnHIB_4^-$ were (reasonably) assumed to be the half of those the divalent ions. The mobilities of $LnHIBAc^+$ may be between $LnAc_2^+$ and $LnHIB_2^+$ and the values were evaluated on the assumption that the mobilities of $LnHIB_2^+$, $LnHIBA^+$ and $LnAc_2^+$ are inversely correlated with the square roots of the formula weights of the ions[13]. Then the mobility of $LnHIBAc^+$ can be given as

$$m_0(LnHIBAc^+) = 0.447\, m_0(LnHIB_2^+) + 0.553\, m_0(LnAc_2^+) \qquad (8)$$

By the use of these assumptions, the mobilities that should be determined independently could be reduced to those of $LnAc^{2+}$ and $LnHIB^{2+}$.

As shown in Table III, the mobilities of Ln^{3+} are similar but decrease slightly according to the atomic number. Therefore, it is probably that the complex ions may have similar mobilities when the coordination number and the ligands are the same. Although the stability constants of $LnHIBAc^+$ have not been reported, the values may be between $LnHIB_2^+$ and $LnAc_2^+$.

The evaluation of the mobilities and stability constants was based on a computational method applying the least-squares technique to the observed seventeen R_E values for Ln–Gd and the twelve R_E values for Tb–Lu (Figs. 2, 4 and 6). Good agreement was obtained between the observed and simulated R_E values; the mean errors were less than 1.1% for all lanthanoids and the individual errors were less than $ca.$ 3%. When the mixed ligand complexes were not taken into account, the

agreement was unsatisfactory, especialy for the observed R_E values with electrolyte systems 14–17, confirming the formation of LnHIBAc$^+$ complexes.

Table IV shows the simulated R_E values, concentrations and effective mobilities for La, Sm, Gd, Ho, Tm and Lu. The evaluated mobilities of the complex ions and the reported mobilities of Ln^{3+} are shown in Fig. 7 and Table V. As expected, the evaluated mobilities of the complex ions were very similar. For LnAc^{2+} the values were in the range $47.4 \cdot 10^{-5}$ (La) to $47.0 \cdot 10^{-5}$ cm^{2}V^{-1} sec^{-1} (Dy, Tm and Yb) and for LnHIB^{2+} they were in the range of $41.3 \cdot 10^{-5}$ (La) to $37.8 \cdot 10^{-5}$ cm^2 V^{-1} sec^{-1} (Dy). For monovalent ions of LnAc$_2^+$ and LnHIB$_2^+$ they were half of the above values from the assumption and for LnHIBAc$^+$ the values were in the range $22.3 \cdot 10^{-5}$ (La) to $21.5 \cdot 10^{-5}$ cm^2 V^{-1} sec^{-1} (Dy and Yb). Fig. 7 also shows the evaluated stability constants of log β (LnHIBAc$^+$) at $I = 0$ and the reported stability constants of LnAc$_2^+$ and LnHIB$_2^+$ corrected to $I = 0$. For the light lanthanoids the stability constants of LnHIBAc$^+$ were similar with those of LnHIB$_2^+$ and for others they were between LnHIB$_2^+$ and LnAc$_2^+$.

Using the evaluated constants, the effective mobilities and concentrations of the constituents of the Ln zone were simulated under the isotachophoretic steady state. Fig. 8 shows the dependence of the K$^+$ concentration on the effective mobilities of Ln interacting with Ac$^-$. The leading electrolytes do not contain HIB. From eqn. 6 (in this instance the terms related to HIB should be omitted) the effective mobilities of Ln ions decrease with increasing Ac$^-$ concentration. The profiles of the curves are very similar, namely, an increase in the Ac$^-$ concentration in the leading zone decreased the effective mobilities of Ln to similar extents. Consequently, lanthanoids cannot be separated by complex formation with Ac$^-$. Fig. 9 shows the abundances of acetate complexes for La, Sm and Tm. As the stability constants of Sm complexes with Ac$^-$ are the largest among the lanthanoids, as shown in Table III, the abundance of non-complexing Sm^{3+} is the smallest, as shown in Fig. 9. The relatively smaller effective mobility of Sm can be understood as the result of the large abundance of the complexes, *i.e.* the mobility of SmAc^{2+} is *ca.* two thirds of that of Sm^{3+}, that of SmAc$_2^+$ is *ca.* one third of that of Sm^{3+} and that of SmAc^3 is zero, and the formation of these complexes decreases the effective mobility. The similarity of the effective mobilities of La and Tm can be elucidated by the fact that the abundance of LaAc^{2+} is larger than that of TmAc^{2+} but the abundance of LaAc$_2^+$ is smaller than that of TmAc$_2^+$.

