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Selective Separation of Yttrium Ions from Other Rare Earth Ions Using Nonequilibrium Extraction

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An advanced new method for the separation of yttrium ions from other rare earth ions using nonequilibrium extraction in the DTPA–B2EHPA system has been demonstrated. The extraction stages for obtaining yttrium oxide of 99.9% purity from yttrium oxide of 60% purity as a starting material were estimated to be about fifteen, which was the smallest value ever obtained, compared with the usual method (50—100 stages). The mechanism of the extraction reaction is discussed.

We previously reported[1)] for the first time that a new separation method for the purification of yttrium ions was found by using a nonequilibrium extraction method in a DTPA (diethylenetriaminepentaacetic acid) and B2EHPA (bis(2-ethylhexyl)phosphoric acid) / kerosine system. We have continued our investigation of extraction experiments. Recently, Teramoto et al.[2)] reported on the kinetics in the extraction of yttrium and erbium ions using a DTPA–BTMPPA (bis-(2,4,4-trimethylpentyl)phosphinic acid) system. However, they have not reported the extraction of yttrium ions from other rare earth ions using their method. In this paper we thus describe a method for nonequilibrium extraction for the purification of yttrium ions by using the DTPA–B2EHPA system.

Experimental

Materials: A yttrium chloride solution (1 mol dm^{-3}) was prepared by dissolving yttrium oxide of 99.9% purity (purchased from Rhone Poulence) in concd HCl; the solution was then heated in order to remove any excess HCl. An erbium chloride solution (1 mol dm^{-3}) was prepared by a similar procedure. A rare earth chloride solution was prepared from yttrium oxide of 60% purity (purchased from Malaysian Rare Earth Co.) by similar procedure to give a total rare earth concentration of 34 g (Ln_2O_3)/l at pH 0.2. A DTPA (1.0 mol dm^{-3}) solution was prepared by dissolving a DTPA reagent (393.4 g, Tokyo-Kasei) into aqueous ammonia (338 cm^3, 28% as NH_3); the volume of the solution was adjusted to 1.0 dm^3 with water. A 1.0 mol dm^{-3} (monomer base) B2EHPA/kerosine solution was prepared by diluting 348 cm^3 of DP-8R (Daihachi-Kagaku) to 1.0 dm^3 with kerosine. This solution was washed three times with 500 cm^3 of 6 mol dm^{-3} HCl and three times with 500 cm^3 of water, after which the solution was left over night.

Extraction Procedure for the Yttrium–Erbium System: Then, 25 cm^3 each of a yttrium chloride solution and an erbium chloride solution was added to a prepared 700 cm^3 of distilled water in a 1 dm^3 beaker under stirring. A 100 cm^3 volume of a DTPA solution was added to the mixture solution, and the pH adjusted to ca. 8 (TOA pH Meter, HM-30S) by concd HCl. Finally, the volume of the solution was adjusted to 1.0 dm^3 with water, and generally called a "feed solution". A 100 cm^3 volume of the feed solution was transferred to a 300-cm^3 separatory funnel; a 100 cm^3 volume of the B2EHPA solvent was then added to the solution (phase ratio S/F=1.0). Shaking was started immediately with a shaker (Yamato Scientific Co. Model SA-31) under vigorous shaking conditions; an emulsion was observed throughout the extraction process at room temperature (23—25 °C). After the designated time, the phases were separated into aqueous and organic parts by natual standing, during which the separation speed was quick. The total amount of rare earth ions in the aqueous phase were precipitated quantitatively as oxalates upon the addition of an oxalic acid solution. The precipitate was ignited at 800 °C for 1 h to obtain rare earth oxides, the concentrations of which were determined gravimetrically.

