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The Effect of Consecutive Complex Formation on the Separation of Rare Earths by Electromigration

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The effect of a complexing agent with which rare earths consecutively form complexes on the separation of an adjacent pair of rare earths by electromigration was investigated. By assuming the complexes ML and ML_2 to be formed, the relation of the separation factor, the difference in the zone mobility of the two rare earths, to the ligand-ion concentration was derived and examined for the separation of the La-Ce and Ce-Pr pairs by using nitrilotriacetic acid (NTA), which is known to form the ML and ML_2 complexes with rare earths. It is found that the separation factor is affected not only by the difference in the first (k_1) or the second (k_2) consecutive formation constant of the two elements to be separated, but also by the value of the k_1/k_2 ratio.

In a previous paper,[1] it was reported that the separation of an adjacent pair of rare earths by using a complexing agent in electromigration is considerably influenced by the ligand-ion concentration and that when only one complex, ML, is assumed to be formed, the optimum ligand-ion concentration for their separation can be predicted from the values of the formation constants of the complexes. It was also suggested that, in the case where the consecutive formation of complexes, ML, $ML_2, \cdots, ML_n$, takes place, the range of ligand concentrations suitable for separation becomes wider compared with the case where only one complex is formed. However, the previous work was not extended beyond qualitative discussions. It appears to require further investigation for verification.

This paper will deal with the effect of a complexing agent with which rare earths consecutively form complexes on the separation of an adjacent pair of rare earths by electromigration. When two complexes, ML and ML_2, are assumed to be formed, the relation of the separation factor to the ligand-ion concentration has been derived and examined for the separation of the La-Ce and Ce-Pr pairs by using nitrilotriacetic acid (NTA), which is known to form the ML and ML_2 complexes with rare earths.

The Separation Factor for Two Kinds of Rare Earths. When the ML and ML_2 complexes are consecutively formed, the equilibria in solution can be expressed as follows:

$$M + L = ML \qquad (1)$$

$$ML + L = ML_2 \qquad (2)$$

where the charges are omitted for the sake of simplicity. The equilibrium constant of each process, *i.e.*, the first (k_1) and second (k_2) consecutive formation constants, are given by $k_1=[ML]/([M][L])$ and $k_2=[ML_2]/([ML][L])$. When the two species, M and ML, are equilibrated, the equation expressing the zone

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[1] E. Ohyoshi, This Bulletin, **43**, 1387 (1970).

mobility has previously been derived.[1,2] From a similar point of view, the following equations can be given for the system of the above equilibria, the attainment of which is rapid:

$$u([\mathrm{M}] + [\mathrm{ML}] + [\mathrm{ML}_2]) = u_{\mathrm{M}}[\mathrm{M}] + u_{\mathrm{ML}}[\mathrm{ML}] + u_{\mathrm{ML}_2}[\mathrm{ML}_2] \tag{3}$$

$$u = \frac{u_{\mathrm{M}} + u_{\mathrm{ML}}k_1[\mathrm{L}] + u_{\mathrm{ML}_2}k_1k_2[\mathrm{L}]^2}{1 + k_1[\mathrm{L}] + k_1k_2[\mathrm{L}]^2} \tag{4}$$

where u, u_{M}, u_{ML}, and u_{ML_2} are the mobilities of the zone, M, ML, and ML_2 respectively.

Since the charge of the complex tends to become more and more negative with the progress of the consecutive complex formation, the difference in the zone mobility of the two elements should be taken as the separation factor, S:

$$\begin{aligned} S &= u - u' \\ &= \{(u_{\mathrm{M}} - u_{\mathrm{ML}})(k_1' - k_1)(\mathrm{L}) \\ &\quad + (u_{\mathrm{M}} - u_{\mathrm{ML}_2})(k_1'k_2' - k_1k_2)[\mathrm{L}]^2 \\ &\quad + (u_{\mathrm{ML}} - u_{\mathrm{ML}_2})k_1k_1'(k_2' - k_2)[\mathrm{L}]^3\}/ \\ &\quad \{(1 + k_1[\mathrm{L}] + k_1k_1[\mathrm{L}]^2)(1 + k_1'[\mathrm{L}] + k_1'k_2'[\mathrm{L}]^2)\} \end{aligned} \tag{5}$$

where it is assumed that $u_{\mathrm{M}} = u'_{\mathrm{M}}$, $u_{\mathrm{ML}} = u_{\mathrm{ML}}$, and $u_{\mathrm{ML}_2} = u'_{\mathrm{ML}_2}$. Equation (5) suggests that the greater the difference in the mobility of M, ML, and ML_2, or the greater the difference in the first or the second consecutive formation constants of the two elements, the larger the value of S.

