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FURTHER RESULTS ON BEHAVIORS OF RARE EARTH METAL IONS IN CENTRIFUGAL PARTITION CHROMATOGRAPHY WITH DI(2-ETHYLHEXYL) PHOSPHORIC ACID

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ABSTRACT:

In centrifugal partition chromatography (CPC) of rare earth metal ions (RECl_3) by the use of di(2-ethylhexyl)phosphate (D2EHPA) as "separator" in the stationary phase, effects of number of microcells and stationary solvent were investigated for improving separation. By increasing the number of microcells from 1200 (3 cartridges) to 2400 (6 cartridges), the peak resolution value (R) for the separation of PrCl_3 versus NdCl_3 was improved from 0.37 to 0.62. Heavier RE ions (ErCl_3 and YbCl_3) was able to separate almost completely by using CHCl_3 as stationary solvent. This result suggests that by adjusting these two factors, in addition to adjusting $[\text{HCl}]$ in the mobile phase (previously reported), almost whole series of adjacent couples of RE ions will be effectively separated by CPC with acidic D2EHPA. In contrast, neutral tri-n-butyl phosphate (TBP) was found to be a poor separator.

INTRODUCTION

In the preceding papers(1,2) we reported that adjacent pairs of lighter rare earth (RE) metal ions from LaCl_3 to SmCl_3 can be effectively separated by a centrifugal countercurrent type chromatography (centrifugal partition chromatography (CPC)) by using di-(2-ethylhexyl)phosphate (D2EHPA), the most familiar extractant, as "separator" in the stationary phase. In the papers (1,2) we emphasized the importance of adjustment of concentration of HCl ($[\text{HCl}]$) in the aqueous mobile phase, which is one of the key factors for obtaining effective separations. This is basically reasonable because the separation is governed by acid-base interactions of D2EHPA with the RE ions.

In addition, as exemplified in the separation of SmCl_3 from EuCl_3 , the use of toluene which is more polar than n-heptane was effective for RE ions of higher atomic number. Independent of our work, Akiba, et al. also succeeded effective separations of RE ions of La, Pr, Nd, Sm, Eu, Gd, Tb, and Dy by the use of a related phosphonate of PC-88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) as separator in kerosene solvent.(3) Although their mobile phase was aqueous (H, Na) Cl_2CHCOO solutions containing 20%-ethylene glycol, they also used mobile phase of higher pH value, similarly to our case, for the separations of RE ions of higher atomic number.

Since D2EHPA has long been mainly used for large-scale separating extraction of RE ions, it seems to be important to clarify the behaviors of RE ions in CPC using this phosphate. This kind of informations will be useful in replacing the familiar extraction techniques with industrial-scale CPC. Hence, some key factors other than $[\text{HCl}]$ were examined for improving separations by the use of D2EHPA separator. The target of our

present study was focused on the effect of number of microcells on the separations of CeCl_3 , PrCl_3 and NdCl_3 , and effect of solvent polarity in the stationary phase for the separations of RE ions heavier than EuCl_3 .

YbCl_3 was chosen as a typical heavier RE ion because it is the second heaviest element of the RE series which is readily available commercially, and in addition, the CPC behaviors of LuCl_3 will be easily extrapolated on the basis of those of YbCl_3 . Similarly, ErCl_3 was chosen as a typical sample for predicting the behaviors of TmCl_3 , HoCl_3 and other RECl_3 s somewhat lighter than ErCl_3 .

Finally, for comparison of separating abilities of acidic and neutral phosphates as separator, tri-n-butyl phosphate (TBP), again one of the classical extractants, was tested.

EXPERIMENTAL

Materials: Rare earth metal ions were obtained from commercial suppliers and used without further purification: $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (Wako, >98%), $\text{PrCl}_3 \cdot 7\text{H}_2\text{O}$ (Kanto, first grade), $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ (Wako, >97%), $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (Wako, first grade) $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ (Wako, 99.9%), $\text{Nd}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ (Wako, 99.9%), $\text{Sm}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ (Wako, 99.9%), $\text{Eu}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ (Nakarai, first grade), and tri-n-butyl phosphate (TBP) (Wako, extra pure grade). Other reagents and solvents were the same as used in the preceding paper.(1)

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, and other apparatuses were used as in the case of the preceding work.(1)

Chromatographic procedures:

