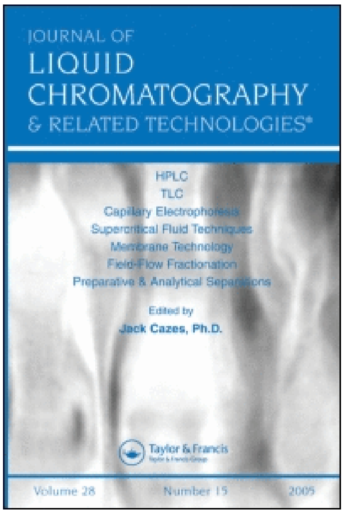

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SEPARATION OF LIGHTER RARE EARTH METAL IONS BY CENTRIFUGAL COUNTER-CURRENT TYPE CHROMATOGRAPHY WITH DI-(2-ETHYLHEXYL)PHOSPHORIC ACID

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ABSTRACT:

A centrifugal countercurrent type chromatography (Centrifugal Partition Chromatography) was applied to separations of lighter rare earth metal ions ($LaCl_3$, $CeCl_3$, $PrCl_3$, $NdCl_3$, $SmCl_3$ and $EuCl_3$) first time. The results obtained by using di-(2-ethylhexyl)phosphate (D2EHPA) showed that this technique is successfully usable for the laboratory-scale separations, though the numbers of theoretical plate calculated from the chromatograms were considerably lower than expected. The values of separation factors for the adjacent RE ions were found to be substantially parallel to those obtained by single stage extraction method, indicating that our chromatography involves a multi-stage extraction process as in the cases of organic samples.

INTRODUCTION

Recently, application of centrifugal force(1-3) in the continuous extraction method has opened a new quick technique for separation, isolation, purification, and concentration of a variety organic(2-7) and inorganic ions.(8) The results of centrifugal countercurrent type chromatography was found to be able to successfully applied for costless selective liquid-membrane transport systems.(9) Our work described here is the first report showing the usefulness of this type of technique for lighter rare earth (RE) metal ions.

Centrifugal continuous extraction method is now developing under two types of name: a) Centrifugal Countercurrent Chromatography (CCC) and b) Centrifugal Partition Chromatography (CPC). Difference of these two chromatography is mainly based on the difference in their machinery constitutions for effectuating the application of centrifugal force in the continuous extraction processes. Namely, the former employs the Itoh's "seal-free planet coil centrifuge",(2) and the latter the Murayama's "microcell cartridges" together with rotary seal joints.(3) However, the fundamental chemical aspects involved in both of these chromatographies are almost identical.

For the separation of rare earth metal ions the single-stage liquid-liquid extraction by using di-(2-ethylhexyl)phosphate (D2EHPA) or related phosphates(10-18) has been studied extensively, and its applications to a column chromatography(19) and a 20-stage mixer-settler method(20) have already been reported. Recently, extractions by using liquid surfactant membranes have also been investigated.(21) Our results of the separation by using of a centrifugal countercurrent method reported here can be used in advancing the studies on purification and/or concentration of rare earth metal ions by this type of quick and effective centrifugal countercurrent-type chromatographic techniques aiming to industrial-scale applications.

EXPERIMENTAL

Materials: Lighter rare earth metal ions were obtained from commercial suppliers and used without further purification: $LaCl_3$ $7H_2O$ (Wako, first grade), $CeCl_3$ $7H_2O$ (Wako, >98%), $PrCl_3$ $7H_2O$ (Kanto, first grade), $NdCl_3$ $6H_2O$ (Wako, >97%), $SmCl_3$ $6H_2O$ (Nakarai, first grade) and $EuCl_3$ $6H_2O$ (Nakarai, extra pure grade). Di-(2-ethylhexyl)phosphoric acid (D2EHPA) (Nakarai, 99%), n-heptane (Nakarai, extra pure grade), xylenol orange (Wako, analytical grade) and hexamethylenetetramine (Wako, extra pure grade) were used without further purification. Deionized water was used throughout the experiments.