Fig. 10 shows the dependence of the K$^+$ concentration on the abundance of La, Sm and Gd complexes with HIB in the isotachophoretically separated zones. The leading electrolytes do not contain Ac$^-$. The abundances of non-complexing Ln^{3+} quickly decrease with an increase in the K$^+$ or HIB concentration, as expected from the large stability constants of HIB complexes. With acetate complexes the main species are one-coordinated but with HIB complexes the main species are two-coordinated, and even four-coordinated species are formed to a small extent. For the heavier lanthanoids the simulational calculation did not converge to the steady state. This phenomenon occurred with Tb at a K$^+$ concentration less than 4 mM, with Dy at a K$^+$ concentration less than 6 mM, and so on. This was caused by the decrease in the pH of the lanthanoid zone to an isotachophoretically unallowable extent accompanied by a strong interaction between the heavy lanthanoids and HIB. According to simulation, the lower limit of the pH of the sample zone at the steady state

TABLE IV

OBSERVED AND SIMULATED R_E VALUES OF La, Sm, Gd, Ho, Tm AND Lu, AND EFFECTIVE MOBILITIES AND CONCENTRATIONS OF ZONE CONSTITUENTS (25°C)

No. = Number of electrolyte system shown in Table I. R_E = Ratio of potential gradients, E_S/E_L. Dev. = Deviation (%). m_S = Effective mobility (cm² V⁻¹ sec⁻¹) × 10⁵ of sample ion. pH_S = pH of sample zone. C_S = Total concentration (mM) of sample zone. P_1, P_2 and P_3 = Abundances (%) of LnAc²⁺, LnAc₂⁺ and LnAc₃ complexes, respectively. P_4, P_5, P_6 and P_7 = Abundances (%) of LnHIB²⁺, LnHIB₂⁺, LnHIB₃ and LnHIB₄⁻, respectively. P_8 = Abundances (%) of mixed-ligand complexes LnHIBAc⁺. C_B = Total concentration (mM) of non-complexing buffer ion (acetate for systems 1-8 and 14-17, α-hydroxyisobutyrate for systems 9-13). $\bar{m}_B$ = Effective mobility (cm² V⁻¹ sec⁻¹) of buffer ion × 10⁵ of non-complexing additive ion (α-hydroxyisobutyrate). $\bar{m}_A$ = Effective mobility (cm² V⁻¹ sec⁻¹) of additive ion × 10⁵. C_A = Total concentration (mM) of non-complexing additive ion × 10⁵. κ = Conductivity of zone (mS/cm). I = Ionic strength of sample zone × 10³.

Ln	No.	R_E Obsd.	Calcd.	Dev.	$\bar{m}_S$	pH_L	C_S	P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8	C_B	$\bar{m}_B$	C_A	$\bar{m}_A$	κ	I
La	1	1.40	1.41	−0.6	51.5	4.71	1.77	43.0	3.9	0.2						8.85	−14.4			0.40	7.91
	2	1.49	1.51	−1.2	47.6	4.69	2.90	49.8	6.5	0.4						13.9	−12.9			0.59	11.9
	3	1.54	1.55	−0.4	46.2	4.69	3.45	51.8	7.8	0.5						16.3	−12.4			0.68	13.8
	4	1.60	1.61	−0.4	44.2	4.67	4.39	54.2	9.7	0.8						20.2	−11.7			0.82	16.8
	5	1.66	1.66	0.1	42.6	4.66	5.34	55.6	11.5	1.1						24.1	−11.1			0.95	19.6
	6	1.70	1.71	−0.4	41.2	4.64	6.32	56.5	13.1	1.4						28.4	−10.6			1.08	22.4
	7	1.78	1.76	1.2	39.7	4.63	7.49	57.0	14.9	1.9						33.1	−10.1			1.22	25.6
	8	1.85	1.84	0.7	37.7	4.63	9.45	57.1	17.5	2.6						40.3	−10.1			1.45	30.6
	9	1.92	1.95	−1.6	37.3	4.30	2.27				53.7	24.8	1.0	0.0		6.32	−9.57			0.33	7.01
	10	2.03	2.03	0.2	35.8	4.32	2.68				53.0	27.7	1.3	0.0		7.15	−9.92			0.37	7.93
	11	2.10	2.10	0.2	34.5	4.31	3.10				52.2	30.1	1.6	0.0		8.06	−9.54			0.40	8.81
	12	2.15	2.16	−0.4	33.4	4.29	3.52				51.2	32.3	1.9	0.0		9.07	−9.14			0.44	9.64
	13	2.26	2.22	1.8	32.5	4.31	3.95				50.2	34.3	2.2	0.0		9.78	−8.72			0.47	10.5
	14	1.61	1.61	0.2	44.9	4.66	3.27	44.2	6.0	0.4	11.5	0.7	0.0	0.0	8.4	15.2	−8.54	0.72	0.9	0.66	13.2
	15	1.72	1.70	1.3	42.6	4.69	3.15	36.3	4.4	0.2	22.0	2.6	0.0	0.0	14.3	13.0	−12.1	1.46	−0.7	0.62	12.6
	16	1.76	1.78	−0.9	40.7	4.68	3.10	29.1	3.1	0.1	30.7	5.6	0.1	0.0	17.6	11.4	−12.5	2.22	−2.2	0.58	12.1
	17	1.84	1.85	−0.3	39.1	4.65	3.10	22.9	2.1	0.1	37.4	9.1	0.2	0.0	18.5	10.2	−12.5	2.99	−3.5	0.56	11.7
Sm	1	1.60	1.63	−2.0	44.4	4.66	1.88	60.4	12.0	0.5						8.61	−12.2			0.35	6.67
	2	1.75	1.77	−1.1	40.6	4.64	3.10	61.6	17.8	1.1						13.5	−10.7			0.51	9.89
	3	1.79	1.82	−1.8	39.2	4.63	3.70	61.3	20.1	1.4						15.8	−9.47			0.58	11.4
	4	1.92	1.90	0.8	37.3	4.62	4.73	60.2	23.5	2.0						19.7	−9.06			0.69	13.7
	5	2.00	1.97	1.2	35.7	4.60	5.76	58.7	26.4	2.6						23.5	−8.53			0.80	15.9
	6	2.03	2.04	−0.6	34.4	4.58	6.82	57.2	28.9	3.2						27.7	−8.12			0.90	18.0