Extraction Procedure for Yttrium Oxide of a 60% Purity System: (A) The separation procedure for light rare earth ions (La—Ga) from the rare earth chloride solution: It is generally said that the separation of the light rare earth ions from a chloride solution with the B2EHPA solvent should be easy using the usual extraction method involving a counter-current multistage. Hereupon, our purpose is not only the separation of yttrium ions from light rare earth ions, but also the separation of yttrium ions from middle-heavy rare earth ions. Therefore, the following procedure was carried out: A 100 cm^3 volume of the rare earth chloride solution was transferred to a 300-cm^3 separatory funnel; a 100-cm^3 volume of the B2EHPA solvent was then added to the solution. The funnel was shaken with the shaker under the usual vigorous shaking condition for 10 min. Then, both phases were separated into an aqueous and organic phases by natulal standing, and the total amount of rare earth ions in the organic phase were back-extracted with 6 mol dm^{-3} HCl. The total amount of back-washed rare earth ions were precipitated quantitatively as oxalates at pH 1. The oxalates were ignited at 800 °C for 1 h to obtain rare earth oxides, which were used as the source of a starting material for the following separation procedure, (B). These extraction procedures were performed several times to prepare the desired amounts of the starting material for the procedure, (B). The average molecular weight of the oxides was determined by an analytical procedure (which is hereinaftermentioned).

(B) Separation procedure for yttrium from middle-heavy (Tb~Lu) rare earth ions: A definite amount of the rare earth oxides obtained from procedure (A) was dissolved in concd HCl by the usual procedure. Then, a definite amount of DTPA solution was added to the rare earth chloride solution under stirring. The molar ratio of $[DTPA]_T/[Ln^{3+}]_T$ became 1.1 under the conditions. The pH was adjusted to 8.6, and a solution of total rare earth ions, $[Ln^{3+}]_T$, was prepared to be 0.1 mol dm^{-3} with water, called a "feed solution". A 100 cm^3

volume of the feed solution was transferred to a 300-cm^3 separatory funnel, and a 100 cm^3 volume of the B2EHPA solvent was added to the solution (phase ratio S/F=1.0). The funnel was shaken vigorously with the shaker for 10 or 20 min. After the designated time, the organic and aqueous phases were separated by natural standing during which the separation speed was quick. The total amount of rare earth ions in the organic phase were back-extracted with 6 mol dm^{-3} HCl, and the all ions were precipitated quantitatively as oxalates at pH 1 upon the addition of an oxalic acid solution. The oxalates were ignited by a similar procedure (A) to obtain the rare earth oxides, which were used as the source of the next stage (2th). These procedures were continued until the 7th stage. At each stage, extraction was performed several times in order to prepare the desired amounts of the source of rare earth oxides, which were employed in the following stage.

Analytical Procedure: In the yttrium–erbium system, the weighed rare earth oxides (ca. 0.1 g) were dissolved in concd HCl in a 50 cm^3 beaker; the volume of the solution was adjusted to 25 cm^3 with distilled water. The concentration of erbium ions in the solution was determined spectrophotometrically by measuring the absorbance at 521 nm (Hitachi Model 323, Recording Spectrophotometer). The concentration of erbium ions in the aqueous phase was easily determined by using the relation between the above-measured concentration and the ratio of the first weight of the total rare earth oxides to the weight of the sampled rare earth oxides (ca. 0.1 g). Then, the concentration (mol dm^{-3}) of yttrium ions in the aqueous phase was determined by using the weight of the yttrium oxide obtained by the difference between the first weighed total rare earth oxides and the summed weigth of erbium oxide calculated from the concentration of the measured erbium ion. The concentration of each type ion in the organic phase was estimated by subtracting that of each type ion in the aqueous phase from that of each type ion in the feed solution.

In yttrium oxide of a 60% purity system, the average molecular weight of the rare earth oxides was, (for the first time), determined by using the following analytical procedure; The weighed rare earth oxides were dissolved in concd HCl, and the solution was adjusted to a constant volume with water. After a definite amount of the solution was pipetted in a beaker, the concentration of the solution was diluted to ca. 1×10^{-2} mol dm^{-3} with water. The pH was adjusted to 7—7.5 with aqueous ammonia and a hexamine solution. Then, two or three drops of BT indicator were added to the solution, and the concentration of the rare earth ions in the solution was titrated with a 0.1 mol dm^{-3} of the DTPA standard solution. The average molecular weight (M_{av} (g mol^{-1})) was determined from the following equation. $M_{av}=W/(10^{-3}\cdot X\cdot C)$, where W(g) was the weight of sampled rare earth oxides, X (cm^3) the titer, and C (mol dm^{-3}) the concentration of the DTPA standard solution. The value of this M_{av} can be also used as a standard guide regarding the purity of yttrium oxide in rare earth oxides. The concentrations of the other rare earth oxides in the purified yttrium oxide were also determined by spark-source emission spectrometry.

