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Study of the Mixed Ligand Complexes of Heavy Rare Earth Elements by Electromigration

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The formation of the mixed ligand complexes of heavy rare earth elements with α-hydroxyisobutyric acid (AHIB or HA) and nitrilotriacetic acid (NTA or H_3L) was studied by electromigration. The equations expressing the zone mobility as a function of the concentrations of the two ligands were derived with or without the mixed ligand complexes, MLA^-. The experimental results showed that the MLA^- complexes were formed. The formation constants for the Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), and Lu(III) complexes were determined. The results obtained by using the two series of solutions, with varying $[L^{3-}]$ at a constant $[A^-]$ and with varying $[A^-]$ at a constant $[L^{3-}]$, were in good agreement. The stability trend was in an ordinary decreasing sequence of: Lu>Yb>Tm>Er>Ho>Dy>Tb.

The separation factor, the difference in the zone mobilities of two adjacent rare earth elements, is enhanced by the consecutive formation of complexes, ML_n.[1] This enhancement becomes more appreciable the closer the first and the second formation constants are to each other. This means that when various species, such as M, ML, and ML_2, are coexisting, more effective separation can be expected. If some mixed ligand complexes, such as MLA, were to be formed with another ligand A other than the binary complexes, ML_n, separation would be more improved. Therefore, it seems that a system containing two different ligands is more favorable for separating heavy rare earth elements than the conventional system. In this case, however, it is assumed that the formation constants of the mixed ligand complexes increase with increasing atomic number as observed in the case of the binary complexes, ML_n. To justify this assumption, it is necessary to obtain the data on the formation of the mixed ligand complexes of the heavy rare earth elements.

This work includes the results of a study on the mixed ligand complexes of the heavy rare earth elements with AHIB and NTA by paper electromigration.

Experimental

All chemicals used were of G.R. grade. The rare earth nitrate solutions of 2.0×10^{-2} mol dm^{-3} were prepared by dissolving the respective oxides in nitric acid. Mixed sample solutions of Tb(III), Dy(III), Er(III), and Yb(III), and of Tb(III), Ho(III), Tm(III) and Lu(III) at the same concentration of 1.5×10^{-4} mol dm^{-3} (pH≈1) were prepared. The other solutions were prepared as follows. Either AHIB(HA) or NTA (H_3L) was dissolved in chloroacetate buffer solution of pH 2.0 to give a concentration from 0.1 to 1.0 mol dm^{-3} or 10^{-3} to 10^{-2} mol dm^{-3}, respectively. By using the acid dissociation constants of AHIB[2] ($pK_{HA}=3.79$) and NTA[3] ($pK_{H_3L}=1.75$, $pK_{H_2L^-}=2.47$ and $pK_{HL^{2-}}=9.71$), the ligand ion concentrations are calculated to be $1.33-13.3\times10^{-3}$ mol dm^{-3} (A^-) and $2.33—23.3\times10^{-12}$ mol dm^{-3} (L^{3-}). The zone mobilities calculated by using these values of $[A^-]$ and $[L^{3-}]$ were found to agree well with the observed ones. In these concentration ranges, successive formation of the AHIB complexes proceeds, while that of the NTA complexes does not. The final ionic strength was adjusted to 0.1 with sodium chloride. In NaCl solution of 0.1 mol dm^{-3}, no appreciable complex formation of rare earth elements with chloride was observed.

Paper electromigration was carried out as described previously.[4]

Results and Discussion

The Effect of Two Ligands on the Zone Mobility of the Heavy Rare Earth Elements. At first, the experiment was carried out by using AHIB and NTA separately; the results are shown in Figs. 1a(AHIB) and 1b(NTA). In the ligand concentration ranges used here, the predominant complex species formed with NTA is ML, that is, the range of $[L^{3-}]$ is too low to form the ML_2 complex. On the other hand, various forms of complexes (MA^{2+}, MA_2^+, MA_3, and MA_4^-) are formed with increasing concentration of AHIB. In both cases, the zone mobility of each rare earth becomes close to each other with increasing ligand concentrations, but