Apparatus: Centrifugal partition chromatography was performed by using a Centrifugal Partition Chromatograph - L. L. apparatus, Model NMF (Sanki Engineering, LTD) with cartridges of Model 240W. The pumping system was Model LBP-V (Sanki Engineering, LTD), and the injection valve system was of a Model CPC-FCU II (Sanki Engi- neering, LTD). A HITACHI spectrophotometer Model 200-20 was used for quantitative analysis of RE ions in the fractions eluted.

Chromatographic procedures: Three high resolution type cartridges (Model 240W) containing 400 microcells per cartridge were equipped in series (total 1200 microcells). Solution of 0.1M D2EHPA in n-heptane (stationary phase) was filled in the microcells by the following procedures: the solution of stationary phase was pumpued at maximum speed under centrifugation (400 rpm) while the mode-valve was turned to "ascending mode", then the stationary phase solution was kept recycling for 10-15 min to remove gaseous materials completely.

Next, the valve was turned to "descending mode", and a given concentration of aqueous HCl solution (mobile phase) was pumped in a descending fashion through the microcells under centrifugal force (800 rpm), adjusting to a given elution speed (1.12 + 0.02 ml min^{-1}). The n-heptane solution (23 ml) in the dead spaces was eluted during this procedure, and ca. 40 ml (containing 1.3 g of D2EHPA) of stationary phase was retained in the microcells. When "descending elution" is employed it is necessary to avoid carefully introducing gaseous materials in the microcells; otherwise, the gaseous materials stay in the microcells to cause troubles, e.g. leaking of the stationary phase out of the microcells during chromatography, together with instability in the rate of elution. After the elution was stabilized for ca. 1 hr, sample solution (0.54 ml) was charged through the sample injecting valve.

Analysis of fractions: The eluted aqueous mobile phase was collected at the end of the chromatographic line at 5 min's intervals. From each fraction 2 ml-aliquots were taken, and aqueous solutions of 5.60×10^{-4} M xylenol orange (1 ml) and 0.5 M hexamethylenetetramine hydrochloride buffer (2 ml) were added, resulting in 5 ml of aqueous solutions of pH 5.6 containing 1.12×10^{-4} M of xylenol orange and 0.2 M hexamine buffer. Concentrations of the RE ions thus colored were determined from the intensities of absorption spectra at 420 nm (22), by comparing with the pre-calibrated values.

RESULTS AND DISCUSSION

The samples of lighter RE ions used in this work were aqueous solutions of $LaCl_3$, $CeCl_3$, $PrCl_3$, $NdCl_3$,

$SmCl_3$ and $EuCl_3$. Under centrifugation the mobile phase (aqueous HCl solution) was pumped through the microcell-cartridges (400 microcells per cartridge; total 1200 (= 3 x 400) microcells were used) containing 0.1M D2EHPA in n-heptane solution as the stationary phase. The fractions collected were analyzed by absorption spectroscopy at 420nm after treating with xylenol orange.

Figure 1 shows the results of chromatographic complete separation of one-to-one mixture of La^{3+} and Ce^{3+} ions, an adjacent pair of the lightest RE ions, together with showing the excellent reproducibility of the experiments (curve a). In this case total 0.02M $RECl_3$ (0.54 ml) was charged and eluted with 0.050N + 0.001 aq. HCl by "descending" method.

When Pr^{3+} ion was charged under the same conditions, it was eluted considerably later than the Ce^{3+} ion peak (curve b), and it is clear that the separation between La^{3+} and Pr^{3+} ions is also complete. The separation between Ce^{3+} and Pr^{3+} ions was considerably good but the tail of the peak of Ce^{3+} ion was slightly overlapped with the peak-front of Pr^{3+} ion. Under the conditions used it appears possible to obtain about 75% yields of pure Ce^{3+} and Pr^{3+} ions from 1:1 mixture of these ions.

