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S. M. Corrêa; G. Arbilla; M. S. Carvalho

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## Modeling and Separation of Rare Earth Elements by Countercurrent Electromigration: A New Separation Column

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S. M. CORRÊA

INSTITUTO DE QUÍMICA  
UNIVERSIDADE FEDERAL DO RIO DE JANEIRO  
RIO DE JANEIRO, BRAZIL  
E-MAIL: graciela@iq.ufRJ.br

INSTITUTO DE ENGENHARIA NUCLEAR  
CNEN  
RIO DE JANEIRO, BRAZIL  
E-MAIL: machado@cnen.gov.br

G. ARBILLA\*

INSTITUTO DE QUÍMICA  
UNIVERSIDADE FEDERAL DO RIO DE JANEIRO  
RIO DE JANEIRO, BRAZIL  
E-MAIL: graciela@iq.ufRJ.br

M. S. CARVALHO

INSTITUTO DE ENGENHARIA NUCLEAR  
CNEN  
RIO DE JANEIRO, BRAZIL  
E-MAIL: machado@cnen.gov.br

### ABSTRACT

The separation of a samarium (90%) and europium (10%) mixture in  $\alpha$ -hydroxy isobutyric acid was performed in a new countercurrent electromigration system. The mobilities of these elements were estimated, and samarium of better than 99.9% purity was obtained. The equilibrium of multicoordinate complexes of these elements

\* To whom correspondence should be addressed.

with  $\alpha$ -hydroxy isobutyric acid ( $\alpha$ -HIBA) plays an important role in the separation process. The equilibrium concentrations of the involved species were calculated by a computational procedure, and a kinetic study of the complexation reaction was also performed.

## INTRODUCTION

Countercurrent electromigration (CCEM) is an electrodialysis technique that uses a counterflow of electrolyte toward the direction of the relevant migration species. This counterflow enhances the separation process by increasing the competition between the migration zones.

This technique was introduced by Wagener (1–4) in the 60s for the separation of alkaline metals. Also, Medeiros (5) worked on research with heavy elements, Alleluia (6) and Nukatsuka et al. (7) on the lanthanide elements, Bilal et al. (8) on the separation of actinides from radioactive waste, Makarova et al. (9) on berkelium, cerium, plutonium, and thorium, and Carvalho (10) on uranium and thorium.

These authors used different column designs. Bilal (8) employed an open square profile, Medeiros (5), Alleluia (6), and Carvalho (10) an open triangle profile, and Lyubimov (11) and Brewer et al. (12) a “U” tube type.

The column used in our work (13) was designed to optimize the separation process of the rare earth elements and to avoid the experimental difficulties described by these authors such as uncontrolled high temperatures, loss of electrolyte by evaporation, and difficulties with sampling. All the cited columns were employed for analytical purposes while our column was designed as a separation device to obtain rare earth elements.

Despite the good experimental results reported for lanthanide separation by this technique, a detailed explanation of the complex equilibrium of the involved species and a description of the separation phenomenon is not available in the literature. The experimental conditions were adjusted in an empirical way based on previous work (5, 10). The success of such experiments depends mainly on the type of complexing agent, its concentration, and the solution pH. So, one of the goals of this paper is to formulate and solve theoretical equations of the complex equilibrium to achieve some understanding of the separation process.

The rare earth elements samarium and europium were chosen because at the Instituto de Engenharia Nuclear in Rio de Janeiro the rare earth elements separated from monazite sands are purified by the liquid–liquid extraction technique and the samarium contains a small quantity of europium ( $< 10\%$ ).

## EXPERIMENTAL

The separation column used in this work is shown in Fig. 1. It is made of acrylic in a cylindrical shape, 0.8 m i.d., 1.1 m in length, with walls 0.08 m