When the values of k_1 and k_1' are much larger than those of k_2 and k_2', Eq. (5) can be simplified to Eq. (6) or (7) in a range of either low or high ligand concentrations.

$$S_{(\mathrm{l})} = \frac{(u_{\mathrm{M}} - u_{\mathrm{ML}})(k_1' - k_1)[\mathrm{L}]}{(1 + k_1[\mathrm{L}])(1 + k_1'[\mathrm{L}])} \tag{6}$$

$$S_{(\mathrm{h})} = \frac{(u_{\mathrm{ML}} - u_{\mathrm{ML}_2})(k_2' - k_2)[\mathrm{L}]}{(1 + k_2[\mathrm{L}])(1 + k_2'[\mathrm{L}])} \tag{7}$$

Equations (6) and (7) exhibit only two species, either M and ML or ML and ML_2, present in the respective range. As was shown by the relation of S to [L] expressed by Eq. (6) presented in the previous paper,[1] $S_{(\mathrm{l})}$ has its maximum at:

$$[\mathrm{L}] = \{1/(k_1k_1')\}^{1/2} \tag{8}$$

An expression of Eq. (7) similar to that of Eq. (6) indicates that if $k_2' > k_2$, $S_{(\mathrm{h})}$ also has its maximum at:

$$[\mathrm{L}] = \{1/(k_2k_2')\}^{1/2} \tag{9}$$

where $\mathrm{d}S_{(\mathrm{h})}/\mathrm{d}[\mathrm{L}] = 0$. Hence, when $k_1 \gg k_2$ and $k_1' \gg k_2'$, S takes two maxima in a range of low or high ligand concentrations.

Experimental

The sample solution was prepared as has been described previously.[1] The concentration of La^{3+}, Ce^{3+}, or Pr^{3+} was 3×10^{-4} M. The electrolyte solutions were prepared as follows. Nitrilotriacetic acid (Dotite NTA), plus a small amount of NaOH, was dissolved in solutions of different pH's (1.86—4.80) to give concentrations from 10^{-3} to 10^{-2} M. Mixtures of 0.05 M HCl and 0.05 M NaCl (pH<2.1), biphthalate buffer solutions (pH 2.2—3.0), and acetate buffer solutions (3.5—4.8) were used to prepare solutions of various concentrations of the nitrilotriacetate ion, $[\mathrm{L}^{3-}]$ ranging from 10^{-12} to 10^{-8} M. Considering the dissociation of NTA, the ionic strength of the solutions was finally adjusted so as to maintain them at 0.05. The chemicals used were of a G. R. grade.

The procedure for paper electromigration was essentially the same as that described previously.[1] In this experiment, the sample was spotted at the center of the paper strip, since the zone may migrate toward either the cathode or the anode, depending on the degree of complex formation. The migrating zone was detected by studying the color reaction with Arsenazo III.

Results and Discussion

The Concentration of NTA. For the rapid attainment on the paper strip of the equilibria expressed by Eqs. (1) and (2), an amount of a complexing agent sufficient to enable us to neglect the amount bound to the metal must be used. By using solutions of the same concentration of the ligand ion, obtained by adjusting the pH, the zone mobility was measured as a function of the total NTA concentration. From the results it was found that, at concentrations above 2.5×10^{-3} M, the mobility was almost constant, but it was lowered at 1.25×10^{-3} M. Hence, NTA concentrations ranging from 2.5×10^{-3} to 1.0×10^{-2} M were used.

Determination of u_{M}, u_{ML}, and u_{ML_2}. Since there is an appreciable difference between the first and the second consecutive formation constants of rare earth-NTA complexes (the value of k_1/k_2 is of the order of 10^3), Eqs. (6) and (7) can be applied in the ranges of both low and high ligand concentrations. The rearrangement of Eqs. (6) and (7) leads to these expressions:

$$u = \frac{1}{k_1[\mathrm{L}] + 1}(u_{\mathrm{M}} - u_{\mathrm{ML}}) + u_{\mathrm{ML}} \tag{6'}$$

$$u = \frac{1}{k_2[\mathrm{L}] + 1}(u_{\mathrm{ML}} - u_{\mathrm{ML}_2}) + u_{\mathrm{ML}_2} \tag{7'}$$

