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Studies on the Separation of Rare Earths. Determination of the Optimum Concentration of Ligand Ion Used in Electromigration

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An attempt to determine the optimum concentration of ligand ion for the separation of adjacent pairs of rare earth elements by electromigration was made using the method employed for the determination of the stability constant of complex. To examine the theory, separation of lanthanum and cerium, and cerium and praseodymium was carried out using α-hydroxyisobutyric acid as a complexing agent. From the results, factors necessary for the separation of all kinds of rare earth elements were discussed.

Studies on the separation of rate earth elements by electromigration have been carried out. Successful results are obtained when α-hydroxyisobutyric acid[1-3] is used as a complexing agent. In most cases, however, the conditions for the separation are arbitrary.

In recent years, the theory of electromigration of metal and complex ions derived by Kiso[4] was applied to the separation of rare earth elements and justified experimentally.[5] Shvedov and Stepanov[6] proposed the method of determination of the stability constant of complex by electromigration. The results obtained were in good agreement with those by potentiometry.

In order to find the optimum condition for the separation based on the difference in the stability of complex of two elements, it is most important to choose a suitable concentration of ligand ion depending on the stability of complexes to be formed. In the present investigation, it is intended to determine the optimum concentration of ligand ion for the separation of rare earth elements using the method proposed by Shvedov and Stepanov which is simpler than that by Kiso. Factors affecting the separation are also discussed.

Determination of the Optimum Concentration of Ligand Ion. When a metal, M, forms a complex, ML, in solution the following equilibrium may be established (the charges are omitted for simplicity):

$$M + L = ML \tag{1}$$

The equilibrium constant of process (1), *i.e.*, stability constant, is expressed by

$$K = \frac{[ML]}{[M][L]} \tag{2}$$

According to Shvedov and Stepanov, when an electric field is applied to such solution, the over all migration of a metal can be expressed as the sum of two components one of which governs the

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[1] K. Buchtela, K. Aitzetmuller and F. Grass, *Atomkernenergie*, **10**, 264 (1965).

[2] K. Aitzetmuller, K. Buchtela and F. Grass, *J. Chromatog.*, **22**, 431 (1966).

[3] K. Aitzetmuller, K. Buchtela and F. Grass, *Anal. Chim. Acta*, **38**, 249 (1967).

[4] Y. Kiso, *J. Sci. Hiroshima Univ.*, **27**, No. 1, 17 (1963).

[5] Y. Kiso, I. Yamada, Y. Yamamoto and M. Shinagawa, This Bulletin, **38**, 695 (1965).

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

transfer in the form of metal ions and the other the transfer in the complex form.

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

where u, u_M and u_{ML} are the mobilities of zone, of metal ion and of complex ion, respectively. Equation (3) can be brought into the form

$$[ML]/[M] = (u-u_M)/(u_{ML}-u) = K[L] \tag{4}$$

From Eq. (4), Shvedov and Stepanov determined the stability constant of the complex ML with measurements of u_M, u_{ML} and u. By rearrangement of Eq. (4), the zone mobility u is given as follows.

$$u = \frac{u_{ML}K[L] + u_M}{1 + K[L]} \tag{5}$$

To separate M_1 from M_2, in the first case where $u_{ML}>0$, *e.g.*, α-hydroxyisobutyric acid, lactic acid, *etc.*, the ratio of zone mobility of each metal u_1/u_2 can be taken as the separation factor S. Hence, it is important to find the condition under which S takes the maximum value. In the case of rare earth elements, the difference in mobility of metal or complex ions of two kinds of element is neglected. Thus we have

$$S = \frac{u_1}{u_2} = \frac{(1+K_2[L])(K_1[L]+u_M/u_{ML})}{(1+K_1[L])(K_2[L]+u_M/u_{ML})} \tag{6}$$

Differentiating with respect to [L], we get

$$\frac{dS}{d[L]} = \frac{(1-u_{ML}/u_M)(K_2-K_1)(1-u_{ML}/u_M K_1K_2[L]^2)}{\{(u_{ML}/u_M K_2[L]+1)(1+K_1[L])\}^2} \tag{7}$$

In the case of $K_2>K_1$, with an increase in [L], S increases and reaches maximum at $dS/d[L]=0$, and then decreases. At $dS/d[L]=0$, we have

$$[L] = \left(\frac{u_M/u_{ML}}{K_1K_2}\right)^{1/2} \tag{8}$$

S takes the maximum value. It can be seen that this concentration of ligand ion is the optimum one for separating M_1 from M_2.