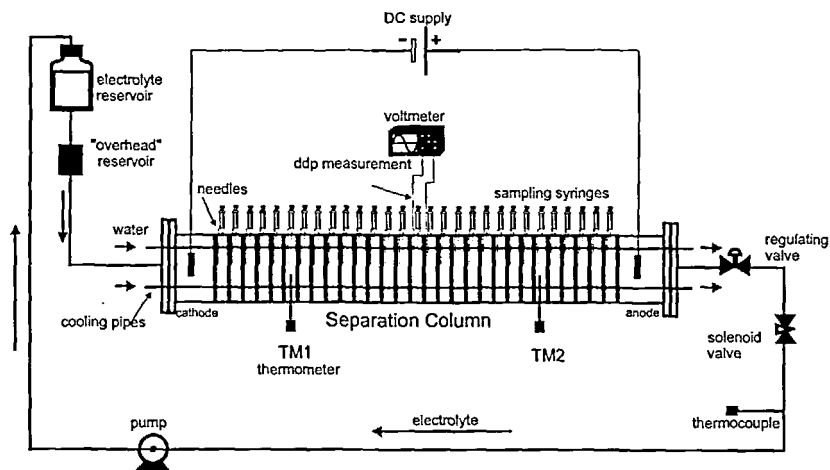


FIG. 1 Apparatus for CCEM separation of rare earth ions.

thick. The extremities are closed by flanges. The column is divided into 30 chambers, each one with an approximate volume of 0.1 L. These chambers are separated by disks made of a nylon web with 7700 wires per meter. The cathode and anode are made of a platinum web of 0.06 m<sup>2</sup> area and are located in chambers placed at the extremities of the column. These chambers are provided with a vertical open tube to purge the oxygen and hydrogen produced by the process.

In all chambers a silicon septum is placed on the top, where the potential differences between the chambers are measured and the liquid is sampled.

There are 5 mL syringes extending through the silicon septums to each chamber. The liquid inside the column is sampled by the syringes (the column has a little positive pressure).

In order to estimate the mobility of the elements and to follow the separation, the potential differences between the separation chambers are measured. This procedure, introduced by Wagener (1-4), has the advantage of avoiding continuous chemical analysis. Small stainless steel needles are fixed on the superior part of each chamber through the silicon septum. One extremity of each needle is inside the electrolyte and the other is connected to a voltmeter.

In order to remove the heat generated from the system, a cooling system consisting of a 50-L thermostatic bath with a circulation pump and a regulation valve is used. This bath is capable of maintaining the cooling water up to 5°C. This cooling water passes through a manifold that divides the flux to five glass tubes in a homogeneous radial distribution inside the column, and then comes back to the bath to form a closed system.

The electrolyte feeding is done by an outer tank in an upper position. In order to maintain a constant velocity of the electrolyte that crosses the column, an overhead valve which guarantees a constant feeding pressure is employed. Therefore, the electrolyte velocity can be regulated either by adjusting the height of the feeding tank or by regulating an outside needle valve.

As the liquid leaves the column it passes through a solenoid valve, enters an intermediary tank, and then is lifted to the feeding tank by air lift transport, so the electrolyte is recycled in a closed system. The total net volume of the liquid is about 4 L.

The system temperature is monitored by two thermocouples of Cr-Al (K type) located at Chambers 8 (TM1) and 22 (TM2), with the extremities located at the center of the column. Another thermocouple is positioned at the electrolyte exit of the column. This thermocouple is plugged to a temperature set-up adjusted to 60°C. If the temperature reaches this value, the DC source, the refrigeration system, and the circulating pump are disconnected and the solenoid valve closes to avoid sample loss.

The DC supply is a high potential Siemens equipment that reaches 3 kV and 1 A.

In all experiments the sodium and potassium mixture was prepared from their respective carbonates. Samarium and europium were prepared from their respective oxides (spectrography standard), dissolved in nitric acid, and evaporated to dryness by using an infrared lamp to remove excess acid. The residue was diluted in 0.01 M  $\alpha$ -HIBA. All samples were diluted to 5 mL and injected in the middle of the column. After injection of the rare earth ions it was necessary to purge the electrolyte to eliminate excess nitrate ion because it has a negative charge and will migrate to the anode, accelerated by the electrolyte flux. It was observed that the generated electric current was higher in the presence of nitrate ion because of its high conductance. This ion was purged until it was no longer detected by an appropriate reagent.

Each chamber was sampled (4 mL) after all separations, and the concentrations of the alkaline ions were analyzed by flame photometry. The mixture of rare earth ions were analyzed by spectrophotometry with arsenaze III reagent. The europium ion was analyzed by polarography with the differential pulse technique, using 0.01 M  $\alpha$ -HIBA as the support electrolyte, rather than ammonium chloride, as an innovation in this method.

Potassium was employed as an electrode protector in the separation of the rare earth ions. An excess of hydroxyl ions occurs at the cathode chamber as a consequence of the production of hydrogen gas. This high pH causes an undesirable hydrolysis of the involved species.