We found that the retention time of the RE ions highly depends on the concentration of HCl in the mobile phase, in consistent with the conclusion of extraction experiments that the extraction with D2EHPA involves a cation-exchanging processes based on acid-base interaction (eq.1):(16)

$$3(HG)_2 + RE^{3+} \rightleftharpoons RE(HG_2)_3 + 3H^+ \qquad (1)$$

where G denotes the phosphate anion. A typical example of HCl-concentration dependence is shown in Figure 1 (curve c), in which the separation between La^{3+} and

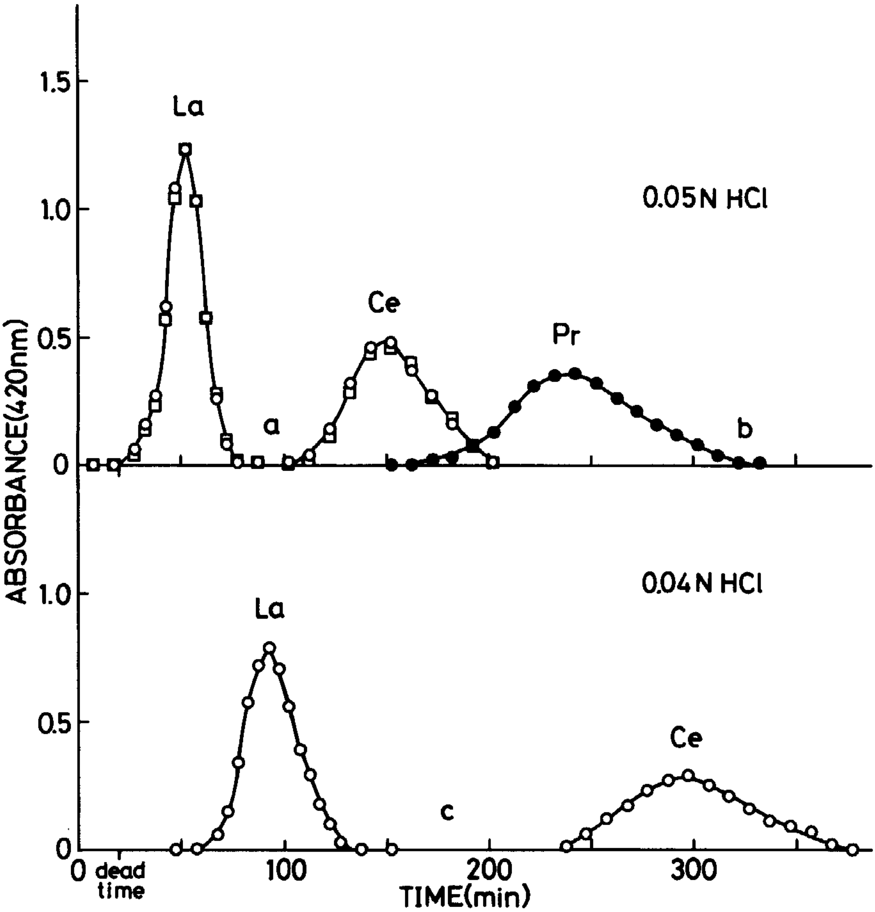

FIGURE 1. Centrifugal partition chromatograms of $LaCl_3$, $CeCl_3$, and $PrCl_3$ at room temperature with D2EHPA/n-heptane stationary phase. Curve (a) shows reproducibility of chromatography by using a binary mixture (0.54 ml) of $LaCl_3$ (0.01 M) and $CeCl_3$ (0.01 M); mobile phase, 0.050N HCl: —○— First run, and —□— second run. Curve (b) is the chromatogram of 0.54 ml of $PrCl_3$ (0.01 M) alone under the same conditions as curve (a). Curve (c) The same sample as the case of curve (a); mobile phase, 0.040N HCl.

Ce^{3+} ions was further improved with a mobile phase of aq. 0.040N HCl.