Hence, by plotting u *vs.* $1/(k_1[\mathrm{L}]+1)$ or $1/(k_2[\mathrm{L}]+1)$, the values of u_{M}, u_{ML}, and u_{ML_2} can be obtained from the intercept and slope. The plots of u *vs.* $1/(k_1[\mathrm{L}^{3-}]+1)$ and $1/(k_2[\mathrm{L}^{3-}]+1)$ for lanthanum, cerium, and praseodymium are shown in Figs. 1 and 2, where k_1 and k_2[3] are the first and second consecutive formation constants of the La(III)-, Ce(III)-, and Pr(III)-NTA complexes. The concentration of L^{3-} is calculated by dividing the total concentration of NTA by the α coefficient,[4] which is a function of the pH. The linear relationship obtained in both Figs. 1 and 2, proves that Eqs. (6) and (7) can be applied to these ranges of $[\mathrm{L}^{3-}]$. From the intercept and slope of the lines, the values of u_{M}, u_{ML}, and u_{ML_2} are given as 0.014, 0, and -0.011 cm²/V min respectively. The value of 0 given for u_{ML} is consistent with the fact that the ML

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[2] V. P. Shvedov and A. V. Stepanov, *Radiokhimiya*, **1**, No. 2, 62 (1959).

[3] T. Moeller, and R. Ferris, *Inorg. Chem.*, **1**, 49 (1962).

[4] A. Ringbom, "Complexation in Analytical Chemistry," Translated ed. by N. Tanaka and H. Sugi, Sangyo Tosho Pub. Co., Ltd., Tokyo (1965), p. 35.

complex is a neutral species.

Effect of the Ligand-ion Concentration on the Separation Factor. To verify Eq. (5), the separation of the La-Ce and the Ce-Pr pairs was carried out at various concentrations of the nitrilotriacetate ion, L^{3-}. In Fig. 3, the separation factor, S, the difference in the zone mobilities of lanthanum and cerium or of cerium and praseodymium observed (points) and calculated from Eq. (5) (the solid or dotted line) is given as a function of $[L^{3-}]$. From the fact that the points obtained experimentally are observed to be close to the lines, Eq. (5) is found to be verified. As has been described above, when $k_1 \gg k_2$ as in this case, the plots of S *vs.* $[L^{3-}]$ for both the La-Ce and the Ce-Pr pairs yield curved with two maxima at $[L^{3-}]=2.51\times10^{-11}$ and 2.72×10^{-8} M for the La-Ce pair, and at $[L^{3-}]=1.12\times10^{-11}$ and 8.92×10^{-9} M for the Ce-Pr pair, as calculated by Eqs. (8) and (9) (Fig. 3). These curves show that S varies with the degree of complex formation, that is, as M forms ML, S reaches the first peak and then decreases with a subsequent increase in the fraction of ML; after passing through the minimum where almost all of the metal exists in the form of ML, S again increases with the formation of ML_2, reaches a second peak, and then decreases with the completion of the formation of ML_2.

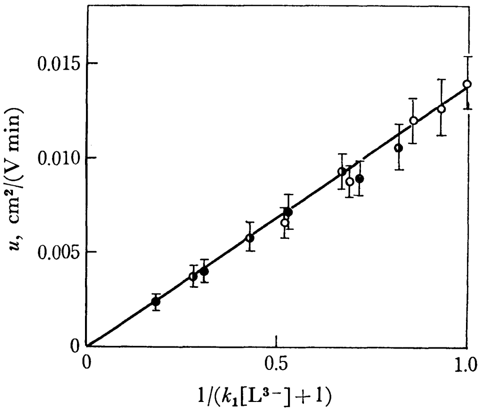

Fig. 1. A plot of u *vs.* $1/(k_1[L^{3-}]+1)$ for La ○, Ce ◑, and Pr ●.
L^{3-} = nitrilotriacetate ion

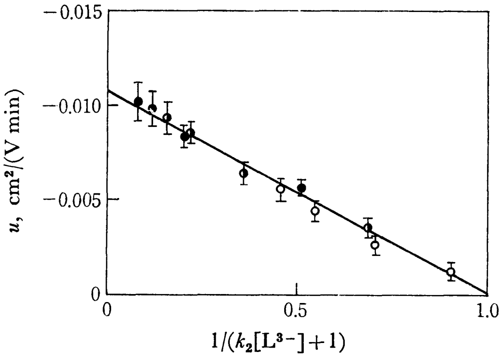

Fig. 2. A plot of u *vs.* $1/(k_2[L^{3-}]+1)$ for La ○, Ce ◑, and Pr ●.
L^{3-} = nitrilotriacetate ion