### Reactants

All the reactants used in the experiments, their specifications, and their sources were as follows.  $\alpha$ -HIBA, AG (99%) Fluka; acetic acid, (100%)

Merck; nitric acid, (95%) Merck; difenilamine, (extra pure) Merck; sulfuric acid, (98%) Merck; arsenaze III, (extra pure) Baker; potassium carbonate, CGS Carlo Erba; sodium carbonate, ACS Merck; potassium chloride, ACS Carlo Erba; samarium oxide, Spectrography standard Johnson Matthey Chemicals; europium oxide, Spectrography standard Johnson Matthey Chemicals; mercuric metal, ACS Merck.

## **Sodium and Potassium Separation**

### ***Influence of Electrolyte Concentration***

The first experiments were performed in order to find the maximum concentration of electrolyte ( $\alpha$ -HIBA) that could be used. The DC supply reached a maximum potential of 1700 V when an electrolyte concentration of 0.1 M was used. Under these conditions the resulting current was so high that the cooling system wasn't capable of removing the heat generated. The electrolyte was diluted until a maximum operational concentration of 0.01 M was reached, at which point the current was 70 mA at 1700 V and a temperature of 30°C.

### ***Influence of the Nylon Webs***

The equipment and all the operational procedures were tested by separating a 200-mg sodium-potassium mixture (1 : 1) using acetic acid as the complexing agent and also as the support electrolyte. No separation was observed along the column, even after 100 hours of experiment, when the nylon webs were not used. By using the nylon webs, distinct profiles were obtained for the sodium and potassium mixture after a few hours. On this empirical basis, the nylon webs were used in our other experiments.

### ***Influence of Electrolyte Flux with Potassium Ion Only***

In order to determine the influence of the electrolyte flux on the separation process, three experiment were carried out with only the potassium ion in the presence of 0.01 M acetic acid. Each experiment was conducted in a different flux, as shown in Fig. 2.

As may be observed in Fig. 2, the concentration of potassium at equilibrium is a linear function of the electrolyte counterflux, as previously described by Medeiros (5), Alelluia (6), and Carvalho (10). The pH of the buffer solution of the acetic acid and its salt was also determinated. The equilibrium values are shown in Table 1. Predicted pH values are in agreement with these data (13).

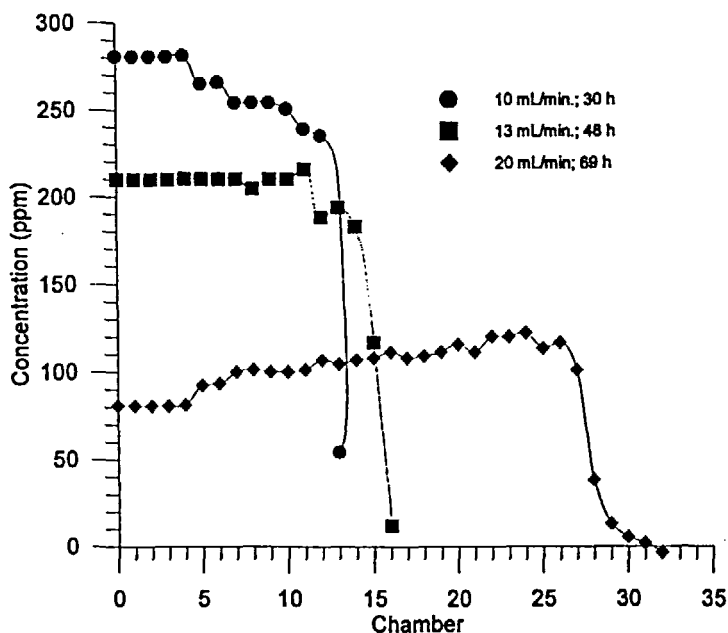


FIG. 2 Potassium experiment with 10, 13, and 20 mL·min<sup>-1</sup> (1700 V, 110 mA, 30°C in 30, 48, and 69 hours).

### Sodium and Potassium Separation

A total of 13 experiments were carried out using such different parameters as flux, current, injection mass, and electrolyte concentration to adjust the operational conditions.