The separation between La^{3+} and Nd^{3+} ions was found to be also complete as shown in Figure 2 (curve a), where concentration of HCl was 0.070N to shorten the total retention times. Under this condition the complete separation between La^{3+} and Pr^{3+} ions was still retained. Pr^{3+} and Nd^{3+} ions showed considerably different retention times (curve a and b), but because of broadness of the peaks resolution of these two curves was not so good under the conditions used. When the concentration of HCl was decreased to 0.060N, the separation of Pr^{3+} vs. Nd^{3+} ions was somewhat improved to allow to concentrate these ions to a considerable extent (curve c and d). For the separation of the last pair of ions, peak broadening became significant, and it seems better to test by other stationary phase or by using a microcell cartridge with much higher theoretical numbers of plate.

Separation between Nd^{3+} and Sm^{3+} ions was almost complete with a 0.140N HCl mobile phase as shown in Figure 3 (curve a). It turned to be complete when a 0.120N HCl mobile phase was used (curve b), although peak broadening for the Sm^{3+} ion was considerable.

Chromatography of an equimolar binary mixture of Sm^{3+} and Eu^{3+} ions by using the D2EHPA/n-heptane stationary phase resulted in extremely significant peak-broadening and was not suitable for the purpose of purification. However, the use of D2EHPA/toluene stationary phase gave considerably good resolution of the mixture as shown in Figure 4.

Table 1 compares separation factors ((α) calculated from (eq. 2)) obtained by our countercurrent type chromatography with those of literature values obtained by corresponding extraction methods using D2EHPA.(19)