(1) **Effect of Number of Cartridges for Separation of CeCl_3 , PrCl_3 , and NdCl_3 with D2EHPA Separator:** Three or six high resolution type cartridges (Model 240W) containing 400 microcells per cartridge were equipped in series (total 1200 or 2400 microcells). Dead volume: 25 ml. Mode: descending mode. Stationary phase: 0.1M D2EHPA in n-heptane. Mobile phase: aqueous HCl solution ($1.12 \pm 0.02 \text{ ml min}^{-1}$); 0.06 M aq.-HCl for separation of CeCl_3 and PrCl_3 ; 0.07 M aq.-HCl for separation of PrCl_3 and NdCl_3 . Rotation: 800 rpm. Temperature: room temperature. Sample size: 0.54 ml of 0.02 M RECl_3 (containing equimolar amounts of RE_1 and RE_2 ions). Detection: Xylenol orange method as described in the preceding paper.(1)

(2) **Behaviors of YbCl_3 and ErCl_3 with D2EHPA Separator:** Number of cartridges: 3. Dead volume: 23 ml for toluene, and 24 ml for CHCl_3 . Mode: descending mode for toluene, and ascending mode for CHCl_3 . Stationary phase: 0.1M D2EHPA in toluene or CHCl_3 . Mobile phase: $1.12 \pm 0.02 \text{ ml min}^{-1}$; 0.20 M aq.-HCl for YbCl_3 (toluene), 0.15 M aq.-HCl for YbCl_3 (CHCl_3), and 0.10 M aq.-HCl for separation of YbCl_3 and ErCl_3 . Rotation: 1200 rpm for YbCl_3 (toluene), and 700 rpm for CHCl_3 systems. Temperature: room temperature. Sample size: 0.54 ml of 0.02 M for a binary RECl_3 sample (containing equimolar amounts of RE_1 and RE_2 ions), and 0.01 M YbCl_3 . Detection: the same as in the case of (1).

(3) **TBP separator System for $\text{RE}(\text{NO}_3)_3$:** Number of cartridges: 3. Dead volume: 25 ml. Mode: descending mode. Stationary phase: neat TBP. Mobile phase: $1.12 \pm 0.02 \text{ ml min}^{-1}$; 1.00 M and 1.50 M LiNO_3 . Rotation: 1200 rpm. Temperature: room temperature. Sample size: 0.54 ml of 0.01 M $\text{RE}(\text{NO}_3)_3$ ($\text{RE} = \text{Nd, Sm, Eu and Yb}$), and 0.02 M for binary $\text{RE}(\text{NO}_3)_3$ sample (containing equimolar amounts

of $\text{Nd}(\text{NO}_3)_3$ and $\text{Sm}(\text{NO}_3)_3$ Detection: the same as in the case of (1).

RESULTS AND DISCUSSION

(1) Effect of Number of Microcells for Separation of CeCl_3 , PrCl_3 , and NdCl_3 with D2EHPA Separator:

Effect of the number of cartridges on the chromatographic behaviors of binary mixtures of $\text{PrCl}_3/\text{NdCl}_3$, and $\text{CeCl}_3/\text{PrCl}_3$ were examined with 0.1 M n-heptane solution of D2EHPA as stationary phase. With 0.07 M aqueous HCl solution as mobile phase, peak resolution (R) of the former mixture was improved (0.62) in the 6-cartridge (containing 2400 microcells) system relative to the 3-cartridge (containing 1200 microcells) system (0.37) (TABLE 1). This is mainly due to the increase of numbers of effective theoretical plate (ca. 1.5 times for PrCl_3 , and ca. 3 times for NdCl_3). Since the separation factors (α) were the same for the both cases (1.7), two-peak chromatogram was obtained with the 6-cartridge system as shown in Figure 1.

TABLE 1. EFFECT OF NUMBER OF MICROCELLS ON SEPARATION PARAMETERS FOR EQUIMOLAR $\text{CeCl}_3/\text{PrCl}_3$ AND $\text{PrCl}_3/\text{NdCl}_3$ BINARY MIXTURES.^a

RE_1	RE_2	No. of micro-cells	[HCl] (M)	$n(\text{RE}_1)$	$n(\text{RE}_2)$	R	α
Ce	Pr	1200	0.05	41	54	0.77	1.7
Ce	Pr	2400	0.06	48	61	0.85	1.7
Pr	Nd	1200	0.07	31	28	0.37	1.4
Pr	Nd	2400	0.07	47	82	0.62	1.4

a) Stationary phase: 0.1 M D2EHPA in n-heptane. 400 microcells are contained in one cartridge. n: Effective theoretical number of plate, R: peak resolution, and α : separation factor.