The best separation was attained with an electrolyte flux of 15 mL·min<sup>-1</sup>, a temperature of 31°C, a potential of 1700 V, and a current of 110 mA. The

TABLE I  
Equilibrium Values

$C_{eq}$ (ppm)	Flux (mL·min <sup>-1</sup> )	pH
250	10	4.5
210	13	4.2
120	20	3.7

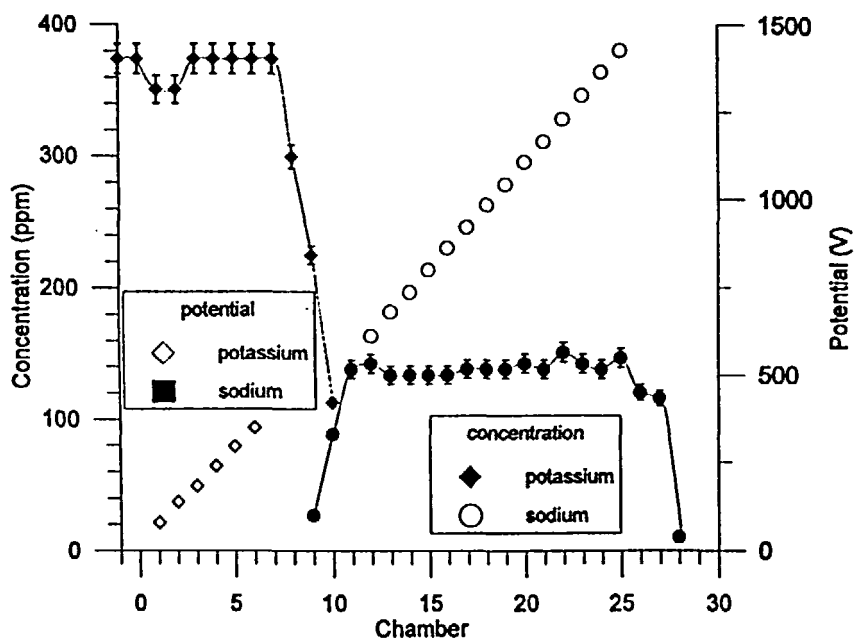


FIG. 3 Sodium and potassium separation in acetic acid 0.01 M after 40 hours (1700 V, 110 mA, 31°C, and 15 mL·min<sup>-1</sup>) and ddp's measurements.

profile after 40 hours of separation is shown in Fig. 3. Figure 3 also displays the ddp values, where the mixture region (Chambers 8 to 10) was not taken into account.

The velocity of each species can be expressed as

$$v_i = m_i E$$

where  $v_i$  = velocity of specie  $i$ ,  $m_i$  = mobility of specie  $i$ , and  $E$  = electric field. At the steady state, the migration velocity is equal to the countercurrent electrolyte velocity:

$$v_{K^+} = v_{Na^+}$$

$$m_{K^+} E_{K^+} = m_{Na^+} E_{Na^+}$$

The ionic mobility of one of the species can be estimated by using the other as a reference from the slopes of the straight lines obtained by plotting the potential against the chamber number (Fig. 3).



Hirokawa (14) reported ionic mobilities of  $72.5 \times 10^{-5}$  and  $50.7 \times 10^{-5}$   $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$  for potassium and sodium, respectively, at  $30^\circ\text{C}$ . The ratio of these values is 1.43, which is the same value obtained from Fig. 3.

## Samarium and Europium Separation

### Determination of the Mobility of Samarium and Europium

In order to estimate the ionic mobilities of samarium and europium, some experiments were performed using 0.01 M  $\alpha$ -HIBA as the supporting electrolyte. The operational conditions were 1700 V, 100 mA, and  $12 \text{ mL} \cdot \text{min}^{-1}$  at  $30^\circ\text{C}$ . This high current is due to the high conductivity of 0.01 M  $\alpha$ -HIBA compared with the 70 mA of 0.01 M acetic acid. The concentration profile after 107 hours of experiment is displayed in Fig. 4.

The ddp measurements were performed after this sampling. The calculated samarium mobility was  $44.4 \times 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ . This result is similar to the Hirokawa et al. (14) value of  $39.6 \times 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ . The deviation is about 12%.