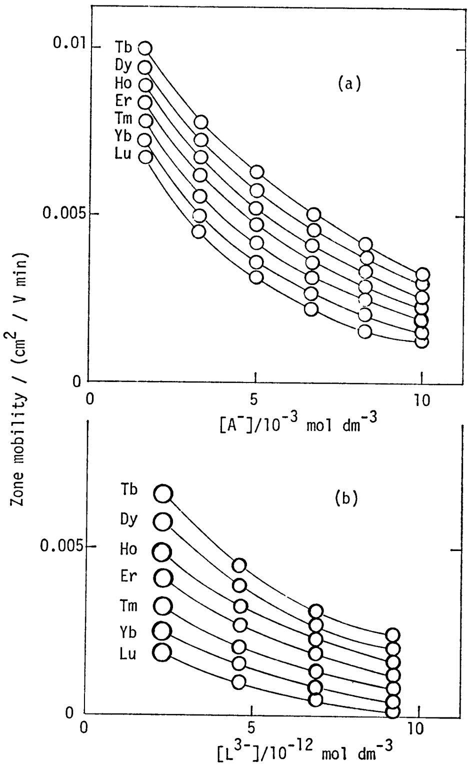

Fig. 1. Plots of the zone mobility *vs.* $[A^-]$(1a) or $[L^{3-}]$-(1b).

the range of AHIB concentration suitable for separation is broader than that of NTA. By lowering the concentration of NTA, the difference in the zone mobility becomes larger than that in the case of AHIB, but the zone width also becomes larger. This would be due to the large difference in the mobility between M^{3+} and ML. It may thus be concluded that AHIB generally gives better separation than NTA.

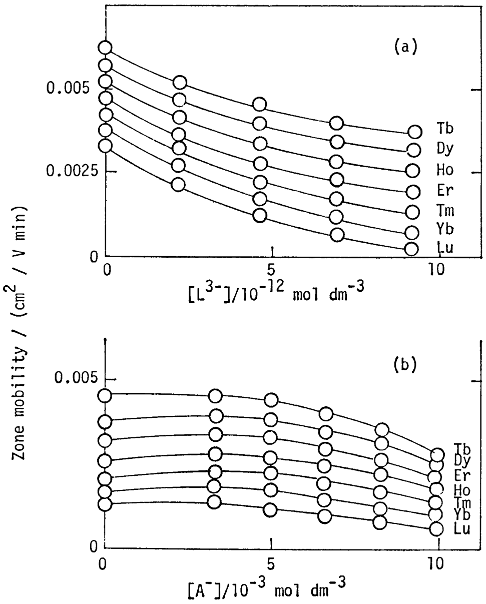

Fig. 2. (a): Plots of the zone mobility *vs.* $[L^{3-}]$ at $[A^-]=5.0\times10^{-3}$ mol dm^{-3}. (b): Plots of the zone mobility *vs.* $[A^-]$ at $[L^{3-}]=4.7\times10^{-12}$ mol dm^{-3}.

To examine the effect of mixed complexing agents on the zone mobility, experiments were done using mixtures of AHIB and NTA as electrolyte solutions. The results are shown in Fig. 2; $[L^{3-}]$ was varied at a constant $[A^-]$(2a) and $[A^-]$ was varied at a constant $[L^{3-}]$(2b). The zone location is found to be much more affected by increasing $[L^{3-}]$ than by increasing $[A^-]$. The formation of the neutral complexes with NTA considerably alters the zone mobility. In general, the zone is located between the limits found in cases where AHIB or NTA is separately used at the same concentration. With increasing concentration of AHIB, however, the zone mobility becomes lower than those in either case where the respective agent is separately used (Fig. 2b). This suggests that some mixed ligand complexes of the rare earth elements with NTA and AHIB, possibly as anionic species, might be formed, and that the zone mobility of each element is lowered.