$$\alpha = t_R(RE_2)/t_R(RE_1) \qquad (2)$$

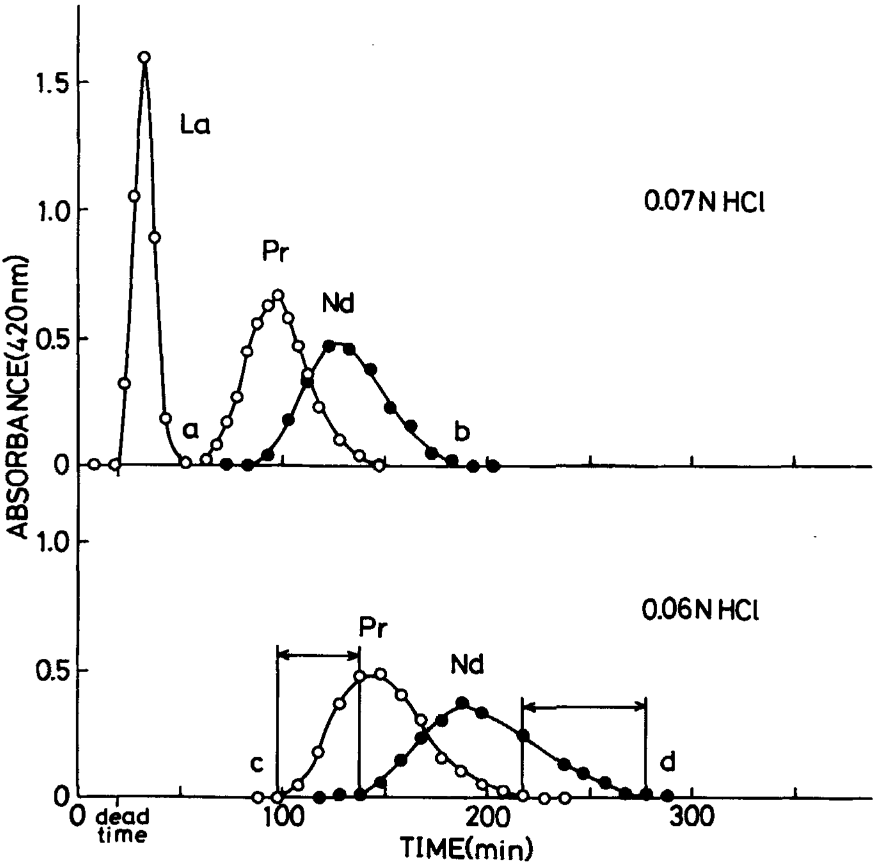

FIGURE 2. Centrifugal partition chromatograms of $LaCl_3$, $PrCl_3$, and $NdCl_3$ at room temperature with D2EHPA/n-heptane stationary phase. Curve (a): sample; a binary mixture of (0.54 ml) of $LaCl_3$ (0.01 M) and $PrCl_3$ (0.01 M); mobile phase, 0.070N HCl. Curve (b): sample; 0.54 ml of $NdCl_3$ (0.01 M) alone under the same conditions as curve (a). Curve (c): sample; 0.54 ml of $PrCl_3$ (0.01 M) alone, and curve (d): sample; 0.54 ml of $NdCl_3$ (0.01 M) alone. Mobile phase, 0.060N HCl. The ranges indicated on the chromatograms are those of the fractions of high-purity RE ions.

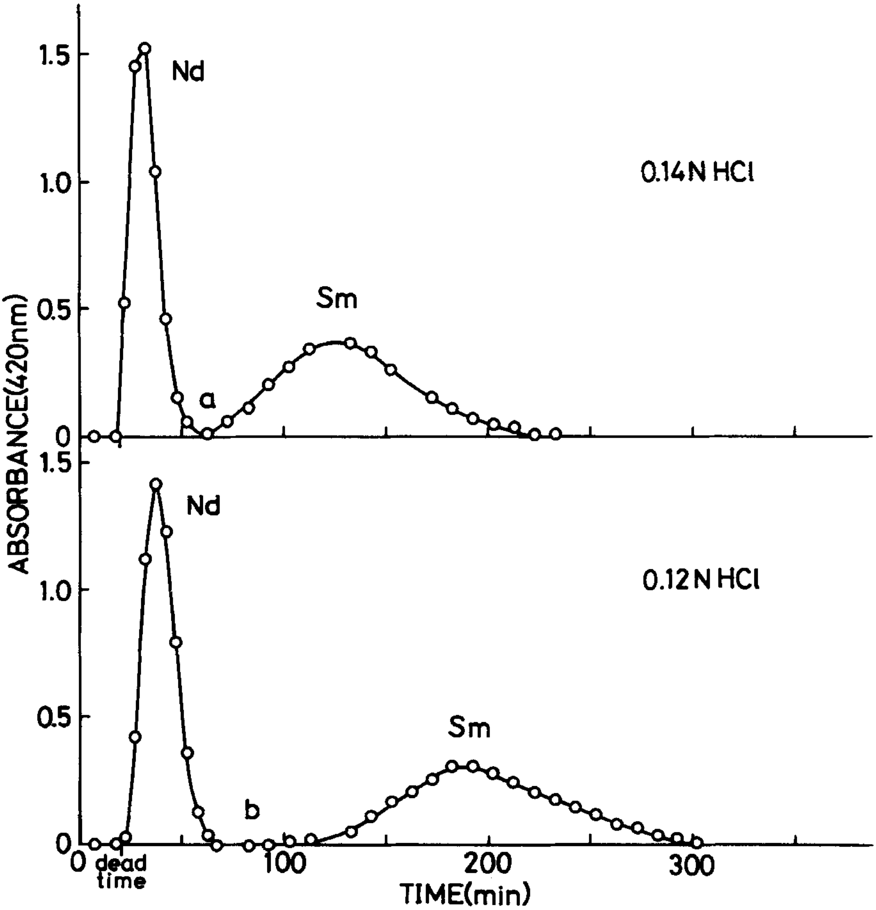

FIGURE 3. Centrifugal partition chromatograms of a binary mixture of $NdCl_3$ and $SmCl_3$ at room temperature with D2EHPA/n-heptane stationary phase. Sample; 0.54 ml of $NdCl_3$ (0.01 M) and $SmCl_3$ (0.01 M); Curve (a): mobile phase, 0.140N HCl. Curve (b): mobile phase, 0.120N HCl.

