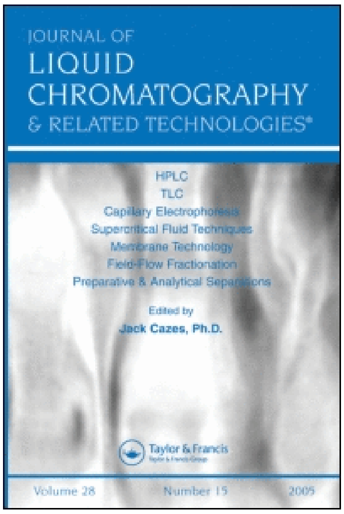

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SEPARATION OF LIGHT LANTHANOIDS BY CENTRIFUGAL PARTITION CHROMATOGRAPHY IN 30% TBP EXTRACTION SYSTEM

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ABSTRACT

Separation of light lanthanoids(III) with centrifugal partition chromatography (CPC) in 30% tri·n·butyl phosphate (TBP) extraction system with the aid of salting-out agent lithium nitrate ($LiNO_3$) was investigated. Carbon tetrachloride (CCl_4) and n·dodecane were used as diluents to control the density difference between mobile and stationary phases.

By a batch method, it was proved that distribution ratios (D) and separation factors (α) of several light lanthanoids increased with the $LiNO_3$ concentration in 1 M ($mol \cdot dm^{-3}$) nitric acid in the aqueous phase. Addition of CCl_4 to 30% TBP-n·dodecane organic phase resulted in a decrease of the D values, holding the α values constant.

On the basis of these data, separations of Ce, Pr and Eu with a CPC apparatus were successfully performed by decreasing the density difference. Although the chromatogram data differed considerably from the batch data owing to the concentration effect of the lanthanoids, satisfactory separation was obtained in 30% TBP-35% n·dodecane-35% CCl_4 and 5 M $LiNO_3$-1 M HNO_3 (α(Pr/Eu): 5.8, resolution(Pr/Eu): 2.0).

INTRODUCTION

Centrifugal partition chromatography (CPC) is a liquid-liquid extraction separation method in which the centrifugal force enables not only dispersion of a mobile phase in a stationary phase but also separation of the both phases (1). Therefore, CPC is suitable for separations of macroamounts of chemical species in relatively short time.

The method has been initially developed for purification of organic substances (1). Recently it has been applied to separation of lanthanoids(III) in the pH region with various extractants, such as EHPA (2), HDEHP (3)(4), and Cyanex 272 (5).

Tri·n·butyl phosphate (TBP) is widely used as an extractant of U and Pu in the nuclear fuel cycle and applicable in the acid region. Lanthanoids are not extracted with TBP from nitric acid (HNO_3) solutions less than several M ($mol \cdot dm^{-3}$), but they are extracted from concentrated nitrate solutions due to salting-out effects (6). Separation factors among them in concentrated nitric acid solution increase also with the concentration of nitrate ions (7).

The authors have applied the TBP extraction system to the separation of lanthanoids with CPC by using lithium nitrate ($LiNO_3$) as a salting-out reagent. In CPC separation, pump pressure for supplying the mobile phase is represented as follows (8):

$$P = K \cdot \Delta\rho \cdot R^2 \qquad [1]$$

where P is the pump pressure (MPa), K is a constant, $\Delta\rho$ is the density difference between the mobile and the stationary phases ($g \cdot cm^{-3}$) and R is the rotational speed of the partition cells (rpm). Since the density of the mobile phase increases with addition of $LiNO_3$, it is necessary to increase the density of the organic phase in order to operate the CPC apparatus under reasonably low pump pressure. If the pressure is increased beyond about 4 MPa, serious leaks of the mobile phase may occur.

Carbon tetrachloride (CCl_4, ρ: 1.6 $g \cdot cm^{-3}$) and n·dodecane (ρ: 0.75 $g \cdot cm^{-3}$) are suitable diluents for controlling the density of the organic phase at a constant percentage of TBP. In this paper, the effects of $LiNO_3$ as salting-out reagent and CCl_4 as diluent in 30% TBP-n·dodecane system on distribution ratios (D) of light lanthanoids were examined by a batch method. After that, the separation of lanthanoids with the CPC apparatus for 30% TBP-n·dodecane-CCl_4 as organic phase and 3-5 M $LiNO_3$-1 M HNO_3 as aqueous phase was demonstrated.

