The Separation of Rare Earths by Paper Electromigration and Focusing Chromatography

By Yoshiyuki KISO,* Itsuko YAMADA, Yuroku YAMAMOTO
and Mutsuaki SHINAGAWA**

(Received February 21, 1964)

Paper electromigration has been used for the separation of rare earths by Maki,1) Sato et al.,2) Pučar and Jakovac,3) Kawamura,4) and Shvedov and Stepanov.5) Moreover, Schumacher and Friedli6) separated rare earths successfully by a new technique, " electorophoretic ion-focusing," i. e., focusing chromatography. However, comparatively little attention has been paid to the theoretical study. In a previous paper7) one of the present authors has derived a theory of the migration of soluble metal complexes. The present experiment was carried out to examine its applicability to the separation of rare earths by the two procedures of ordinary paper electromigration7) and focusing chromatography.8)

The Theory of Separation by Electromigration

In the paper electromigration, the zone mobility in a complexing agent-background electrolyte solution is given by the following equation7):

$$\begin{aligned} U=1/2\cdot U_{\mathrm{M}}\{&(1+(m-n)/m\cdot r_{\mathrm{MA}}/r_{\mathrm{M}}) \\ &+(1-(m-n)/m\cdot r_{\mathrm{MA}}/r_{\mathrm{M}})\cdot \\ &\tanh\,[2.303/2\cdot(\mathrm{p}K_{\mathrm{MA}}-\mathrm{p}C_{\mathrm{H}_n\mathrm{A}}+p\beta)]\} \qquad (1) \end{aligned}$$

$$\begin{aligned} p\beta=1/(1&+(\mathrm{H})/K_n+(\mathrm{H})^2/k_nk_{n-1}+\cdots \\ &+(\mathrm{H})^n/K_nK_{n-1}\cdots K_1) \end{aligned}$$

where U is the zone mobility; U_{MA}, the mobility of the complex species MA; m, the charge of the single metal ion; n, the all over number of hydrogen ions dissociated from the ligand donor, $\mathrm{H}_n\mathrm{A}$; r_{M} and r_{MA}, the ionic radii of the single and complex species; K_{MA}, the stability constant of the complex species; $C_{\mathrm{H}_n\mathrm{A}}$, the concentration of the complexing agent, and K_1-K_n, the consecutive dissociation constants of the complexing agent.

On moist paper, the zone mobility of ions is less than the mobility in a free solution because of the more tortuous path of the ions through the networks of fiber forming the paper or possibly because of other factors related to the affinity of the ion with the medium.9) This relation is given by:

$$U_{\mathrm{Z}}=\rho U_{\mathrm{F}} \qquad \rho<1 \qquad (2)$$

where U_{Z} is the zone mobility; ρ, the obstructive factor and U_{F}, the mobility in a free solution. The zone mobility, U, in Eq. 1 corresponds to U_{Z} in Eq. 2. In the case of EDTA complexes of rare earth elements, Eq. 1 turns into a simpler form, since $m=3$, $n=4$ and $r_{\mathrm{MA}}\approx r_{\mathrm{M}}$ for rare earth.7)

$$\begin{aligned} U_{\mathrm{RE}}\approx U_{\mathrm{M}}\{1/3+2/3\cdot[&\tanh\,(2.303/ \\ &2\cdot(\mathrm{p}K_{\mathrm{MA}}+\mathrm{p}C_{\mathrm{H_4A}}+p\beta))]\} \qquad (3) \end{aligned}$$

with

$$\begin{aligned} p\beta=1/(1&+(\mathrm{H})/K_4+(\mathrm{H})^2/K_4K_3 \\ &+(\mathrm{H})^3/K_4K_3K_2+(\mathrm{H})^4/K_4K_3K_2K_1) \qquad (4) \end{aligned}$$

The mobility-pH (U-pH) curves in Fig. 1 were obtained by putting the values of K_{MA} for rare earths,10) the K_i ($i=1$—4) values and $\mathrm{p}C_{\mathrm{H_4A}}=2.3$ ($C_{\mathrm{H_4A}}=5\times10^{-3}\,\mathrm{M}$) into Eq. 3.