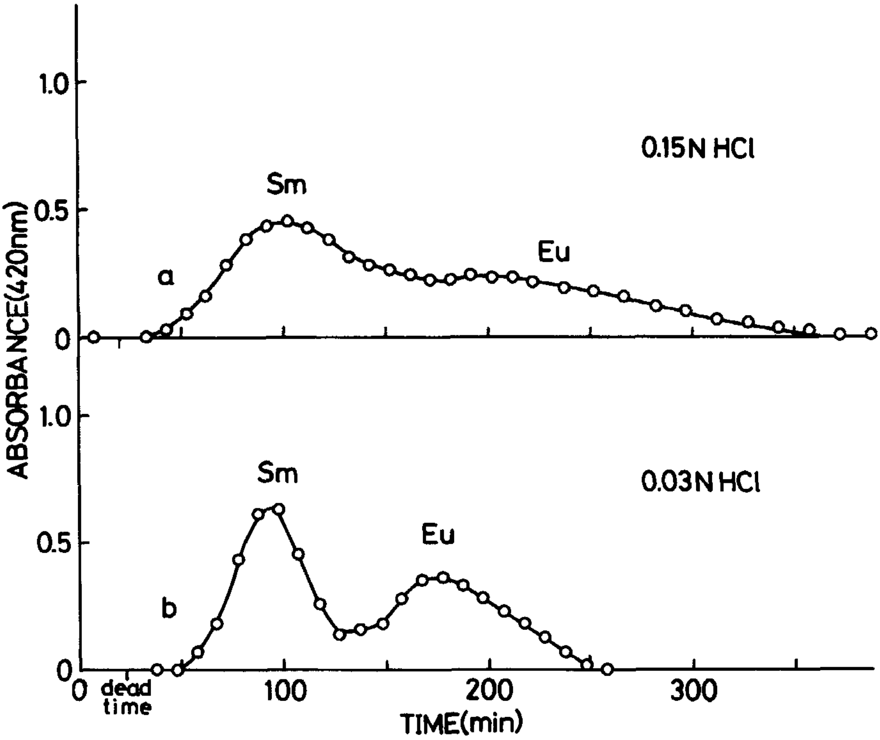

FIGURE 4. Centrifugal partition chromatograms of a binary mixture of $SmCl_3$ and $EuCl_3$ at room temperature. Sample; 0.54 ml of $SmCl_3$ (0.01 M) and $EuCl_3$ (0.01 M). Curve (a): Stationary phase: 0.1M D2EHPA in n-heptane, mobile phase, 0.150N HCl. Curve (b): Stationary phase: 0.1M D2EHPA in toluene, mobile phase, 0.03N HCl.

where, t_R is the apparent retention time, RE_2 and RE_1 are RE ions of higher and lower atomic numbers, respectively.

Although the experimental conditions of these two systems are different and no detailed comparison is possible, our countercurrent type chromatographic results were found to be substantially parallel to the single stage extraction data. (Interestingly, our results by using chlorides of RE ions agreed relatively

TABLE 1. COMPARISON OF SEPARATION FACTORS BETWEEN CENTRIFUGAL PARTITION CHROMATOGRAPHY AND EXTRACTION METHOD.

RE_1	RE_2	Separation Factor (α)		
		CPC[a]	Extraction[b]	
		($RECl_3$)	($RE(OCl_4)_3$)	($RECl_3$)
La	Ce	3.9-4.1	3.0	2.4
Ce	Pr	1.7	2.1	2.8
Pr	Nd	1.4	1.4	1.7
Nd	Sm	9.2-9.3	6.8[c]	5.0[c]
Sm	Eu	2.3(2.2[d])	1.9	2.2

a) This work: 0.1 M D2EHPA in n-heptane. b) 0.54 M D2EHPA in toluene was used for extraction of trace amounts of RE ions.(19) c) Calculated by the equation: $\alpha_{Nd,Sm} = \alpha_{Nd,Pm} X \alpha_{Pm,Sm}$. d) Stationary phase: 0.1M D2EHPA in toluene.