	No.																				
	7	2.18	2.11	3.1	33.0	4.57	8.09	55.3	31.4	3.9						32.2	−7.40			1.02	20.5
	8	2.24	2.21	0.9	31.2	4.56	10.2	52.4	34.7	5.1						39.3	−7.05			1.20	24.3
	9	2.57	2.61	−1.6	27.9	4.01	2.16				43.8	42.9	5.5	0.3		6.29	−6.70			0.25	4.83
	10	2.75	2.74	0.2	26.4	4.02	2.60				41.2	45.5	6.7	0.4		7.07	−6.52			0.27	5.46
	11	2.87	2.86	0.2	25.3	4.02	3.02				38.9	47.5	7.7	0.5		7.94	−6.29			0.30	6.03
	12	2.95	2.96	−0.6	24.3	3.99	3.43				37.0	49.0	8.7	0.6		8.93	−6.02			0.32	6.55
	13	3.13	3.07	1.7	23.4	4.01	3.87				35.1	50.3	9.7	0.8		9.59	−5.93			0.34	7.09
	14	1.91	1.94	−1.9	37.1	4.62	3.30	53.0	15.9	1.0	12.2	1.6	0.0	0.0	15.9	14.6	−9.09	0.63	5.74	0.54	10.8
	15	2.11	2.09	0.8	34.5	4.65	3.07	42.8	11.4	0.6	23.5	6.7	0.3	0.0	27.2	12.3	−9.72	1.30	3.78	0.50	10.2
	16	2.22	2.22	−0.3	32.4	4.64	3.00	32.7	7.6	0.4	31.7	13.9	0.8	0.0	32.0	10.8	−9.91	2.00	1.89	0.47	9.71
	17	2.37	2.35	0.8	30.7	4.60	3.03	24.0	4.8	0.2	36.6	21.6	1.7	0.1	31.6	9.71	−9.72	3.03	0.15	0.44	9.27
Gd	1	1.50	1.59	−2.6	45.6	4.67	1.83	53.1	11.4	0.5						8.65	−11.8			0.36	6.95
	2	1.72	1.72	−0.5	41.5	4.64	3.03	55.7	17.3	1.0						13.5	−10.4			0.52	10.3
	3	1.77	1.78	−0.9	40.0	4.63	3.62	55.8	19.7	1.4						15.9	−9.88			0.59	11.8
	4	1.86	1.86	−0.5	38.0	4.62	4.63	55.3	23.2	1.9						19.8	−9.24			0.70	14.1
	5	1.97	1.94	1.3	36.3	4.60	5.64	54.4	26.2	2.5						23.6	−8.76			0.81	16.4
	6	2.01	2.01	−0.1	34.9	4.58	6.70	53.2	28.8	3.2						27.7	−8.27			0.91	18.5
	7	2.13	2.08	2.1	33.5	4.57	7.95	51.7	31.4	3.9						32.3	−7.89			1.03	21.0
	8	2.22	2.20	1.0	31.5	4.56	10.1	49.2	34.9	5.2						39.3	−7.47			1.21	24.8
	9	2.83	2.83	−0.2	25.6	3.82	1.94				38.6	44.9	10.2	0.4		6.66	−5.51			0.23	3.95
	10	3.05	3.01	1.2	24.1	3.84	2.38				35.6	46.8	12.2	0.5		7.42	−5.37			0.25	4.48
	11	3.17	3.17	0.1	22.9	3.83	2.78				33.2	48.1	13.9	0.7		8.32	−5.18			0.27	4.94
	12	3.26	3.29	−1.2	21.9	3.81	3.17				31.2	49.0	15.4	0.8		9.37	−4.94			0.29	5.35
	13	3.44	3.44	−0.1	20.9	3.82	3.60				29.3	49.7	16.9	1.0		10.0	−4.86			0.30	5.78
	14	1.91	1.95	−2.1	37.0	4.62	3.22	43.6	13.9	0.9	18.4	3.3	0.1	0.0	16.9	14.6	−10.2	0.60	9.63	0.54	10.9
	15	2.17	2.14	0.9	33.6	4.63	3.07	30.5	8.5	0.5	31.7	12.1	1.0	0.0	25.4	12.3	−11.1	1.27	6.81	0.49	10.0
	16	2.35	2.34	0.4	30.9	4.60	3.10	20.0	4.8	0.2	37.7	22.4	2.8	0.1	25.8	10.9	−11.2	1.97	4.10	0.44	9.26
	17	2.53	2.52	0.4	28.7	4.53	3.22	12.9	2.6	0.1	39.1	30.9	5.0	0.1	22.2	9.82	−10.8	2.68	1.74	0.41	8.60
Ho	1	1.52	1.52	0.2	47.8	4.69	1.77	44.7	7.3	0.7						8.73	−13.5			0.37	7.46
	2	1.64	1.64	−0.1	43.7	4.66	2.91	49.6	11.6	1.7						13.7	−11.9			0.55	11.1
	3	1.67	1.70	−1.5	42.1	4.65	3.47	50.6	13.5	2.3						16.0	−11.3			0.62	12.7
	4	1.77	1.78	−0.5	39.9	4.63	4.43	51.3	16.2	3.3						19.9	−10.6			0.74	15.2
	5	1.82	1.85	−1.8	38.1	4.61	5.40	51.3	18.5	4.4						23.8	−9.97			0.85	17.6
	6	1.93	1.92	0.3	36.5	4.59	6.40	50.9	20.5	5.5						28.0	−9.37			0.96	19.9
	7	2.04	2.00	1.8	34.8	4.57	7.59	50.1	22.6	6.8						32.6	−8.87			1.07	22.4
	8	2.17	2.13	2.0	32.6	4.55	9.61	48.4	25.3	8.9						39.7	−8.29			1.25	26.3
	14	1.99	2.00	−0.7	36.0	4.61	3.08	30.9	7.2	1.1	29.3	8.2	0.4	0.0	18.1	14.5	−12.0	0.52	14.2	0.53	10.8