Estimation of the Formation Constants of the Mixed Ligand Complexes. If there are no mixed ligand complexes in solutions containing M, H_3L, and HA, the species in equilibrium would be M, ML, MA, MA_2, MA_3, and MA_4 under the present experimental conditions (the charges are omitted for simplicity). When the equilibria among these species are rapidly attained under the electric field, the zone mobility u_{AL} can be related to the mobility and the amount of each species.[1,4,5)

$$\begin{aligned} u_{AL}([M]+[ML]+[MA]+[MA_2]+[MA_3]+[MA_4]) &\\ = u_M[M] + u_{ML}[ML] + u_{MA}[MA] + u_{MA_2}[MA_2] &\\ + u_{MA_3}[MA_3] + u_{MA_4}[MA_4], &\qquad (1) \end{aligned}$$

where u means the mobility of the respective species. Using the overall formation constants of the above complexes, β's, Eq. 1 can be brought into the form:

$$\begin{aligned} u_{AL}(1+\beta_{ML}[L]+\beta_{MA}[A]+\beta_{MA_2}[A]^2+\beta_{MA_3}[A]^3+\beta_{MA_4}[A]^4) &\\ = u_M + u_{ML}\beta_{ML}[L] + u_{MA}\beta_{MA}[A] + u_{MA_2}\beta_{MA_2}[A]^2 &\\ + u_{MA_3}\beta_{MA_3}[A]^3 + u_{MA_4}\beta_{MA_4}[A]^4, &\qquad (2) \end{aligned}$$

where $\beta_{ML}=[ML]/([M][L])$ and $\beta_{MA_n}=[MA_n]/([M][A]^n)$.

When H_3L or HA is separately used at the same concentrations as the above case, the appropriate following equation is applicable:

$$u_L(1+\beta_{ML}[L]) = u_M + u_{ML}\beta_{ML}[L] \qquad (3)$$

$$\begin{aligned} u_A(1+\beta_{MA}[A]+\beta_{MA_2}[A]^2+\beta_{MA_3}[A]^3+\beta_{MA_4}[A]^4) &\\ = u_M + u_{MA}\beta_{MA}[A] + u_{MA_2}\beta_{MA_2}[A]^2 + u_{MA_3}\beta_{MA_3}[A]^3 &\\ + u_{MA_4}\beta_{MA_4}[A]^4, &\qquad (4) \end{aligned}$$

where u_L or u_A is the zone mobility given by using H_3L or HA separately. Combining Eq. 2 with Eqs. 3 and 4, we obtain

$$\begin{aligned} (u_{AL}-u_L)(1+\beta_{ML}[L]) + (u_{AL}-u_A)(\beta_{MA}[A]+\beta_{MA_2}[A]^2 &\\ +\beta_{MA_3}[A]^3+\beta_{MA_4}[A]^4) + u_M - u_A = 0. &\qquad (5) \end{aligned}$$

The left hand side of Eq. 5 can be calculated using the values of u_{AL}, u_L, u_A, and u_M obtained experimentally, as well as the overall formation constants of the respective complexes reported in the literature. The experimental results showed that Eq. 5 does not become zero, except for the case of Tb(III) at low values of [L] and [A]. Negative values which decrease with increasing [L] and [A] are obtained for all the elements. This indicates that the values of u_{AL} observed are smaller than those predicted by Eq. 5, which was derived by assuming that no mixed ligand complexes were formed. Hence, some mixed ligand complexes with negative charges other than the above complexes should be present in the mixed ligand solutions.

Assuming the mixed ligand complex to be MLA^-, Eq. 2 can be modified to the form:

$$\begin{aligned} u_{AL}(1+\beta_{ML}[L]+\beta_{MA}[A]+\beta_{MA_2}[A]^2+\beta_{MA_3}[A]^3+\beta_{MA_4}[A]^4 &\\ +\beta_{MLA}[L][A]) = u_M + u_{ML}\beta_{ML}[L] + u_{MA}\beta_{MA}[A] &\\ + u_{MA_2}\beta_{MA_2}[A]^2 + u_{MA_3}\beta_{MA_3}[A]^3 + u_{MA_4}\beta_{MA_4}[A]^4 &\\ + u_{MLA}\beta_{MLA}[L][A], &\qquad (6) \end{aligned}$$

where u_{MLA} is the mobility of MLA and $\beta_{MLA}=[MLA]/([M][L][A])$. Combining Eq. 6 with Eqs. 3 and 4, we obtain

$$\begin{aligned} (u_{AL}-u_L)(u_{MLA}-u_{AL})^{-1}(1+\beta_{ML}[L])+(u_{AL}-u_A)(u_{MLA}-u_{AL})^{-1} &\\ \times (\beta_{MA}[A]+\beta_{MA_2}[A]^2+\beta_{MA_3}[A]^3+\beta_{MA_4}[A]^4) &\\ + (u_M-u_A)(u_{MLA}-u_{AL})^{-1} = \beta_{MLA}[L][A]. &\qquad (7) \end{aligned}$$

If u_{MLA} is known, the left hand side of Eq. 7 can be obtained as a function of the product of [L] and [A]. If a linear relation is obtained between the left hand side of Eq. 7 and the product of [L] and [A], the formation constant of MLA^- can be determined from the slope of the line.