The differences between zone mobilities for two kinds of rare earths reach a maximum at the mean value of their pS's, which represent the pH values at the points of inflection of the U-pH curves.

The pS values for EDTA complexes of various rare earths vary with the concentration of EDTA. From the relations in Figs. 1 and 2, it can be predicted that, in one fixed pH of a background solution, one can separate only a few kinds of rare earths. However, all 15 different kinds of rare earths can probably be

---

* Present address; Research Reactor Institute, Kyoto University, Kumatori, Osaka.

** Department of Nuclear Engineering, Faculty of Engineering, Osaka University, Higashinoda, Miyakojima-ku, Osaka.

1) M. Maki, *Japan Analyst*, **5**, 571 (1956).

2) T. R. Sato, H. Diamond, W. P. Norris and H. H. Strain, *J. Am. Chem. Soc.*, **74**, 6154 (1952).

3) Z. Pučar and Z. Jakovac, *J. Chromatog.*, **3**, 477 (1960).

4) S. Kawamura, Lecture at the Symposium of Radiochemistry of the Chemical Society of Japan, Tokai, October, 1960.

5) V. P. Shvedov and A. V. Stepanov, *Radiokhimya*, **2**, 198, 201 (1960).

6) E. Schumacher and W. Friedli, *Helv. Chim. Acta*, **44**, 1829 (1960).

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

8) M. Shinagawa and Y. Kiso, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 1019 (1961).

9) R. A. Bailey and L. Yaffe, *Can. J. Chem.*, **38**, 1871 (1960).

10) Schwarzenbach, R. Gut and A. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

separated by selecting EDTA solutions of several desired pHs as successive background solutions.

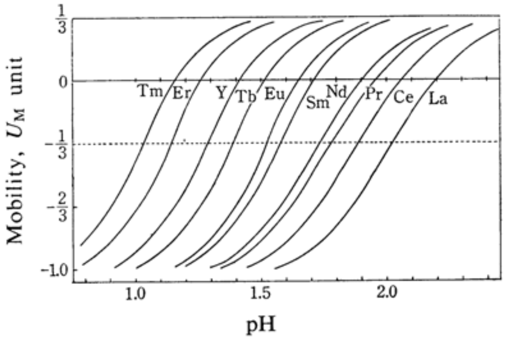

Fig. 1. Theoretical mobility-pH curves of REs-EDTA complexes in 5×10^{-3} M EDTA.

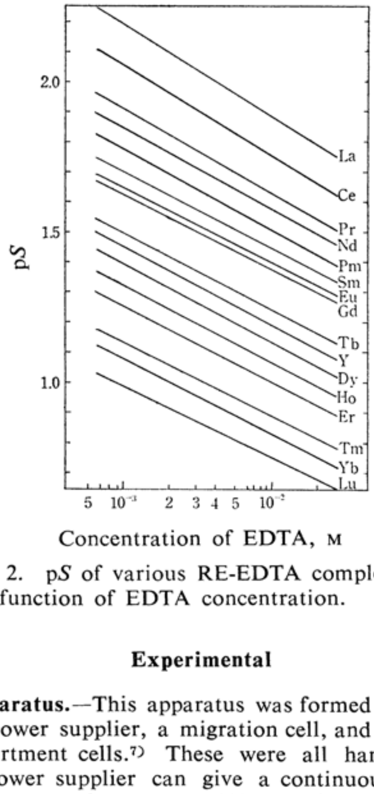

Fig. 2. pS of various RE-EDTA complexes as a function of EDTA concentration.

Experimental

Apparatus.—This apparatus was formed of a high d. c. power supplier, a migration cell, and 20 multi-compartment cells.⁷⁾ These were all hand made. The power supplier can give a continuously variable output voltage up to 1000 V. against the multi-compartment cells. By using a large migration cell ($4\times30\times7$ cm^3) containing carbon tetrachloride and a water-flowing jacket, the temperature in the migration cell was kept constant; thus the evaporation of water from the paper was also prevented.