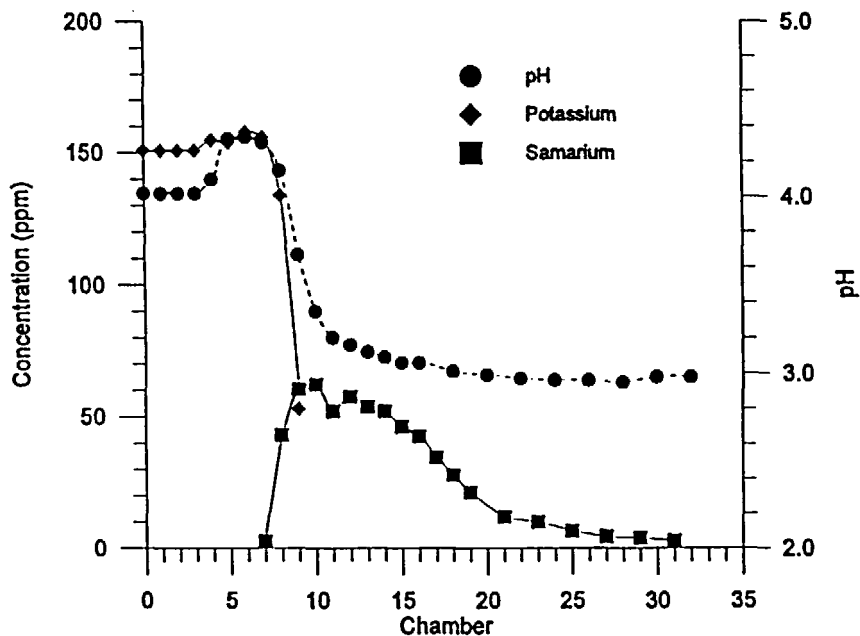


FIG. 4 Potassium and samarium separation in  $\alpha$ -HIBA 0.01 M after 107 hours (1700 V, 90 mA,  $12 \text{ mL} \cdot \text{min}^{-1}$ , and  $27^\circ\text{C}$ ).

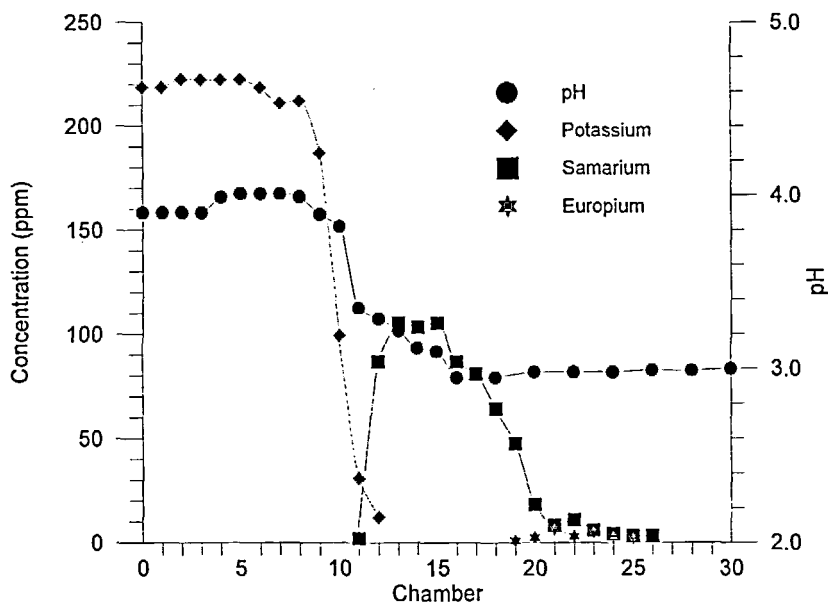


FIG. 5 Separation of samarium and europium (9:1) with potassium in  $\alpha$ -HIBA 0.01 M after 88 hours (1700 V, 90 mA, 12 mL $\cdot$ min $^{-1}$ , 28°C).

The same procedures were carried out for the europium ion after 96 hours of experiment. The mobility was estimated as  $36.5 \times 10^{-5}$  cm $^2$  $\cdot$ V $^{-1}$  $\cdot$ s $^{-1}$ . This value is also in good agreement with the Hirokawa et al. (14) value of  $40.6 \times 10^{-5}$  cm $^2$  $\cdot$ V $^{-1}$  $\cdot$ s $^{-1}$ . The deviation is about 10%.

### ***Samarium and Europium Separation***

The last experiment was the separation of a prepared mixture of samarium and europium (9:1), also in 0.01 M  $\alpha$ -HIBA solution. In this experiment a potential between the electrodes of 1700 V and a counterflux of 10 mL $\cdot$ min $^{-1}$  were used. The results after 88 hours are shown in Fig. 5.