Results and Discussion

Yttrium–Erbium System: The extraction data are summarized in Table 1. The changes in the extraction fraction E (%) of yttrium (Y^{3+}) and erbium (Er^{3+}) ions are plotted as a function of the shaking time, (t), in Fig. 1. The plots show that the extraction rate of yttrium ions is faster than that of erbium ions.[1] Furthermore, the change in the separation factor, ($\beta^{Y-Er}(=D^Y/D^{Er})$, ratio of the distribution ratio (D) for Y to Er) are plotted against the time, in Fig. 2. It was found that the value of β^{Y-Er}

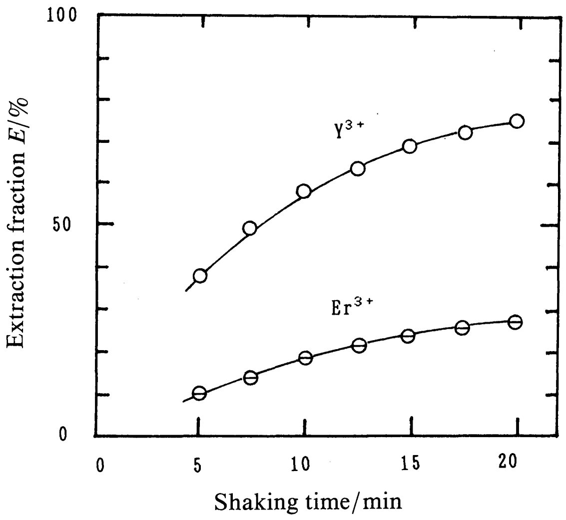

Fig. 1. Relationships between the extraction fraction (E(%)) of yttrium ions (○) and erbium ions (⊖), and the shaking time.

Table 1. Extraction Data of Y^{3+} and Er^{3+} Ions from a Solution[a] Containing DTPA with 1 mol dm^{-3} B2EHPA/Kerosine[b] at Room Temperature (24 °C)

Shaking time/min	Aqueous phase		Organic phase		Extr. fraction		β^{Y-Er}
	$[Y^{3+}]_T$	$[Er^{3+}]_T$	$[Y^{3+}]$	$[Er^{3+}]$	Y^{3+}	Er^{3+}	
	10^{-2} M[c]		10^{-2} M[c]		%		
5	1.57	2.25	0.93	0.25	37.2	10.0	5.4
7.5	1.30	2.15	1.20	0.35	48.0	14.0	5.8
10	1.07	2.06	1.43	0.44	57.2	17.6	6.4
12.5	0.92	1.99	1.58	0.51	63.2	20.4	6.6
15	0.80	1.94	1.70	0.56	68.0	22.4	7.4
17.5	0.70	1.87	1.80	0.63	72.0	25.2	7.6
20	0.65	1.84	1.85	0.66	74.0	26.4	7.9

a) Molar ratio $[DTPA]_T/([Y^{3+}]_T+[Er^{3+}]_T)=2.0$, pH=ca. 8. b) Phase ratio S/F=1.0. c) M=mol dm^{-3}.