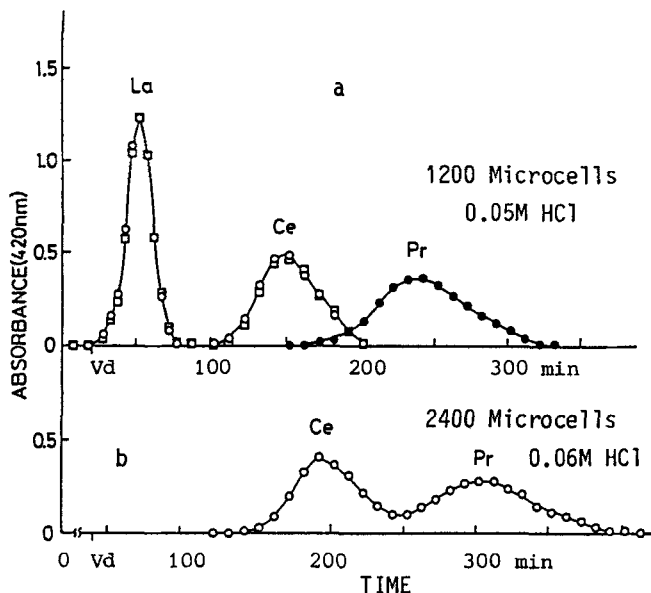


FIGURE 1. Effect of number of microcells on separation of an equimolar binary mixture of PrCl_3 and NdCl_3 by centrifugal partition chromatography with D2EHPA/n-heptane stationary phase. Curve (a): 1200 microcells; $[\text{HCl}] = 0.07 \text{ M}$. (1) Curve (b): 2400 microcells; $[\text{HCl}] = 0.07 \text{ M}$.

For the case of binary $\text{CeCl}_3/\text{PrCl}_3$ mixture, the effect of increasing the number of cartridges was not so important when the value of α was identical (1.7). Namely, the result of using 6 cartridges with 0.06 M $[\text{HCl}]$ was only slightly better (n_{Ce} and n_{Pr} was only 1.17 and 1.13 times, respectively, resulting in only 1.10 times higher R value) than that of using 3 cartridges with 0.05 M $[\text{HCl}]$ (Figure 2). This is due to that chromatographic behaviors of such a lighter RE system can be

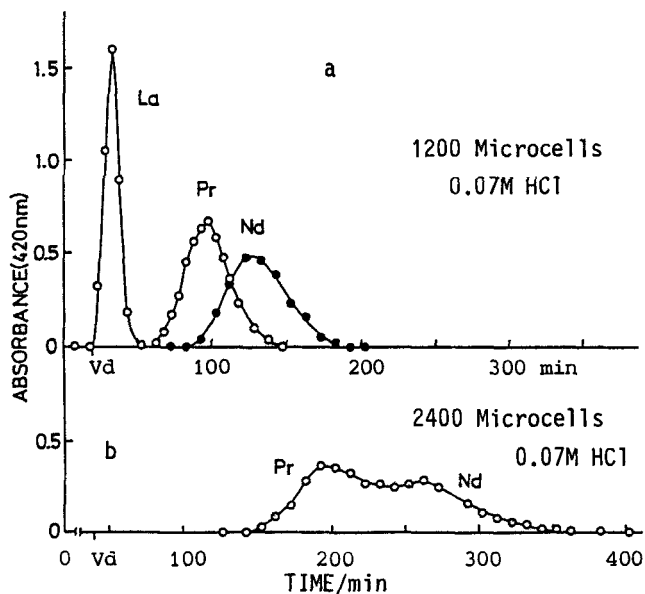


FIGURE 2. Effect of number of microcells on separation of an equimolar binary mixture of CeCl_3 and PrCl_3 by centrifugal partition chromatography with D2EHPA/n-heptane stationary phase. Curve (a): 1200 microcells; $[\text{HCl}] = 0.05 \text{ M}$. (1) Curve (b): 2400 microcells; $[\text{HCl}] = 0.06 \text{ M}$.

well controlled by the concentration of HCl in the mobile phase, and this type of $[\text{HCl}]$ -controlling is more convenient for practical applications than by increasing the number of cartridges.

Our conclusion from this experiment is that increase of the number of microcells is effective when the peak-broadening is considerably significant, i.e., for RE ions of higher atomic numbers.