TABLE IV (continued)

| Ln	No.	R_E Obsd.	R_E Calcd.	Dev.	$\bar{m}_S$	pH_L	C_S	P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8	C_B	$\bar{m}_B$	C_A	$\bar{m}_A$	κ	I
	15	2.42	2.39	1.2	30.2	4.58	3.12	14.9	2.9	0.4	39.8	26.0	2.9	0.0	20.4	12.2	-12.6	1.20	9.45	0.44	9.11
	16	2.72	2.73	-0.5	26.4	4.51	3.29	7.4	1.2	0.1	38.0	38.7	6.6	0.0	15.8	10.8	-12.1	1.90	-5.45	0.38	7.91
	17	3.02	3.02	-0.0	23.9	4.41	3.45	4.1	0.5	0.0	34.1	45.7	10.1	0.1	11.4	9.86	-11.0	2.59	-2.43	0.34	7.07
Tm	1	1.52	1.52	-0.2	47.6	4.69	1.76	44.4	7.0	0.5						8.73	-13.6			0.37	7.48
	2	1.64	1.64	-0.2	43.7	4.66	2.89	49.5	11.4	1.2						13.7	-12.0			0.55	11.1
	3	1.68	1.69	-0.8	42.2	4.65	3.46	50.7	13.2	1.6						16.0	-11.5			0.62	12.8
	4	1.76	1.77	-0.6	40.1	4.64	4.41	51.7	16.0	2.4						19.9	-10.7			0.74	15.4
	5	1.85	1.84	0.5	38.3	4.62	5.38	51.9	18.4	3.2						23.8	-10.1			0.86	17.8
	6	1.91	1.91	0.2	36.8	4.60	6.38	51.7	20.6	4.0						28.0	-9.55			0.96	20.2
	7	1.99	1.98	0.6	35.3	4.58	7.57	51.0	22.8	5.0						32.6	-9.07			1.09	22.8
	8	2.09	2.09	-0.0	33.1	4.57	9.58	49.6	25.7	6.7						39.7	-8.51			1.27	26.9
	14	2.07	2.08	-0.2	34.8	4.60	3.07	27.4	6.2	0.7	32.3	11.7	0.7	0.0	18.8	14.4	-12.2	0.50	15.4	0.51	10.5
	15	2.59	2.57	0.7	28.1	4.55	3.20	10.9	2.0	0.2	38.5	33.3	4.8	0.1	18.0	12.2	-12.6	1.20	9.89	0.41	8.43
	16	2.97	3.00	-0.8	24.1	4.45	3.41	4.9	0.7	0.0	33.7	44.9	9.9	0.2	12.4	10.8	-11.6	1.87	5.52	0.35	7.12
	17	3.36	3.34	0.6	21.6	4.34	3.54	2.5	0.3	0.0	29.0	49.9	14.1	0.4	8.3	9.99	-10.2	2.54	2.42	0.31	6.26