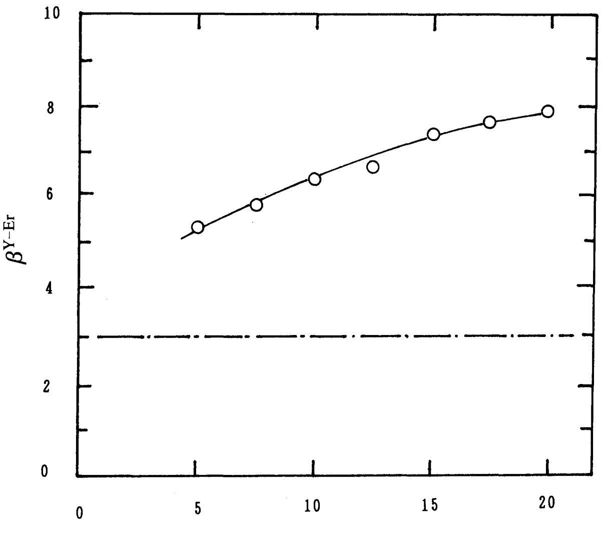

Fig. 2. Relationship between the separation factor ($\beta^{\text{Y-Er}}$) and the shaking time; the value at equilibrium ($\beta_e^{\text{Y-Er}}$) is indicated by the broken line.

increased as the extraction proceeded. This fact is very important from an industrial view point, since the larger separation factor gives a more efficient extraction process having fewer extraction stages. It might thus be important to discuss whether a larger separation factor could be obtained if the extraction could proceed further: In the first place, the separation factor during the equilibrium state, ($\beta_e^{\text{Y-Er}}$), can be calculated from the following equations:

$$\mathrm{Ln^{3+}} + 3(\mathrm{H_2X_2})_{(o)} \overset{K_{ex}}{=} \mathrm{Ln(HX_2)_{3(o)}} + 3\mathrm{H^+}, \tag{1}$$

$$\mathrm{Ln^{3+}} + \mathrm{Z^{5-}} \overset{K_l}{=} \mathrm{LnZ^{2-}}, \tag{2}$$

where K_{ex} is supposed to be the extraction constant, K_l is the complex formation constant, (H_2X_2) is dimeric species of B2EHPA(HX) in kerosine, $Ln(HX_2)_3$ is an extracted species in the organic phase (subscript o), and Z^{5-} is the free DTPA ions. Therefore, the separation factor during equilibrium in a Ln^{3+}(A)-Ln'^{3+}(B) pair system, can be described by Eq. 3, as shown in Appendix.

$$\beta_e^{\text{A-B}} = (K_{ex,A}/K_{ex,B})(K_{l,B}/K_{l,A}) = (D_e^{A}/D_e^{B})(K_{l,B}/K_{l,A}). \tag{3}$$

Thus, in the Y^{3+}(A)-Er^{3+}(B) system, $\beta_e^{\text{Y-Er}}$ was calculated to be 3.0 by substituting the values of D_e^{Y}/D_e^{Er}, (0.62[4]) and $K_{l,Er}/K_{l,Y}$, (4.9[3]) into Eq. 3. This fact tells us that the separation factor, ($\beta^{\text{Y-Er}}$), begins to decrease at the time, (t), at which the maximum value is obtained, and should approach 3.0 during the equilibrium state (shown in Fig. 2) if extraction proceeds to equilibrium. In the second place, in order to obtain information about the time at which the maximum value of the separation factor is obtained, the kinetics of the extraction was carried out according to the rate law of first-order reaction:

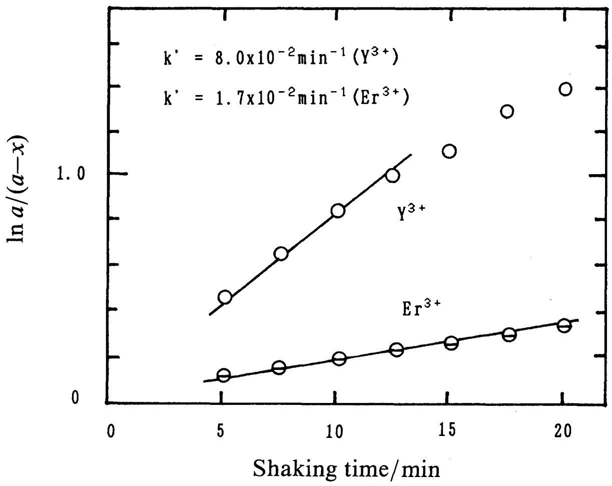

Fig. 3. Relationships between $\ln a/(a-x)$ and the shaking time (t) for yttrium ions (○) and erbium ions (⊖).