TABLE 2. EFFECTIVE NUMBER OF THEORETICAL PLATE (n) AND PEAK RESOLUTION (R) IN CENTRIFUGAL PARTITION CHROMATOGRAPHY.[a]

RE_1	RE_2	Concn. of HCl in mobile phase (M)	$n(RE_1)$	$n(RE_2)$	$R(RE_1$ vs. $RE_2)$
La	Ce	0.04	34	77	2.0
La	Ce	0.05	14	41	1.5
La	Pr	0.07	5	31	1.4
Ce	Pr	0.05	41	54	0.77
Pr	Nd	0.06	33	41	0.44
Pr	Nd	0.07	31	28	0.37
Nd	Sm	0.12	5	21	1.4
Nd	Sm	0.14	3	12	1.1
Sm	Eu	0.15	5	18	0.56
Sm	Eu[b]	0.03	18	27	0.75

a) Stationary phase: 0.1 M D2EHPA in n-heptane.
b) Stationary phase: 0.1 M D2EHPA in toluene.

well with the extraction values obtained by perchlorates rather than chlorides; the reason is unknown in the present stage.) This parallelism indicates that our countercurrent type chromatography is almost simply a multi-stage process of the extraction method, and as long as the data of extraction are obtained carefully the approximate chromatographic separations can be readily predicted as in the cases of many organic samples.

As can be seen from Table 1, the separations of higher members of RE ions than Ce^{3+} ion from La^{3+} ion can be readily realized by our chromatographic technique. On comparing the behaviors of Ce^{3+}, Pr^{3+} and Nd^{3+} ions each other, it is clear that Ce^{3+} and Nd^{3+} ions can be separated if ca. 0.070N HCl is used as mobile phase (see Table 2). Separation of Sm^{3+} and Eu^{3+} ions from Ce^{3+}, Pr^{3+} or Nd^{3+} ion seems to be quite easy.

From our centrifugal countercurrent type experiments by using D2EHPA as stationary phase, values concerning other chromatographic behaviors of lighter RE ions can be summarized as shown in Table 2. In Table 2 tabulated are: number of effective theoretical plate (n), and observed peak resolution (R), which are calculated from the equations (3, 4), respectively:

$$n = 5.55(t_R/w_h)^2 \qquad (3)$$

$$R = 2[(t_R(RE_2) - t_R(RE_1)]/[w(RE_2) + w(RE_1)] \qquad (4)$$

where, w_h is half width of the peak, and w (= $2w_h$) is peak width.

The limit of the use of D2EHPA is found for its significant peak broadening effect for all of the RE ions used, especially for the higher homologues. The values of separation factor were high in this D2EHPA system (see Table 2), but the values of n were much lower than 100, in spite of the number of microcells used was 1200. When the sample ions behave ideally in the stationary phase, the values of n should be quite resemble to that of the number of microcells. (For instance, in the previous combination of alkali metal picrates and dibenzo-crown ether, we observed the values of n almost correspond to the number of microcells (150).(8)

Although our separation experiments with the D2EHPA system were successful in laboratory scale, considerable loss in the n values resulted in quite low values of R which should be improved before this chromatographic technique is applied for industrial scale purification of RE ions. A key origin of the peak broadening can be due to the mechanism of acid-base interaction (eq. 1) between the sample and D2EHPA in the stationary phase. Similar considerable peak broadenings have been observed for the behaviors of optically active mandelic acids with the separator-aided centrifugal partition chromatography by the use of a stationary phase containing brucine, a base.(23)

Our results reported here will stimulate the studies to find new reagents for the stationary phase showing higher n values via interaction mechanisms of other than acid-base type. As exemplified by the separation of Sm^{+3} and Eu^{+3} ions the nature of solvent in the stationary phase greatly alters the resolution (and number of theoretical plate). Certainly, the solvent controls the equlibriums involved in the acid-base interaction, and finding out of an appropriate solvent is also necessary.

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