Lu	1	1.54	1.55	-0.9	46.6	4.68	1.77	45.6	8.6	0.4						8.69	-13.2			0.36	7.32
	2	1.66	1.68	-1.2	42.7	4.66	2.92	50.1	13.7	1.0						13.6	-11.6			0.53	10.9
	3	1.70	1.73	-1.8	41.3	4.65	3.49	51.0	15.9	1.3						16.0	-11.1			0.61	12.5
	4	1.79	1.81	-1.1	39.2	4.63	4.46	51.6	19.1	2.0						19.8	-10.4			0.73	15.0
	5	1.88	1.88	-0.0	37.5	4.62	5.44	51.5	21.8	2.6						23.7	-9.79			0.84	17.4
	6	1.99	1.95	2.2	36.1	4.59	6.46	51.0	24.3	3.3						27.9	-9.23			0.94	19.7
	7	2.03	2.02	0.5	34.6	4.58	7.67	50.1	26.8	4.1						32.4	-8.77			1.06	22.2
	8	2.16	2.13	1.4	32.5	4.57	9.73	48.4	30.2	5.4						39.5	-8.25			1.25	26.3
	14	2.15	2.15	0.0	33.6	4.59	3.19	24.0	6.4	0.5	34.2	16.5	1.4	0.0	15.9	14.4	-12.2	0.50	16.5	0.49	10.0
	15	2.75	2.74	0.3	26.3	4.50	3.40	8.1	1.7	0.1	35.1	39.9	7.7	0.2	12.6	12.2	-12.3	1.19	10.1	0.38	7.75
	16	3.22	3.25	-0.9	22.3	4.38	3.59	3.4	0.5	0.0	28.7	48.9	14.0	0.6	7.9	11.0	-10.9	1.87	5.55	0.32	6.38
	17	3.68	3.65	0.8	19.8	4.25	3.66	1.7	0.2	0.0	24.0	51.9	18.7	1.0	5.0	10.1	-9.18	2.53	2.42	0.28	5.55
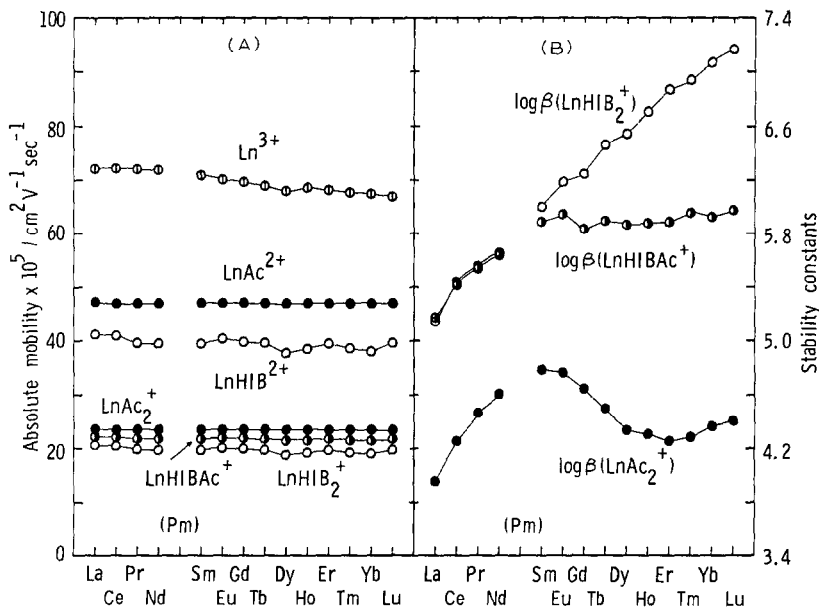
Fig. 7. (A) Evaluated mobilities of complex ions, $LnAc^{2+}$, $LnAc_2^+$, $LnHIB^{2+}$, $LnHIB_2^+$ and $LnHIBAc^+$ and reported mobilities of lanthanoid ions[4,5]. (B) Evaluated stability constants of $LnHIBAc^+$ at $I = 0$ and the stability constants of $LnHIB_2^+$ and $LnAc_2^+$ corrected to $I = 0$ using the reported values[6,8].