$$V = -\mathrm{d}[\mathrm{Ln^{3+}}]_{T,a}/\mathrm{d}t = \mathrm{d}[\mathrm{Ln^{3+}}]_o/\mathrm{d}t = k'[\mathrm{Ln^{3+}}]_{T,a},$$

or

$$\mathrm{d}x/\mathrm{d}t = k'(a-x), \tag{4}$$

where subscript T represents the total concentration of rare earth ions, and subscripts a and o denote an aqueous phase and an organic phase, respectively; a is the total concentration of the Ln^{3+} species initially charged to the aqueous phase, x is the concentration of Ln^{3+} ions extracted in the organic phase at time, (t), and k' is the rate constant. Based on Eq. 4, $\ln a/(a-x)$ was plotted vs. time, (t) for both ions by the use of data in Table 1, as is shown in Fig. 3. It was found that the relationship for both ions is given by almost straight lines passing through the origin. The rate equation should thus be given by Eq. 4. The extraction rate constants, (k'), obtained from the slopes of the lines were 8×10^{-2} min^{-1} (Y^{3+}) and 1.7×10^{-2} min^{-1} (Er^{3+}), respectively. The slope in the Y^{3+} ion system deviated at about 20 min. This fact suggests that this deviation must be due to a backward reaction,[5] also indicating that the time giving a maximum separation factor may be after about 20 min. The phenomenon showing a maximum in the separation factor must therefore be due to a difference in the dissociation rate of the Ln–DTPA complex expressed in Eq. 2 and in the back-extraction rate of $Ln(HX_2)_3$, expressed in Eq. 1 for both ions. Teramoto et al.,[2] however, reported that yttrium ions were extracted faster than 5.5 times that of erbium ions with DTPA and bis(2,4,4-trimethylpentyl)phosphinic acid/butane system. But they[2] said only that their result would be due to the

Table 2. Extraction Conditions of Yttrium Ion from Rare Earth Chloride Solution (60% as Y_2O_3) in Order to Obtain Y_2O_3 of 99.9% Purity by Using Both the Equilibrium and Nonequilibrium (DTPA System) Methods with B2EHPA/Kerosine, and the Values of the Average Molecular Weights (M_{av}) of Rare Earth Oxides Extracted at Each Extraction Stage

Extraction method and its stage	Feed solutions			Shaking time	Av. molecular weight M_{av}
	$[Ln_2O_3]/(g/l)$	pH	R[c]	min	
A[a]-1	34.0	0.2	0	10	126.5
B[b]-1	12.0	8.6	1.1	10	120.0
B[b]-2	11.8	8.6	1.1	10	118.0
B[b]-3	11.5	8.6	1.1	10	115.0
B[b]-4	11.4	8.6	1.1	20	114.6
B[b]-5	11.4	8.6	1.1	20	114.5
B[b]-6	11.4	8.6	1.1	20	114.5
B[b]-7	11.4	8.6	1.1	20	113.6

a) Separation process for light rare earth ions (La—Gd) by the conventional equilibrium extraction method, S/F=1.0. b) Separation process for middle-heavy rare earth ions (Tb—Lu) by our nonequilibrium extraction method, S/F=1.0. c) $[DTPA]_T/[Ln^{3+}]_T$ molar ratio in the feed solutions.