After this time, 40 mL of sample was withdrawn from Chamber 14 where a high concentration of samarium and a minimum of europium were observed. This sample was analyzed; the europium concentration was 70 ppb. This sample was also analyzed in another lab by the same technique using the hanging mercury drop and a value of 80 ppb was found. Taking this conservative value and considering that samarium was present at 102 ppm concentration, samarium was obtained in a purity better than 99.9%.

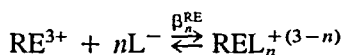
## DISCUSSION

### Equilibrium Study

In order to increase the small mobility differences between the trivalent rare earth ions, and consequently also the separation factor, it is necessary to form multicoordinate complexes. A good complexing agent should form multicoordinate, charged, soluble complexes with equilibrium constants appreciably different and with low conductivities in order to avoid elevated currents during experiments.

Many complexing agents are reported in the literature (13), including the following acids: iminodiacetic, nitriloacetic, ethylenediamine tetraacetic, oxalic, glycolic, fumaric, maleic, formic, lactic, citric, butyric, acetic, and the  $\alpha$ -hydroxy isobutyric ( $\alpha$ -HIBA). The latter shows successful results for all the lanthanides while others, like acetic and lactic acids, may be used for some groups of elements.

When samarium and europium react with  $\alpha$ -HIBA (HL) in an aqueous solution, at least 14 species are found in the equilibrium according to



where RE is samarium and europium, L is  $\alpha$ -HIBA, and  $\beta$  is the stability constant that ranges from 1 to 4. We also have to consider the dissociation of the acid and the water equilibrium. Additional equations were used relating to the mass balance of the RE elements and the ligands and the electroneutrality.

The activity coefficients were taken as unity based on preliminary calculations that gave an approximate value of 0.92 for  $\gamma_{\pm}$ .

In order to simulate the complex-forming equilibrium between the RE elements and  $\alpha$ -HIBA, it is necessary to know the stability constants. These values have been extensively proposed by other authors, show great variation, and are under considerable uncertainty. In this work the values reported by Powell et al. (15) were used since they were obtained in conditions of pH and ionic strength similar to ours.

The set of algebraic equations which contains 14 equations and 14 variables was solved in a microcomputer using a Newton-Raphson subroutine in FORTRAN as a function of free ligand concentration  $[\text{L}^-]$ , as shown in Fig. 6 for samarium. A similar behavior was found for europium. In both simulations the initial concentrations of the metals were 80 mM. The complexes with four ligands were not plotted because their concentrations were below  $10^{-5}$  M.

The concentration of each species was converted with these simulated values to a percentage contribution and compared with the values reported by

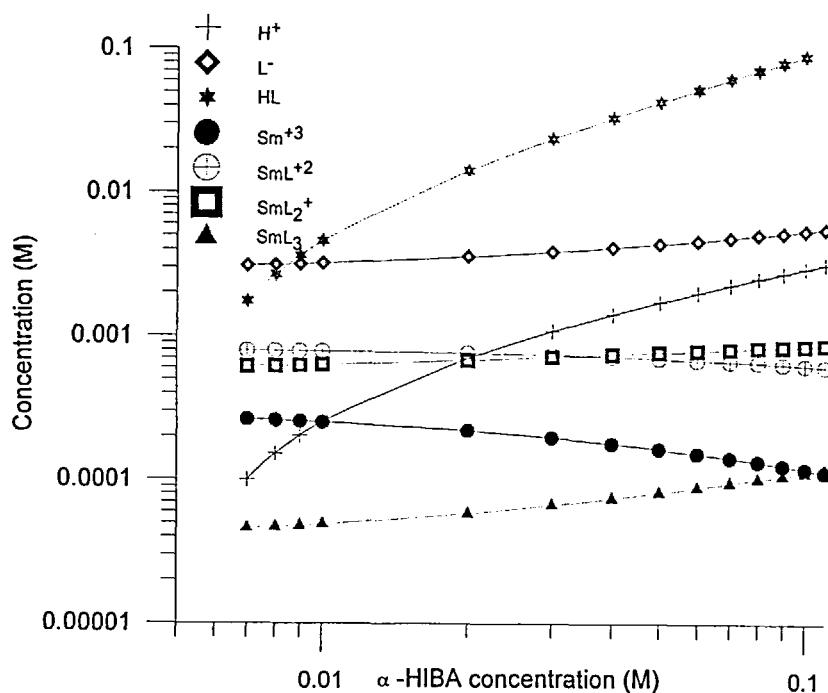


FIG. 6 Simulation of the equilibrium of samarium with  $\alpha$ -HIBA (see text for details).