TABLE V

DETERMINED MOBILITIES AND STABILITY CONSTANTS OF LANTHANOID ACETATE, LANTHANOID-α-HYDROXYISOBUTYRATE AND THE MIXED LIGAND COMPLEXES

m_0 = Absolute mobilities $(cm^2 \ V^{-1} \ sec^{-1}) \times 10^5$. $Log\beta \ (LnHIBAc^+)$ = Thermodynamic overall stability constants of mixed ligand complexes $LnHIBAc^+$.

| Ln	m_0 of complex ions					$Log\beta \ (LnHIBAc^+)$
	$LnAc^{2+}$	$LnAc_2^+$	$LnHIB^{2+}$	$LnHIB_2^+$	$LnHIBAc^+$	
La^{3+}	47.4	23.7	41.3	20.7	22.3	5.18
Ce^{3+}	47.1	23.5	41.1	20.5	22.2	5.42
Pr^{3+}	47.1	23.6	39.7	19.9	21.9	5.54
Nd^{3+}	47.1	23.6	39.6	19.8	21.9	5.64
Sm^{3+}	47.2	23.6	39.6	19.8	21.9	5.89
Eu^{3+}	47.2	23.6	40.5	20.2	22.1	5.95
Gd^{3+}	47.2	23.6	39.9	20.0	22.0	5.84
Tb^{3+}	47.1	23.6	39.7	19.8	21.9	5.90
Dy^{3+}	47.0	23.5	37.8	18.9	21.5	5.87
Ho^{3+}	47.1	23.5	38.6	19.3	21.6	5.88
Er^{3+}	47.1	23.5	39.6	19.8	21.9	5.89
Tm^{3+}	47.0	23.5	38.7	19.3	21.6	5.96
Yb^{3+}	47.0	23.5	38.1	19.1	21.5	5.93
Lu^{3+}	47.1	23.5	39.7	19.8	21.9	5.98
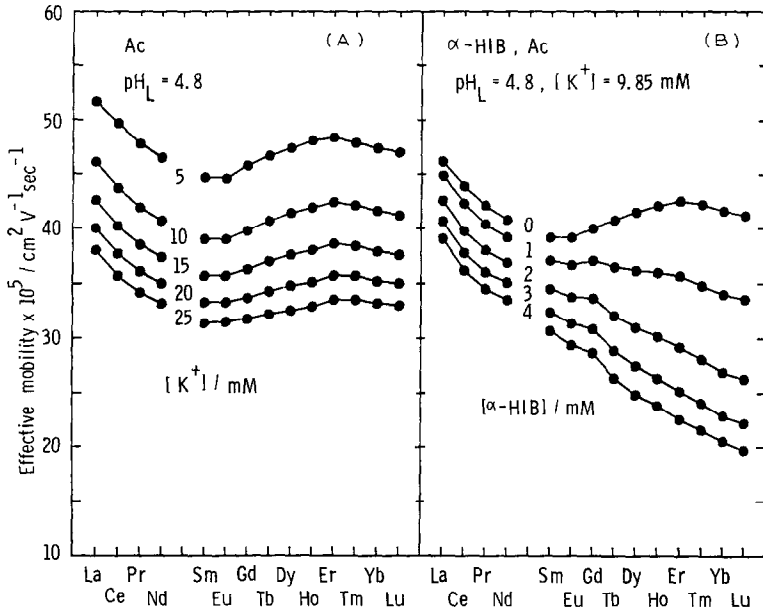
Fig. 8. (A) Dependence on K^+ concentration of the effective mobilities of fourteen lanthanoids coexisting with acetic acid. (B) Dependence on α-hydroxyisobutyric acid concentration of the effective mobilities of fourteen lanthanoids coexisting with acetic acid and HIB.
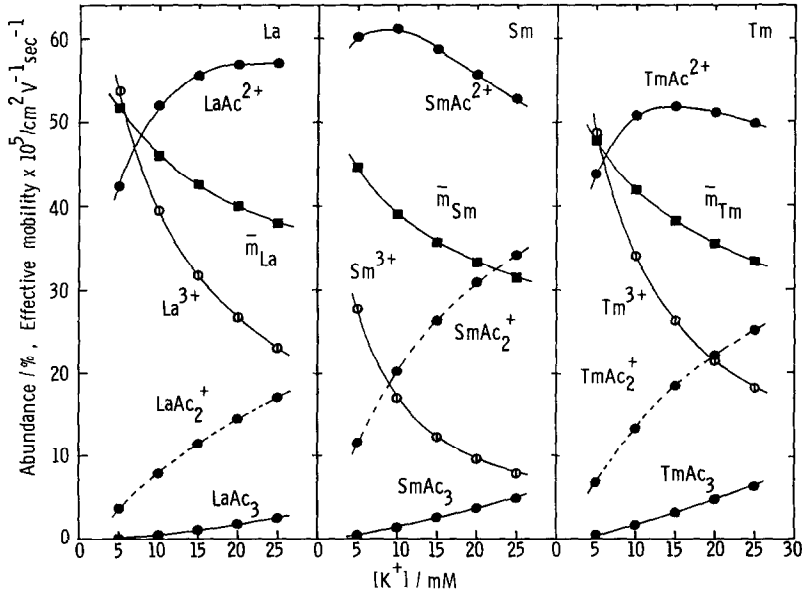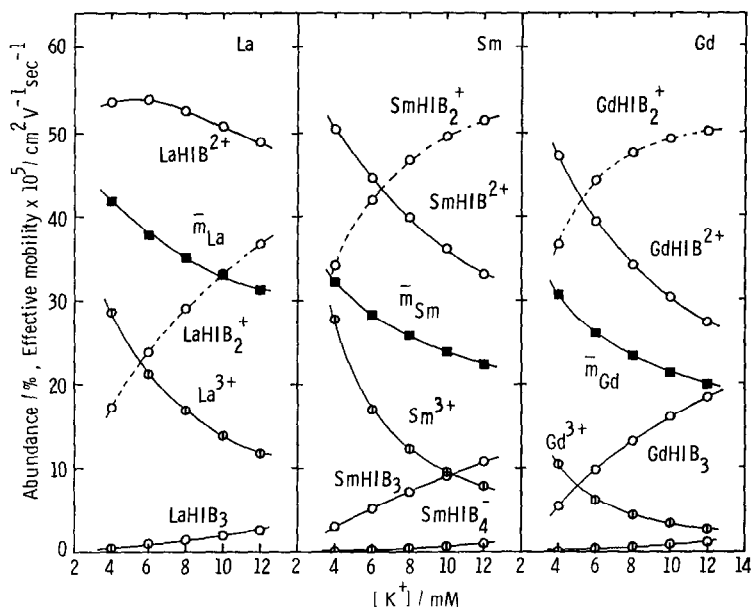