Various values have been reported for the formation constants of the rare earth complexes with NTA and AHIB. We tried to find the most suitable values by comparing the zone mobilities u_L and u_A calculated from Eqs. 3 and 4 with the observed ones. To estimate the mobilities of various complexes required for calculation, $u_{MA}{}^{2+}=0.007$ cm^2/V min[4] and $u_{ML_2}{}^{-}=0.012\pm0.001$ cm^2/V min measured at $I=0.1$ were used. When we consider that the value for $u_{MA}{}^{2+}$ was measured with the presence of MA_2^+, the mobility is roughly proportional to the charge of the species. Hence, the following values might be given for the mobility of each species: $u_{ML}=0$, $u_{MA}{}^{2+}=0.008$, $u_{MA_2}{}^{+}=0.004$, $u_{MA_3}=0$, $u_{MA_4}=-0.004$, and $u_{MLA}{}^{-}=-0.004$ cm^2/V min. The calculation of u_L and u_A was made by using the reported values for the formation constants of the rare earth complexes with NTA[6] and AHIB[7] determined at an ionic strength of 0.1. For all the elements the values calculated for u_L well agreed with those observed, whereas there were appreciable differences between the calculated and observed values of u_A. The values of u_A calculated by using another data for β_{MA_n} at higher ionic strength of 0.2[8] well agreed with the observed ones.

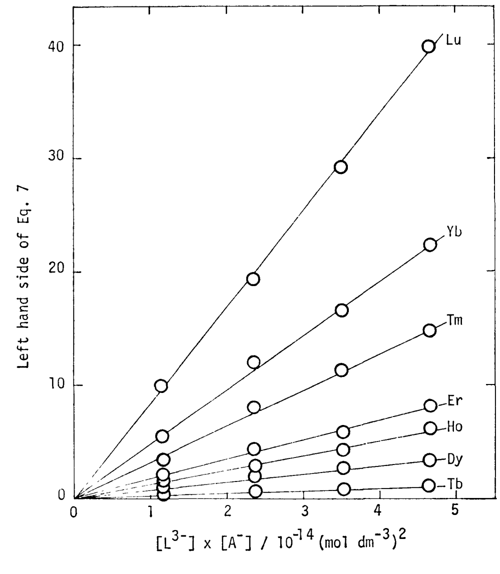

Fig. 3. Plots of the left hand side of Eq. 7 *vs.* $[L^{3-}]\times[A^-]$ at $[A^-]=5.0\times10^{-3}$ mol dm^{-3}.

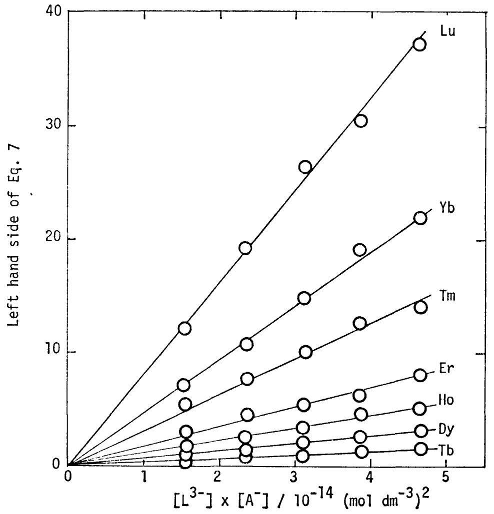

Fig. 4. Plots of the left hand side of Eq. 7 *vs.* $[L^{3-}]\times[A^-]$ at $[L^3]=4.7\times10^{-12}$ mol dm^{-3}.