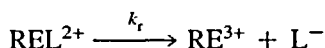
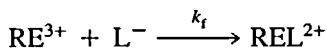
Hirokawa et al. (14, 16) who proposed a simulation for the isotacophoretic separation of the rare earth elements with  $\alpha$ -HIBA as the complexing agent. The deviation of the values is near 20%, and could be imputed to differences in ionic strength, ligand concentration, and mainly to the isotacophoresis method.

### Complexation Kinetics

The possibility of finding isolated species inside the CCEM column was checked by a preliminary study on the kinetics of complexation so time scales for this reaction could be estimated.

It is well known that the variation in enthalpy and entropy of complex formation of the rare earth elements with different complexing agents is difficult to explain if only differences in ionic radii and electronic configurations are considered. The solvent sheath must be taken into account. Graffeo and

Bear (17) employed a relaxation technique (pressure jump) to measure this solvent effect on the formation of these complexes, and they furnished important data of the formation constants for all lanthanides. Although oxalic acid was used in their experiments, a similar behavior was expected for  $\alpha$ -HIBA. It is possible to formulate a set of forward and reverse elementary reactions to describe the hydration and complexation processes. It seems that the complex formation constants are independent of the complexation agent, as reported by Geier (18) who used murexide as the complexing agent. By considering the four-step mechanism proposed by Eigen and Tamm (17) and assuming that hydrolysis is not relevant, the determinant step is the loss of water from the inner hydration shell. Taking the formation of complexes with one ligand as an example, the equilibrium reaction may be expressed as



and using data from Graffeo and Bear (17) and Powell et al. (15):

$$k_f^{\text{Sm}} = 8.2 \times 10^7 \text{ M}^{-1} \cdot \text{s}^{-1} \quad k_f^{\text{Eu}} = 7.7 \times 10^7 \text{ M}^{-1} \cdot \text{s}^{-1}$$

$$k_r^{\text{Sm}} = 8.4 \times 10^4 \text{ M}^{-1} \cdot \text{s}^{-1} \quad k_r^{\text{Eu}} = 6.3 \times 10^4 \text{ M}^{-1} \cdot \text{s}^{-1}$$

The following set of differential equations can be written to calculate the species concentrations as a function of time:

$$d[\text{Sm}]/dt = -k_f^{\text{Sm}}[\text{Sm}][\text{L}] + k_r^{\text{Sm}}[\text{SmL}]$$

$$d[\text{Eu}]/dt = -k_f^{\text{Eu}}[\text{Eu}][\text{L}] + k_r^{\text{Eu}}[\text{EuL}]$$

$$d[\text{L}]/dt = -k_f^{\text{Sm}}[\text{Sm}][\text{L}] - k_f^{\text{Eu}}[\text{Eu}][\text{L}] + k_r^{\text{Sm}}[\text{SmL}] + k_r^{\text{Eu}}[\text{EuL}]$$

$$d[\text{SmL}]/dt = k_f^{\text{Sm}}[\text{Sm}][\text{L}] - k_r^{\text{Sm}}[\text{SmL}]$$

$$d[\text{EuL}]/dt = k_f^{\text{Eu}}[\text{Eu}][\text{L}] - k_r^{\text{Eu}}[\text{EuL}]$$

This set of five ordinary differential equations was solved using the numerical method of Adams-Bashforth (19). Initial concentrations of 0.10 and 0.01 M were used for the  $\text{RE}^{3+}$  and free ligand species, respectively (Fig. 7).

It is observed that an equilibrium condition is established in a few microseconds. This result indicates that once the CCEM column is sampled, the species could not be analyzed as individual compositions because a new equilibrium stage will be reached without relation to the original one.