Fig. 9. Dependence on K^+ concentration of the abundance of non-complexing Ln^{3+}, one-coordinated, two-coordinated and three-coordinated complexes with acetate ions and effective mobilities of La, Sm and Tm. $pH_L = 4.8$.

Fig. 10. Dependence on K^+ concentration of the abundance of non-complexing Ln^{3+}, one-coordinated, two-coordinated and three-coordinated and four-coordinated complexes with α-hydroxyisobutyrate ions and effective mobilities of La, Sm and Gd. $pH_L = 4.7$.

was *ca.* 3.5 when the leading K^+ concentration was in the range 4–12 mM. To improve this the concentration of K^+ should be increased but the safe range is limited for heavy lanthanoids, and above a certain concentration an isotachophoretic steady state could not be achieved. Thus not all lanthanoids could be separated at once isotachophoretically when HIB was used as the complexing agent.

To suppress the pH decrease and achieve an isotachophoretically steady state, the abundances of HIB complexes should be lowered. This could be realized by diluting HIB with weakly complex-forming by weakly interacting acetate ions. Fig. 8B shows the dependence on HIB concentration of the effective mobility of the lanthanoids. The effective mobilities decrease quickly on adding HIB and the decrease is large for the heavy lanthanoids. When 4 mM HIB was added, all lanthanoids could be separated, as already shown in Fig. 6. The simulated mobility of La was 39.1 · 10^{-5} and that of Lu was 19.7 · 10^{-5} cm^2 V^{-1} sec^{-1}. The separation of Eu and Gd was the most difficult and the difference in the effective mobilities was 0.7 · 10^{-5} cm^2 V^{-1} sec^{-1}. Fig. 11 shows the dependence of HIB concentration on the abundances of HIB and acetate complexes. The formation of HIB complexes could be suppressed sufficiently by coexisting acetate complexes and the mixed ligand complexes of LnHIBAc$^+$. A fairly large abundance of LnHIBAc$^+$ was simulated. Without this species, the observed R_E values cannot be simulated accurately.

Hence the isotachophoretic separation of lanthanoids could be explained by an appropriate but small difference in the effective mobilities owing to the different abundances of the complex ions. Fig. 12 shows the simulated isotachopherograms of the observed ones shown in Fig. 6. The agreement is satisfactory.