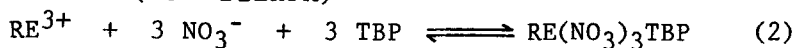
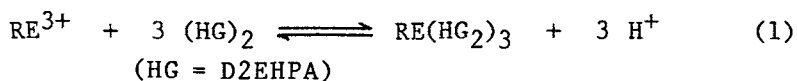
(2) Behaviors of YbCl_3 and ErCl_3 with D2EHPA Separator (Effect of Solvent):

With 0.1 M toluene solution of D2EHPA as stationary phase and with 0.20 M aqueous HCl (almost the maximum [HCl] for our CPC experiment) as mobile phase, an extremely broad peak of YbCl_3 was observed, and its retention value was also high as shown in Figure 3a. But the chromatographic behavior was extensively improved by the use of CHCl_3 as stationary solvent (Figure 3b). Combining our present results with the previous ones,⁽¹⁾ we can conclude that more polar solvent is effective for both shortening the retention times and narrowing the peaks of RE^{3+} ions having higher atomic numbers, i.e., n-heptane for La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} ; toluene for Sm^{3+} , Eu^{3+} , and RE^{3+} ions in near heavier; and CHCl_3 for much heavier ions around Yb^{3+} .

In fact, separation of ErCl_3 from YbCl_3 with 0.1 M D2EHPA solution in CHCl_3 was readily realized at [HCl] = 0.10 M (Figure 3c). This result suggests that the whole range of RE ions will be separated with D2EHPA by adjusting the nature of solvent in the stationary phase, along with adjusting [HCl] in the mobile phase.

(3) TBP Stationary Phase for $\text{RE}(\text{NO}_3)_3$:

D2EHPA is an acidic separator whose key interaction in CPC has been supposed to be relatively strong acid-base type interaction shown as eq 1.^(1,4) In contrast, tri-n-butyl phosphate (TBP) is a neutral phosphate also widely used in extraction of RE ions, and its extraction mechanism is described as the eq 2:⁽⁵⁾



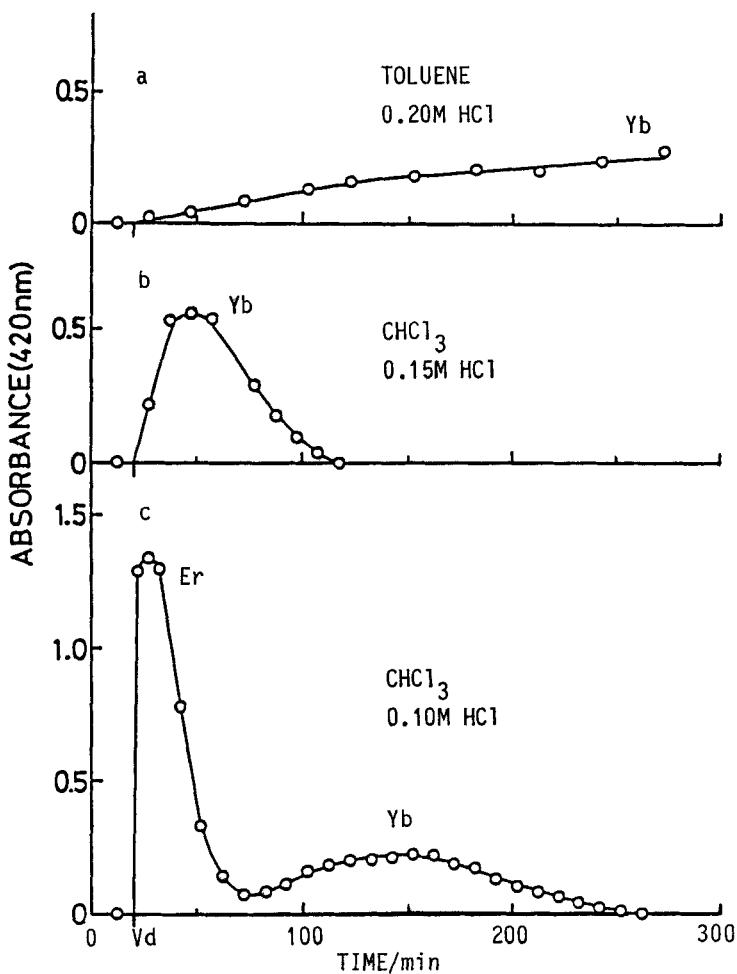


FIGURE 3. Behaviors of Yb^{3+} ion in centrifugal partition chromatography using toluene and chloroform as stationary solvent of D2EHPA. 1200 Microcells. Curve (a): Solvent: toluene; $[\text{HCl}] = 0.20 \text{ M}$. Curve (b): Solvent: CHCl_3 ; $[\text{HCl}] = 0.15 \text{ M}$. Curve (c): Separation of an equimolar binary mixture of ErCl_3 and YbCl_3 by the use of CHCl_3 solvent, where $[\text{HCl}] = 0.10 \text{ M}$.