Obviously this is a rough approximation of the real system but, nevertheless, it gives a reasonable estimation of the time scale of the process. A more

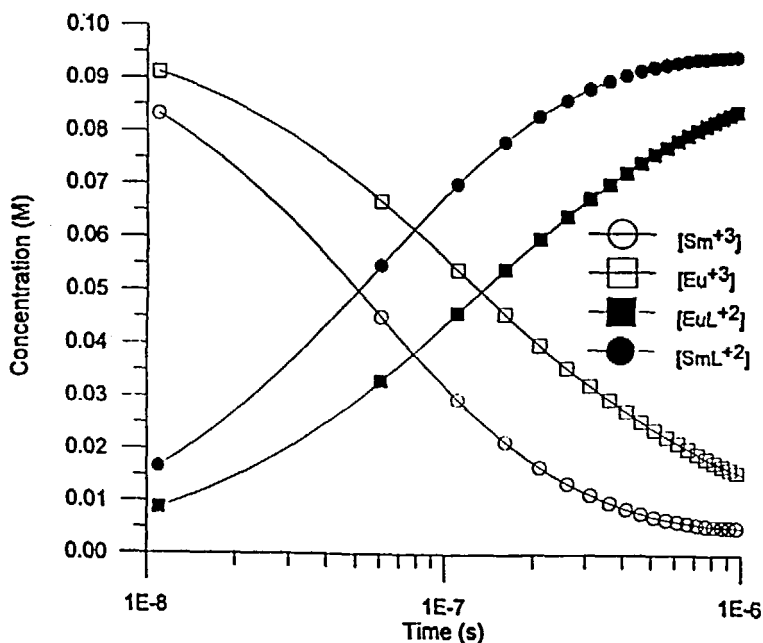


FIG. 7 Reactions of samarium and europium with  $\alpha$ -HIBA (see text for details).

complete description of the system is not feasible at the present stage since rate constants for the individual steps are not available.

## CONCLUSION

The separation factor of adjacent rare earth elements by countercurrent electromigration was highly improved by using a new column design and  $\alpha$ -hydroxy isobutyric acid as a complexing agent. Column performance was enhanced in relation to previous works.

The results show that migration of the ionic species inside the column may be followed by measuring the potential differences between the chambers. This procedure is simpler than continuous chemical analysis and also makes it possible to estimate the unknown ionic mobilities.

This work indicates that it is possible to separate a mixture of samarium (90%) and europium (10%), and to obtain samarium with a purity better than 99.9%. Considering that the physical and chemical properties of rare earth are very similar and that the difference between the ionic mobilities of the

trivalent ions is less than 2%, improving their ionic mobility differences to more than 10% by complexation is an impressive result.

The simulation of the stationary state for the experimental conditions employed demonstrated that the main species present in equilibrium are  $\text{RE}^{3+}$ ,  $\text{REL}^{2+}$ , and  $\text{REL}_2^+$ , and that the  $\text{REL}_3$  and  $\text{REL}_4^-$  species are negligible.

Each complex possesses different mobilities because they have different charges and volumes. A question that arose during our studies was the possibility of the existence of individual complexes in separated zones. It is known that specie  $\text{RE}^{3+}$  has the highest charge and minor volume, and therefore the highest mobility, and so it should be found ahead of the others. Simulation of the kinetic process shows that when this ion becomes free in the presence of an excess of completely dissociated ligand, a new equilibrium stage is reached in relation to the others species. It is assumed that all species migrate together in a unique zone. Hirokawa (14, 16) suggested that these multicoordinate complexes coexist at equilibrium, and this one may be fast enough to maintain a homogeneous migration rate.

The calculations presented in this work were developed in our laboratory and are a powerful tool for studies of the separation of rare earth elements by CCEM (13). These simulations gave a better understanding of the system and assisted in determining the conditions for the experiments.

During the separation process the temperature was not constant along the column. It was observed that where the ion concentrations were higher, the temperature was lower. This variation was no more than 5°C.

It was also found that a nylon web plays an important role in separation. The reason for this is not presently understood and will be investigated in future work.

The results of CCEM can also be predicted for any mixture of elements since the mobilities and such operational data as current, potential, temperature, flux, and injected mass are supplied. This will be theme of a future article, how being prepared, about simulation of the process.

## NOMENCLATURE

$K$	equilibrium constant
$\beta$	overall equilibrium constant
$k$	elementary reaction rate ( $\text{M}^{-1}\cdot\text{s}^{-1}$ )
$\gamma_{\pm}$	mean activity coefficient
$\mu$	effective mobility ( $\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ )

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