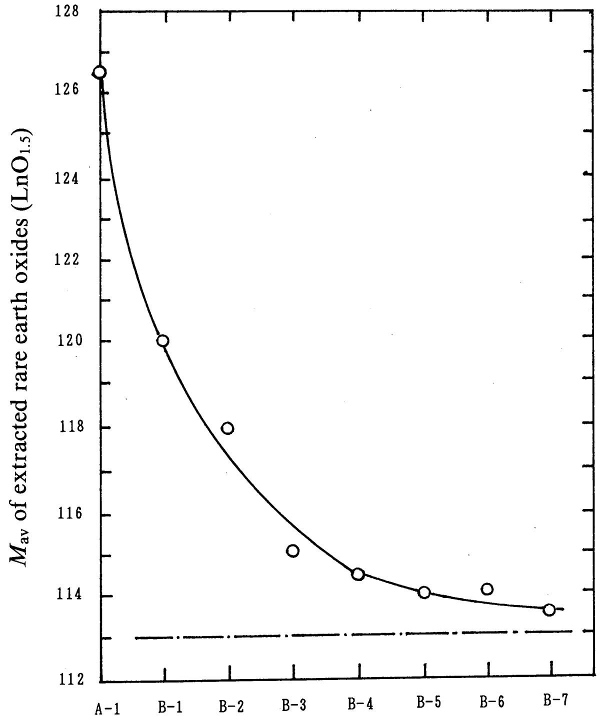

Fig. 4. Relationships between the average molecular weight (M_{av}) in rare earth oxides ($LnO_{1.5}$) extracted at each extraction stage and the number of the stage; symbols A and B on the horizontal axis represent the process for separating light rare earth ions and that of middle-heavy rare earth ions, respectively; the broken line indicates M_{av} of pure $YO_{1.5}$.

dissociation reaction of the $Y^{3+}(Er^{3+})$–DTPA complex, and did not find any phenomenon showing a maximum in the separation factor under their extraction system.

Yttrium Oxide of a 60% Purity System: The extraction conditions in the separation of yttrium and middle-heavy rare earth ions from light rare earth ions (A-1) and in the separations of yttrium ions from middle-heavy rare earth ions (from B-1 to B-7) are summarized in Table 2. The experimental values of the average molecular weights (M_{av}) of the rare earth oxides extracted at each extraction stage (A-1 and B-1—B-7) are also shown in Table 2. The relationship between the extraction stage and the values of M_{av} is given in Fig. 4, showing that the purity of yttrium oxide in the extracted rare earth oxides becomes higher with an increase of the extraction stage (from B-1 to B-7). Supposing that the molecular weight of the other impure rare earth oxides ($Ln'O_{1.5}$) is 170, the purity of yttrium oxide at the 5th (B-5) and 7th (B-7) stage is estimated to be as 73 and 99%, respectively.

Table 3. Concentrations of Rare Earth Impurities (Ln'_2O_3) in Purified Y_2O_3 at the 5th and 7th Stages (B-5 and B-7 on the Table 2)

Elements of impure rare earth (Ln')	Contents of impure rare earth oxides (Ln'_2O_3)/ppm[a]	
	5th (B-5)	7th (B-7)
Tb	>100	30
Dy	>100	100
Ho	90	20
Er	>100	100
Yb	10	30
Lu	—	<20
Ce	>500	>500
La	>500	>500

a) >100 represents 100 ppm$<Ln'_2O_3<$500 and >500 does 500 ppm$<Ln'_2O_3<$1000 ppm.

The concentrations of impure rare earth oxides in purified yttrium oxide at the 5th and 7th stages were then determined by spark-source emission spectrometry. These values are tabulated in Table 3. It was estimated that the purity of yttrium oxide at the 7th stage is 99%. Therefore, the above-mentioned estimation concerning the purity must be true.

It is probable that the purity of yttrium oxide must become 99.9% at the 7th stage if the light rare earth ions

(La, Ce, etc.) are almost completely removed in procedure (A), because the summed amount of the impurities of oxides from Tb to Lu can be calculated to be about 330 ppm. It is generally said that removing light rare earth ions is easy by using the counter-current multistage (about eight stages) extraction method with the B2EHPA solvent because of its large separation factor[4] between yttrium and these ions at the equilibrium state. Furthermore, the above-mentioned procedure to remove light rare earth ions is considered to be essential in our system, because the selective extraction of La and Ce ions must be mainly due to a difference in the dissociation rate between La(Ce)–DTPA complexes and the Y–DTPA complex, as mentioned regarding Y–Er system. This concept is acceptable because the formation constant[3] of the Y–DTPA complex ($10^{22.05}$) is larger than those[3] of the La–DTPA complex ($10^{19.48}$) and the Ce–DTPA complex ($10^{20.5}$). Further, the extraction behavior of Tb, Dy, Ho, Yb, and Lu ions can be easily understood, since these ions have larger values of the formation constant[3] with DTPA than that of yttrium ion as follows: Tb–DTPA ($10^{22.71}$), Dy–DTPA ($10^{22.82}$), Ho–DTPA ($10^{22.78}$), Yb–DTPA ($10^{22.62}$), and Lu–DTPA ($10^{22.44}$). The extraction data shown in Table 3 have thus been explained. Furthermore, the separation factors of yttrium ions (A) to these ions (B) at equilibrium can be calculated from Eq. 3 as follows: La(40), Ce(180), Tb(49), Dy(26), Ho(8), Yb(0.3), and Lu(0.1). Thus, if the extraction time is much longer than the employed 20 min at the 7th stage, it is predicted that the concentration of the La and Ce ions in yttrium oxide is lower and, on the contrary, those of the Yb and Lu ions are higher compared with those shown in Table 3. However, those of Tb, Dy, and Ho can not ne predicted, since the maximum values of the separation factor of yttrium ions to these ions are not yet available.