The TBP-extraction results already published differ considerably from those of D2EHPA, e.g., the order of extractability is not always parallel to the atomic number of RE ions.(5,6) In addition, there was a possibility that milder interaction of neutral TBP might cause narrowing of the chromatographic peaks of RE ions in CPC. In the present study, neat TBP was used as the stationary phase because we intended for testing the maximum efficiency of TBP.

In the extraction procedures with TBP, very high concentration (1N-18N) of aqueous HNO_3 has been employed. However, the use of such a highly concentrated HNO_3 is difficult to use in our CPC machine. Alternatively, aqueous solutions containing salting-out agents, i.e., nitrates of Li, NH_4 , Fe, Al, and Ca, or isothiocyanates of Li, Na, and NH_4 , have been used for the TBP-extraction.(7) Among them LiNO_3 was found to be the most effective, and moreover, detection ability of RE ions by xylenol orange method in the presence of LiNO_3 was also satisfactory. Hence, we chose to use its aqueous solution as our mobile phase.

CPC results obtained with neat TBP as stationary phase and aqueous LiNO_3 as mobile phase, and RE^{3+} (Nd^{3+} , Sm^{3+} , Eu^{3+} and Yb^{3+}) nitrates as sample were considerably poorer than the cases of D2EHPA separator:

(a) Separation of Nd^{3+} versus Sm^{3+} gave $\alpha = 1.2$, and $n = 21$ for Nd^{3+} and 20 for Sm, giving rise to extremely low R value (= 0.15).

(b) Sm^{3+} and Eu^{3+} gave almost the same retention times ($22(V_d) + \text{ca. } 28 = \text{ca. } 50$ min), and the shape of considerably broad peaks was almost identical.

(c) The α value of Yb^{3+} versus Eu^{3+} was considerably high (= 1.9), but significant broadness of these peaks ($n = 14$ for Yb^{3+} and 13 for Eu^{3+}) prevents effective separation ($R = 0.50$).

(d) Retention time of heavier Yb^{3+} ($22(V_d) + \text{ca. } 4 = \text{ca. } 26$ min) was much smaller than Eu^{3+} ($22(V_d) + \text{ca. } 28 = \text{ca. } 50$ min), i.e., the retention times of RE ions is not parallel to their atomic number.

Even considered that the nitrate samples have less affinities for the highly organic phosphate relative to the corresponding chloride samples, the neutral phosphate, TBP, should be concluded as a significantly less effective separator for CPC applications. In contrast, Akiba, et al.(3) obtained effective separations by using PC-88A which shows essentially similar behaviors to our D2EHPA cases.(1,2) Combining the CPC results obtained by us using D2EHPA ($(\text{RO})_2\text{P}(=\text{O})\text{OH}$) in the preceding work(1) plus in this report with those obtained by Akiba et al.(3) using PC-88A ($\text{R}(\text{RO})\text{P}(=\text{O})\text{OH}$) and with those obtained by us using TBP ($(\text{RO})_3\text{P}=\text{O}$), the acidic nature (P-OH) of the phosphorus compounds seems to be a key property for effective separations of RE^{3+} ions in the present stage.

CONCLUDING REMARKS

Since D2EHPA has been widely used in practical extraction of rare earth metal ions, test of its applicability to the centrifugal partition chromatography seems to be reasonable. On the basis of the results of preceding paper(1, 2), behaviors of RE ions in CPC with D2EHPA as separator were further studied. (1) For the binary mixture of Pr^{3+} and Nd^{3+} , whose separation is important for RE-technologies, increase of the number of microcells for obtaining higher number of theoretical plate is shown to be effective. (2) The use of more polar CHCl_3 as the stationary solvent gave promises for separations of heavier series of RE ions including Yb^{3+} and probably Lu^{3+} . (3) Acidic nature of the phosphorus

containing separator is thought to be the key property for effective separation, until a new and effective neutral separator is developed in future. Hence, [HCl]-gradient techniques, addition of an organic material in the mobile phase(3), or other experimental improvements for narrowing the peaks will be of value in the present stage.

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