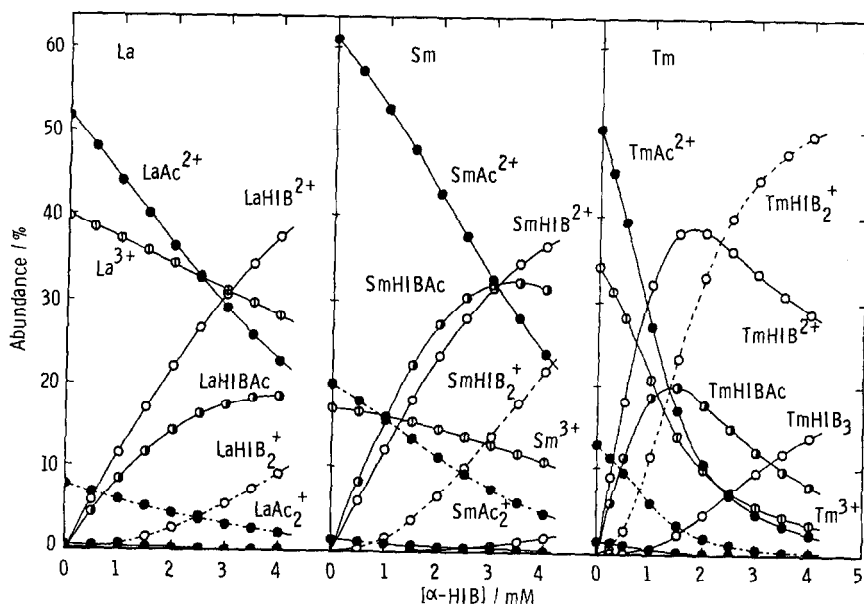Although the electrolyte concentrations used by Nukatsuka *et al.*[1] were very

Fig. 11. Dependence on α-hydroxybutyric acid concentration of the abundance of non-complexing Ln^{3+}, one-coordinated, two-coordinated and three-coordinated complexes with HIB and acetate ions and effective mobilities of La, Sm and Tm. The K^+ concentration is 9.85 mM and $pH_L = 4.8$.
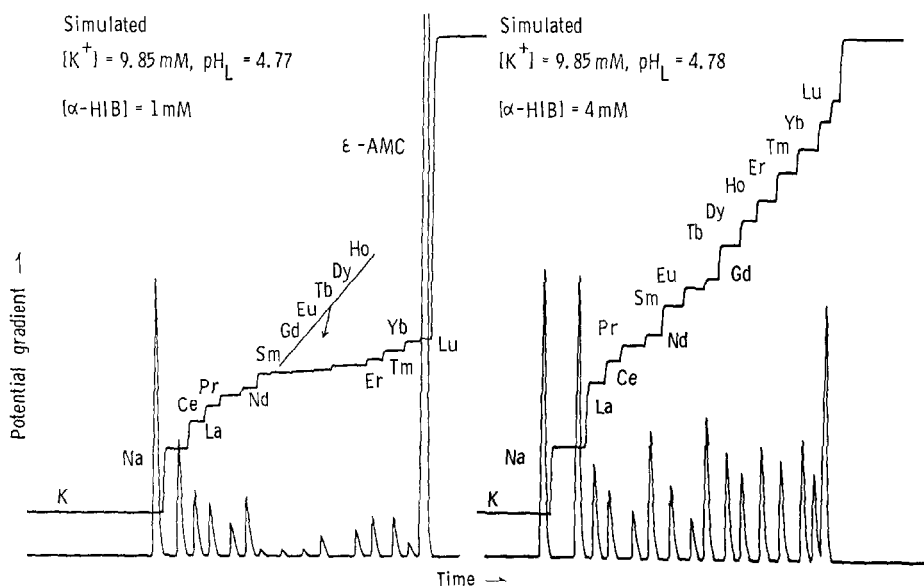

Fig. 12. Simulated isotachopherograms of Na^+ and fourteen lanthanoids coexisting with acetic acid and α-hydroxybutyric acid (1 and 4 mM).

high in comparison with those in this work, a simulation was carried under the reported electrolyte conditions; the K^+ concentration was 25 mM, the HIB concentration was 15 mM and pH$_L$ was adjusted to 4.92 by adding acetic acid. The simulated R_E values were in the range 2.5 for La to 6.5 for Lu. In comparison with the observed R_E values (2.7 for La to 5.9 for Lu) converted from the observed PR values ($PR = 1/R_E$, 0.37 for La to 0.17 for Lu), the agreement was not so good for heavy lanthanoids. The discrepancy suggests the formation of three-coordinated mixed ligand complexes such as $LnHIB_2Ac$. When the precise R_E values under such conditions are available, their stability constants may be evaluated.

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