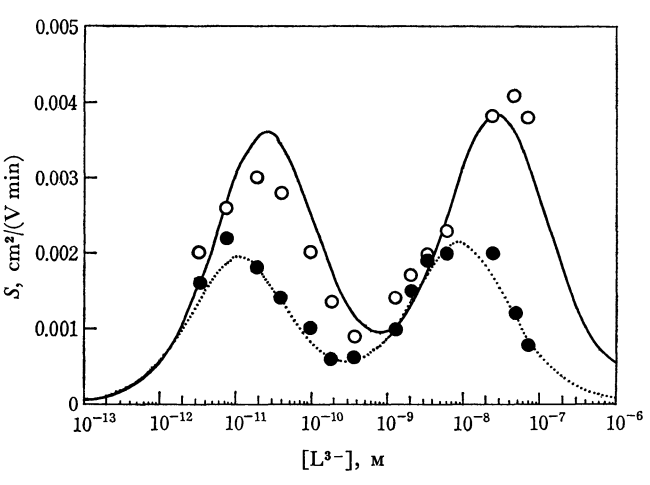

Fig. 3. Plots of S *vs.* $[L^{3-}]$, L^{3-} = nitrilotriacetate ion. Observed values for the La-Ce pair ○ and the Ce-Pr pair ●; Theoretical curves given by Eq. (5) for the La-Ce pair — and Ce-Pr pair …….

In seeking for the effect of the consecutive formation of complexes on the separation factor, we attempt to plot S *vs.* [L], assuming various conditions, in Fig. 4. Curve 1 is a plot of the relation given by Eq. (5) by assuming that $u_{ML}/u_M=0.2$, $u_{ML_2}/u_M=-0.5$, $k_1=10^3$, $k_1'=2k_1$, $k_2=10$, and $k_2'=1.5k_2$. Curves 2 and 3 plot the relations given by the simplified equations (6) and (7) by using the values assumed in curve 1. When we compare these curves, we find that in the range on the lower side of $[L]=\{1/(k_1k_1')\}^{1/2}$ and the higher side of $[L]=\{1/(k_2k_2')\}^{1/2}$ curve 1 agrees well with curves 2 and 3, indicating that only two species, M and ML or ML and ML_2 are present in such ranges. It is noted that, in the range between two maxima where three species M, ML, and ML_2, are coexisting, curve 1 always gives a higher value than those given by curves 2 and 3. This clearly indicates that the formation of both ML and ML_2 serves to enhance the separation factor. To make the three species, M, ML, and ML_2, all present, the value of k_1 must be close to that of k_2. Under the condition assumed in curve 1, if only the k_1/k_2 ratio is varied from 10^2 to 10, the plot

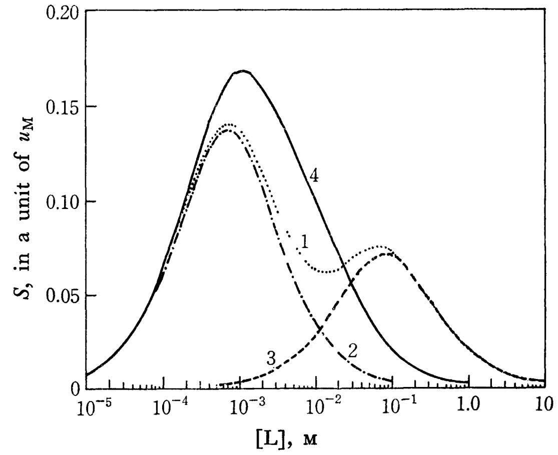

Fig. 4. Effect of the consecutive complex formation on the separation factor.
Curve 1, 4: Plots of S (in a unit of u_M) *vs.* [L] given by Eq. (5) assumed to be $u_{ML}/u_M=0.2$, $u_{ML_2}/u_M=-0.5$, $k_1=10^3$, $k_1'=2k_1$, $k_2'=1.5k_2$, and $k_2=10$ for curve 1 or $k_2=10^2$ for curve 4. Curve 2,3: A plot of $S_{(l)}$ (curve 2) or $S_{(h)}$ (curve 3) *vs.* [L] by using the same values as those in curve 1.

gives curve 4. When we compare curve 1 with curve 4, we find that even when the same difference in the k_1 or k_2 value of two elements is given, the S value is appreciably affected by the ratio of k_1 to k_2. With a reduction in the k_1/k_2 ratio, the two maxima become one, the value of which is considerably enhanced. This suggests that, when the further formation of ML_3, ML_4, $\cdots$, ML_n occurs and when their consecutive formation constants are not very different from each other, the high separation factor may be maintained over a wide range of ligand concentrations.

The above discussion was based on the assumption that $k_1'>k_1$, $k_2'>k_2, \cdots$, $k_n'>k_n$. Hence, when $k_1'>k_1$, $k_2'\simeq k_2, \cdots$, $k_n'\simeq k_n$, we can obtain only the same results as those in the cases when only one complex, ML, is formed.