Using the values of β_{ML},[6] β_{MA_n},[8] and u_{MLA} estimated above, the calculation of the left hand side of Eq. 7 was made. The results as a function of the product of [L] and [A] are shown in Figs. 3 and 4, where [A] or [L] is respectively kept constant. For all the elements, the plots in either Fig. 3 or 4 exhibit linear relations, indicating that the MLA^- complex is present in a mixture of NTA and AHIB solutions at the ligand concentrations studied. The values of β_{MLA^-} for these rare earths were obtained from the slopes of the lines in both Figs. 3 and 4, as listed in Table 1. The two values obtained from Figs. 3 and 4 for each element are in good agreement. The stability trend was in an ordinary sequence, as expected. To obtain further information on the stability of the MLA^- complexes, the values of K^{ML}_{MLA} and K^{MA}_{MLA}, the equilibrium constants of Eqs. 8 and 9 and those of Δ log K and log X defined by Sigel[9] (Eqs. 10 and 11) were calculated:

$$ML + A = MLA \quad k^{ML}_{MLA} = \beta_{MLA}/\beta_{ML}{}^{6)} \tag{8}$$

$$MA + L = MAL \quad k^{MA}_{MAL} = \beta_{MLA}/\beta_{MA}{}^{8)} \tag{9}$$

$$\Delta \log k = \log k^{ML}_{MLA} - \log \beta_{MA}{}^{8)} = \log k^{MA}_{MAL} - \log \beta_{ML}{}^{6)} \tag{10}$$

$$\log X = 2 \log \beta_{MLA} - (\log \beta_{ML_2}{}^{6)} + \log \beta_{MA_2}{}^{8)}). \tag{11}$$

These results are also given in Table 1. For all the elements, Δ log K values are nearly the same but log X

TABLE 1. FORMATION CONSTANTS OF THE MIXED LIGAND COMPLEXES (MLA^-) OF HEAVY RARE EARTHS AT $I=0.1$(NaCl) AND AT 25 °C

Element	log β_{MLA^-}		log K^{ML}_{MLA}	log K^{MA}_{MAL}	Δ log K	log X
	A[a]	B[b]				
Tb(III)	13.4	13.5	1.86	10.53	−1.06	0.69
Dy(III)	13.8	13.8	2.06	10.86	−0.88	1.00
Ho(III)	14.1	14.0	2.15	11.07	−0.83	1.31
Er(III)	14.2	14.2	2.17	11.19	−0.84	1.41
Tm(III)	14.5	14.5	2.28	11.40	−0.82	1.76
Yb(III)	14.7	14.7	2.30	11.57	−0.83	1.88
Lu(III)	14.9	14.9	2.41	11.72	−0.77	1.84

a) Obtained from the plots in Fig. 3. b) Obtained from the plots in Fig. 4.

Table 2. Differences in logarithms of formation constants of the binary and the ternary complexes between adjacent rare earths

Element M_1–M_2	$\log K(M_1) - \log K(M_2)$					
	$K=K^{M}_{MA}$[8]	$K=K^{M}_{ML}$[6]	$K=K^{MA}_{MA_2}$[8]	$K=K^{ML}_{ML_2}$[6]	$K=K^{MA}_{MAL}$	$K=K^{ML}_{MAL}$
Dy–Tb	0.02	0.15	0.19	0.03	0.33	0.20
Ho–Dy	0.04	0.16	0.05	−0.06	0.21	0.09
Er–Ho	0.03	0.13	0.13	−0.09	0.12	0.02
Tm–Er	0.09	0.19	0	−0.03	0.21	0.11
Yb–Tm	0.03	0.18	0.01	0.06	0.17	0.02
Lu–Yb	0.05	0.09	0.17	0.13	0.15	0.11

increases roughly with atomic number, indicating that the heavier the element is, the more the formation of the MLA^- complex is promoted.

Table 2 shows the differences in logarithms of the formation constants of the binary[6,8] and the ternary (Table 1) complexes between adjacent rare earth elements. There are considerable differences in both $\log K^{MA}_{MAL}$ and $\log K^{ML}_{MLA}$ between adjacent elements, suggesting that successive formation of the MLA complexes gives larger differences in the zone mobilities of adjacent elements. On the other hand, formation of the ML_2 complexes reduces the effect on the separation of the metals from dysprosium to thulium, since $K^{ML}_{ML_2}$ for these metals decrease with atomic number. Separation of the heavy rare earth elements would be improved by the formation of the MLA complexes other than the binary complexes ML and MA_n.

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