Appendix

Separation factor $\beta_e^{\text{Ln-Ln}'}$ under equilibrium state:

$$\text{Ln}^{3+} + 3(\text{H}_2\text{X}_2)_{(o)} \overset{K_{ex}}{=} \text{Ln}(\text{HX}_2)_{3(o)} + 3\text{H}^+, \qquad (1)$$

$$\text{Ln}^{3+} + \text{Z}^{5-} \overset{K_1}{=} \text{LnZ}^{2-}. \qquad (2)$$

Supposing that the equilibrium reactions expresssed in Eqs. 1 and 2 are established in the Ln^{3+}(A)–Ln'^{3+}(B) pair system, the distribution factors (D'^{A}_{e} and D'^{B}_{e}) of both ions can be described as follows:

$$D'^{A}_{e} = [\qquad [\text{A}] + [\text{AZ}^{2-}]\}^{-1}, \qquad (3)$$

$$D'^{B}_{e} = [\text{B}(\text{HX}_2)_3]_{(o)}\{[\text{B}] + [\text{BZ}^{2-}]\}^{-1}, \qquad (4)$$

and

$$\beta_e^{A-B} = \{[\text{A}(\text{HX}_2)_3]_{(o)}([\text{B}] + [\text{BZ}^{2-}])\} + \{[\text{B}(\text{HX}_2)_3]_{(o)}([\text{A}] + [\text{AZ}^{2-}])\}^{-1}. \qquad (5)$$

Then, K_{ex} and K_1 for A and B ions, are given as follows:

$$K_{ex,A} = [\text{A}(\text{HX}_2)_3]_{(o)}[\text{H}^+]^3/[\text{A}][\text{H}_2\text{X}_2]^3, \qquad (6)$$

$$K_{ex,B} = [\text{B}(\text{HX}_2)_3]_{(o)}[\text{H}^+]^3/[\text{B}][\text{H}_2\text{X}_2]^3, \qquad (7)$$

$$K_{1,A} = [\text{AZ}^{2-}]/[\text{A}][\text{Z}^{5-}], \qquad (8)$$

$$K_{1,B} = [\text{BZ}^{2-}]/[\text{B}][\text{Z}^{5-}]. \qquad (9)$$

By substituting Eqs. 6, 7, 8, and 9 into Eq. 5, we obtain

$$\beta_e^{A-B} = (K_{ex,A}/K_{ex,B})(1+K_{1,B}[\text{Z}^{5-}])(1+K_{1,A}[\text{Z}^{5-}]). \qquad (10)$$

Since the values of $K_{1,B}[\text{Z}^{5-}]$ and $K_{1,A}[\text{Z}^{5-}]$ are estimated to be much larger than 1.0 by using our experimental initial conditions, Eq. 10 can be approximately represented by

$$\beta_e^{A-B} = (K_{ex,A}/K_{ex,B})(K_{1,B}/K_{1,A}) = (D_e^A/D_e^B)(K_{1,B}/K_{1,A}). \qquad (11)$$

Since the items of $[\text{H}^+]$ and $[\text{H}_2\text{X}_2]$ in Eqs. 6 and 7 are common for both ions, they can be cancelled out in Eq. 11, so that ($K_{ex,A}/K_{ex,B}$) can be represented as (D_e^A/D_e^B).

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