Radioactive Tracers. — Radioactive isotopes, lanthanum-140, cerium-144 and yttrium-90 were imported, while praseodymium-142 and samarium-135 were produced by the JRR-1 at the Japan Atomic Energy Institute. Each 10-mg. portion of those rare earth oxides was irradiated at a flux of 3×10^{11} n/cm^2/sec. for 1—5 hr. The specific activities thus obtained were about 6 mc./g. for samarium-153 and 4 mc./g. for praseodymium-142. Each oxide irradiated was dissolved in hydrochloric acid. The concentration was in the 10^{-3}—10^{-4} M range. The mixed solution was prepared to have a uniform activity of each species.

Background Electrolytes.—The concentration of the EDTA used as the complexing agent was 5×10^{-3}—10^{-4} M. In order to keep constant the ionic strength of the solution (mostly $\mu=0.1$), sodium chloride was added supplementarily. The adsorption of migrant rare earth by the paper was minimized at this ionic strength in a manner shown in a previous report.⁷⁾ The pH of the background electrolyte was adjusted by the addition of sodium hydroxide or hydrochloric acid.

Procedure. — *Ordinary Paper Electromigration.*— First, the paper (Toyo Roshi No. 5, 2×40 cm^2) was cut in half in the long direction. Each sheet of the paper was then uniformly dipped in the background electrolyte solution, and the excess solution on the paper was removed by using other filter paper. Then about 0.005 ml. of the radioactive migrant solution was placed with a glass capillary on a pencil line on the moist paper. The width of the solution placed on the paper was about 1—2 mm. After twenty sheets of paper had been set into the migration cell, the stabilized voltage ranging from 300 to 500 V. was applied for 20—50 min. The water-cooling jacket and carbon tetrachloride in the migration cell were useful in maintaining the initial temperature of the paper during the migration. Even in the more highly-conducting background electrolytes, such as pH 1.0—1.5, no heating was observed during the migration. After the fixed migration time, all the strips were taken out from the cell and dried as fast as possible by an infrared lamp in order to prevent the diffusion of the separated zone.

Focusing Chromatography. — First, a 3-cm.-wide space in the middle of the paper was moistened with the sample solution to be separated; then all the anodic space beside this middle space was moistened with a hydrochloric acid solution adjusted to some selected pH, and finally the rest of the space was moistened with a EDTA solution. In this procedure, particular care was taken to avoid the confusion of the border between the sample and the solution in cathodic or anodic solutions respectively. The other procedure was the same as that used for the ordinary electromigration.

The Detection and Identification of the Migration Zone.—The detection of the radioactive migrant on paper was carried out by the autoradiographic or β-ray counting technique. The identification of radioactive nuclides on paper was carried out by the measurement of the half-life and γ-ray energy.

Results and Discussion

The Effects of the Concentration of the Migrant Ion and the Complexing Agent on the Mobility-pH Curve.—Figure 3 shows the effect of the EDTA concentration on the U-pH curve obtained by a "carrier-free" (yttrium-90) yttrium-EDTA system. In the concentration of 5×10^{-3}—10^{-3} M EDTA, the shift of the U-pH curves of yttrium-EDTA toward the higher pH axis was in agreement with the calculated value, as is shown in Fig. 2. In the range below 5×10^{-4} M EDTA, the shift was more pronounced than was the theoretical shift, and the U-pH curve in the end was close to that of yttrium-hydroxide complex (Y-OH). Using the EDTA concentration higher than 10^{-3} M, the U-pH curve for the yttrium-EDTA complex was the same in the concentration range of the carrier-free ~10^{-3} M of yttrium. Accordingly, in the later experiment, a comparatively high EDTA concentration of 5×10^{-3} M was used in order to make the theoretical analysis and practical use easy.