In the second case, $u_{ML}\leqq 0$, *e.g.*, EDTA, NTA, *etc.*, S should be taken as the difference in the zone mobility of two metals. Thus we get

$$S = u_1-u_2 = \frac{u_{ML}K_1[L] + u_M}{1 + K_1[L]} - \frac{u_{ML}K_2[L] + u_M}{1 + K_2[L]} \tag{9}$$

Differentiation of this equation with respect to [L] leads to the expression

$$\frac{dS}{d[L]} = \frac{(u_M-u_{ML})(K_2-K_1)(1-K_1K_2[L]^2)}{\{(1+K_1[L])(1+K_2[L])\}^2} \tag{10}$$

At $dS/d[L]=0$, we obtain

$$[L] = \{1/(K_1K_2)\}^{1/2} \tag{11}$$

S becomes the maximum.

Comparing the two cases, $u_{ML}>0$ and $u_{ML}\leqq 0$, the optimum concentration of ligand ion in the former case is larger than that in the latter (since $u_M/u_{ML}>1$).

Experimental

Materials. Oxides of lanthanum (Mitsuwa Chemical Co. 99.99%) and praseodymium (Katayama Chemical Industries Co., Ltd. 99.9%) were dissolved in nitric acid. The solution of cerium was prepared by heating $Ce(NO_3)_3\cdot 6H_2O$ (Katayama Chemical Industries Co., Ltd. G. R. grade) with hydrogen peroxide in hydrochloric acid. Mixtures of lanthanum and cerium, and cerium and praseodymium at the same concentration of 10^{-3}M were used as samples. α-Hydroxyisobutyric acid (Tokyo Chemical Industry Co., Ltd. G. R. grade) in varying concentration at the constant ionic strength of 0.1 was used as electrolyte solution.

Procedures. A paper strip (Toyo Roshi No. 50 1×20 cm) was uniformly soaked in the electrolyte solution, and excess solution was removed by pressing between sheets of filter paper. The sample (0.005 m*l*) was then spotted at a point 6.5 cm from the end of the anodic side. The paper was set into a migration cell containing carbon tetrachloride as coolant. A potential gradient of 500 V(D.C.)/16 cm was applied for 15—25 min. After the current was switched off, the paper was dried rapidly under an infrared lamp. The migrating zone was detected by color reaction with Arsenazo III.

Results and Discussion

Measurements of u_M and u_{ML}. Equation (5) can be brought into the form

$$u = \frac{1}{K[L]+1}(u_M-u_{ML}) + u_{ML} \tag{12}$$

Hence, the values of u_M and u_{ML} are obtained from the intercept and the slope of a plot of u *vs.* $1/(K[L]+1)$. Figure 1 gives the linear relationship of u to $1/(K[L]+1)$ for lanthanum and cerium using α-hydroxyisobutyric acid, where K[7] is the stability constant of complex LaL or CeL. The concentration of α-hydroxyisobutyrate ion [L] was

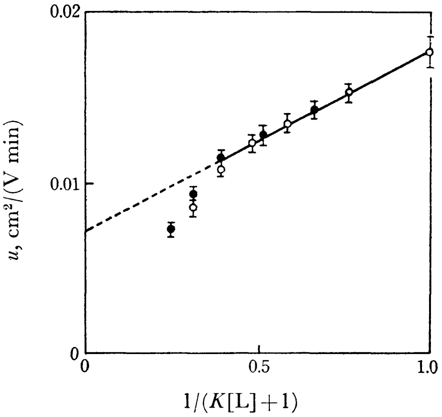

Fig. 1. A plot of u *vs.* $1/(K[L]+1)$ for La ○ and Ce ●.
L=α-hydroxyisobutyrate

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[7] W. R. Stagg and J. E. Powell, *Inorg. Chem.*, **3**, 242 (1964).

calculated from the equation $[L^-]=k_a([HL]_t-[L^-])/[H^+]$, where k_a is the dissociation constant of α-hydroxyisobutyric acid[8] and $[HL]_t$ is the total concentration of α-hydroxyisobutyrate. The deviation of the points from the linearity at high concentration of ligand suggests that the complexes formed are not only ML but also ML_2, ML_3,$\cdots ML_n$ with the increase of concentration of ligand ion. This also accounts for the fact that the zone mobilities of lanthanum are smaller than those of cerium at the same value of $1/(K[L]+1)$ in the range of high concentration of ligand ion (since the value of $k_{1(Ce)}/k_{1(La)}$ is larger than that of $k_{2(Ce)}/k_{2(La)}$, where k_1 and k_2 are the consecutive constants of complexes ML and ML_2). By extrapolation of the straight line in Fig. 1, u_M and u_{ML} are given as 0.0175 and 0.0070 cm²/V min, respectively.