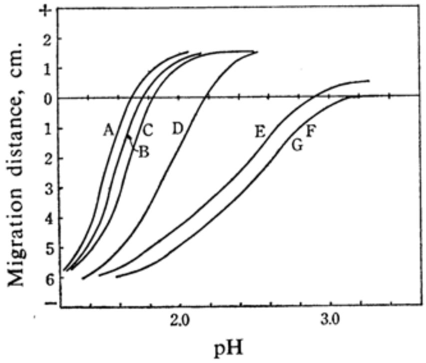

Fig. 3. U-pH curve of yttrium at different EDTA concentration.

Intensity of electric field: 300 V./30 cm., migration time: 33 min., temp: 28±1°C, background electrolyte; EDTA concentration A: 5×10^{-3} M, B: 2×10^{-3} M, C: 10^{-3} M, D: 5×10^{-4} M, E: 2×10^{-4} M, F: 10^{-4} M, G: absent, ionic strength: 0.1 μ, migrant: carrier-free yttrium.

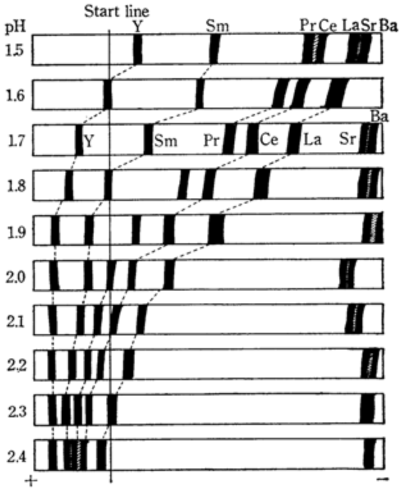

Fig. 4. Separation of RE using ordinary electromigration at different pH for background electrolyte.

Intensity of electric field: 300 V./30 cm., migration time: 50 min., temp.: 25±2°C, background electrolyte: anodic side: pH 1.9—2.1, cathodic side: pH 2.7—4.7 EDTA 5×10^{-3} M, width placed by sample: 3 cm.

The Separation of Rare Earths by Ordinary Paper Electromigration. — From the results shown in Fig. 2, one can evaluate the optimum pH range, 1.7—1.9, for the separation of light rare earths in 5×10^{-3}M EDTA. The autoradiogram trace in Fig. 4 shows the separated patterns under the conditions mentioned above and under other pH conditions close to the former. The separation was unsatisfactory in the pH range higher than 2, but the width of each zone was comparatively narrow. Below pH 1.5, the separated zones of lanthanum, cerium and praseodymium were brought close to those of strontium and barium. The separated pattern of each in Fig. 4 was in good agreement with the expected pattern.

The Separation of Rare Earths by Focusing Chromatography, pH Adjustment in Anodic and Cathodic Sides.—From the theoretical and experimental results in the ordinary electromigration, one can predict that the pH of a background electrolyte solution mixed with a sample (the rare earth to be separated) will also lie between or be close to the respective pS value of rare earths-EDTA in the focusing chromatography process as well as in the ordinary electromigration process. In order to obtain the desired pH condition, one must arrange the initial pHs of the solution on the cathodic and anodic sides. Figure 5 shows the results of the attempt to find a suitable pH arrangement on

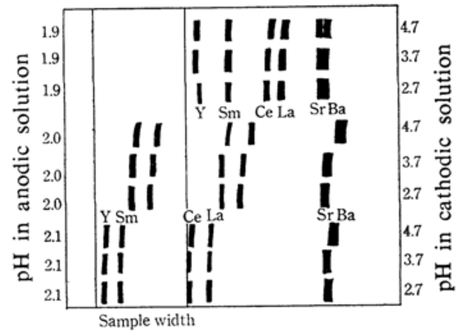

Fig. 5. Focusing chromatographic separation at differant pH gradient.

Intensity of electric field: 800 V./30 cm., migration time: 16 min., temp.: 26±2°C, background electrolyte: anodic side: pH 1.9—2.1, cathodic side: pH 2.7—4.7 (5×10^{-3} M EDTA, width dipped by sample solution: 3 cm.

each side. In Fig. 5, the selected pHs on the anodic side were 1.9, 2.0 and 2.1. These pH values were the same as the suitable ones of a EDTA background solution for the separation of rare earths by the ordinary electromigration method. On the other hand, the pHs of a EDTA solution on the cathodic side were the same as those on the anodic side (which data are not presented in Fig. 5) and higher than those on the anodic side, i. e., 2.7—4.7.

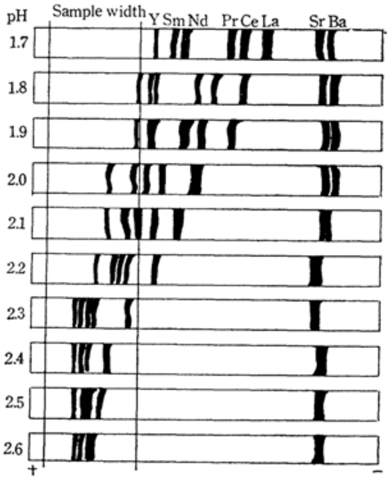

Fig. 6. Focusing chromatogram of RE at different pH in anodic side.

Intensity of electric field: 800 V./30 cm., migration time: 15 min., anodic side: hydrochloric acid, cathodic side: 3×10^{-3} M EDTA, pH 4.7.

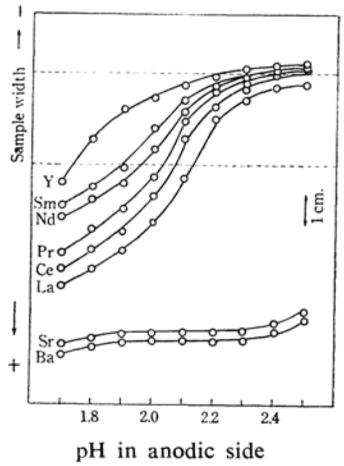

Fig. 7. U-pH curves of RE obtained by focusing chromatography.

Intensity of electric field: 800 V./30 cm., migration time: 15 min., temp.: 21—28°C., cathodic side: 3×10^{-3} M EDTA, pH 4.7.

From the results shown in Fig. 5, it may be concluded that one should be careful to adjust the initial pH on the anodic side since the effect of pH on a resolution and the shift of the relative position for the separated bands are much more intensive than those on the cathodic side, and the pH range to be selective on the anodic side is equal to the optimum one obtained by ordinary electromigration. Figure 6 gives autoradiograms showing the separated pattern of rare earths at different pH arrangements between the anodic and cathodic solutions. The pHs in the anodic solution were selected so that they could be compared with the results shown in Fig. 4. The U-pH curves shown in Fig. 7 were drawn by plotting the separated bands obtained under the same conditions as that of Fig. 6 except for the pH value of the initial sample solution of rare earths. That is, the pH of the sample solution was about 1.2 in Fig. 6 and 1.5 in Fig. 7. The difference between two separated patterns in both Figs. 6 and 7 was probably caused by the different pH values of the sample solution. If the pH of the sample is the same as that of hydrochloric acid on the anodic side, the separated bands will be close to that obtained by ordinary electromigration.

Summary

The optimum pH value and concentration of EDTA for separating rare earths (lanthanum, cerium, praseodymium, neodymium, samarium and yttrium) by the technique of paper electromigration have been evaluated on the basis of the migration theory. The validity of the theory has then been justified experimentally. The best condition for separating was at the range of pH 1.7 — 2.1 of 5×10^{-3} M EDTA. Also, the applicability for focusing chromatographic separation has been examined with several pH arrangements between hydrochloric acid on the anodic side and a EDTA complexing agent solution on the cathodic side. Summarizing the above results, it has been concluded that the initial optimum pH of an anodic solution for separation may be obtained by selecting the pH range close to the expected one for the ordinary electromigration, while the effect of pH in a cathodic solution was not as severe as the former.

Department of Chemistry
Faculty of Science
Hiroshima University
Hiroshima