Separation of Lanthanum and Cerium, and Cerium and Praseodymium. From the values of u_M and u_{ML}, the optimum concentration of ligand ion for the separation of two kinds of rare earth elements can be calculated by Eq. (8). For example, the values for separation of lanthanum and cerium, and cerium and praseodymium are given as $(u_M/(u_{ML}\,k_{1(La)}\,k_{1(Ce)}))^{1/2}=8.04\times10^{-3}$M and $(u_M/(u_{ML}\,k_{1(Ce)}\,k_{1(Pr)}))^{1/2}=5.95\times10^{-3}$M. In the vicinity of these values of ligand concentration, the separation of lanthanum and cerium, and cerium and praseodynium was carried out to examine the theory. Figure 2 gives the separation factor S, the ratio of the zone mobility for two elements observed and calculated from Eq. (6) as a function of the concentration of ligand ion. It is found that the separation factor for the La–Ce pair is larger than that for the Ce–Pr pair at any concentration of ligand ion, indicating that the greater the difference of stability of the complex of two kinds of elements, the greater the effect on their separation. It is noted that at low concentration of ligand ion, both observed and calculated S values are close while with the increase of ligand concentration, a discrepancy between them becomes apparent, that is, the observed values do not decrease even after passing beyond the optimum concentration of ligand ion. The consecutive formation of complexes ML_2, ML_3,$\cdots ML_n$, might proceed with the increase of ligand concentration, though the calculated value from Eq. (6) is assumed to form only one complex ML. Thus, it can be seen that the formation of various complexes by the consecutive reaction makes the range of optimum concentration of ligand wider than cases in which only one kind of complex is possible. From this, the factor affecting the separation is not only the difference in the stability of complex but also the possibility to proceed a consecutive formation of complexes.

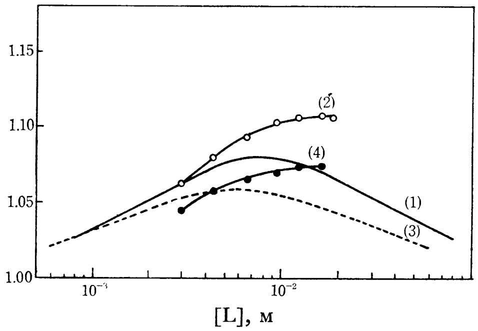

Fig. 2. The separation factor S calculated and observed for La–Ce and Ce–Pr as a function of ligand concentration. (1) calculated, (2) observed for La–Ce; (3) calculated, (4) observed for Ce–Pr.
L=α-hydroxyisobutyrate

In particular, in order to separate all kinds of rare earth elements, it is important to know whether consecutive formation of complexes is taking place or not. If only one complex ML can be formed, the ligand concentration optimum for a pair of light rare earths may greatly differ from that for a pair of heavy rare earths. For example, using the concentration of ligand ion suitable to separate light rare earths, heavy members can not be separated because of the complete formation of complex ML. On the other hand, the concentration suitable to separate the heavy members is so low that the light members remain almost as metal ions. In the case of the consecutive formation of complexes ML, ML_2, $\cdots$ ML_n, as illustrated in Fig. 2, the range of the ligand concentration suitable to separate an adjacent pair is extended toward the higher side because further transformation of ML to ML_2 or of ML_2 to ML_3 gives a different zone mobility to the respective element. Since this extension of the range is observed for any pair of adjacent elements it is probably that a higher part of the range for the last pair of the series (Yb–Lu) and a lower part of that for the first pair (La–Ce) overlap each other. Hence, choosing the ligand concentration at the position of overlapping, it is possible to separate all kinds of rare earths.

Thus, it seems reasonable that the use of α-hydroxyisobutyric acid for the separation of all rare earths gives more successful results as compared with EDTA.

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[8] J. E. Powell and Y. Suzuki, *Inorg. Chem.* **3**, 690 (1964).