EXPERIMENTAL

Reagents

An extractant; TBP (99.8%), two diluents; n·dodecane (95%) and CCl_4 (97.8%) and a salting-out reagent; $LiNO_3$, reagent grade, were used without further purification. Nitrates of Ba and Ce (99.9%) and oxides of Pr (99.5%), Nd, Sm and Eu (99.9%) were dissolved in HNO_3 solution to prepare their stock solutions. Barium was used as an unextractable spike in order to evaluate a dead volume of the CPC chromatogram.

Apparatus

A centrifugal partition chromatograph, Model-LLN, supplied by Sanki Engineering Co. Ltd was used (8). The CPC apparatus was equipped with 6 partition-cell cartridges, Model 250W. Each cartridge has 400 micro cells and total volume of the partition cells was 125 cm^3. A fraction collector was used to fractionate the mobile phase eluted from the CPC apparatus.

An inductively coupled plasma (ICP) spectrometer was employed for determining the concentration of Ba and lanthanoids in the aqueous and organic phases.

Procedures

Distribution ratio of Ba, Ce, Pr, Nd, Sm and Eu were determined by a batch method in the range of 0 to 8 M ($mol \cdot dm^{-3}$) of $LiNO_3$ in 1 M HNO_3 solutions and 0 to 40% of CCl_4 in 30% TBP-n·dodecane organic solvents. The aqueous phase contained 500 $mg \cdot dm^{-3}$ of the respective solutes. The both phases (10 cm^3) were shaken at 25 °C for 3 h.

Separations of Ba, Ce, Pr and Eu with CPC were carried out. Previously the organic phase was charged into the partition cells as the stationary phase, then the aqueous phase was supplied as the mobile phase by a pressurized pump until volume balance between the two phases was equilibrated. Volume percentage of the CCl_4 diluent was selected to keep the $\Delta\rho$ to be constant (0.09 at 2 MPa and 800 rpm). Sample solution of 2.5 cm^3 (Ce:~10, Pr:~15, Eu:~60 $g \cdot dm^{-3}$) was injected through a sample loop to the partition cells. Each solute was eluted with the mobile phase at 800 rpm rotational speed, 25 °C of temperature and 1.5 $cm^3 \cdot min^{-1}$ flow rate.

Analysis of the chromatogram

In the CPC experiments, D, separation factor (α) and resolution between two peaks (R_s) were calculated from the following equations:

$$D = (t_R - t_{RO}) \cdot F / V_s \qquad [2]$$

$$\alpha = D_2/D_1 \qquad [3]$$

$$R_s = 2\cdot(t_{R2}-t_{R1})/(t_{w1}+t_{w2}) \qquad [4]$$

where t_R is the retention time of a solute, t_{RO} is the retention time of Ba, F is flow rate, V_s is the volume of stationary phase and t_w the width at the bottom of peak. Subscript numbers 1 and 2 denote solute 1 and 2. For the estimation of the CPC efficiency the effective theoretical plate number (N_{eff}) was used instead of the theoretical plate number because of too large dead volume (9):

$$N_{eff} = 16\cdot((t_R-t_{RO})/t_w)^2 \qquad [5]$$

RESULTS AND DISCUSSION

Effects of $LiNO_3$ and CCl_4 concentration on the D values

TABLE 1 shows the D values of Ce, Pr, Nd, Sm and Eu, which were obtained by the batch experiments. The D values of Ba were less than 0.001 in all the experiments. The salting-out effect of $LiNO_3$ on the D of lanthanoids in 30% TBP-70% n·dodecane is shown in FIGURE 1. The D values for all the lanthanoids increased with the concentration of $LiNO_3$ and the α values between them also increased. The same tendency was also observed in other 30% TBP-n·dodecane solvents including CCl_4.

The diluent effect of CCl_4 on the D values of lanthanoids in 4 M $LiNO_3$-1 M HNO_3 solution is shown in FIGURE 2. The D values decreased with increasing percentage of CCl_4. This may be a consequence of the decrease of the donicity of TBP with increasing percentage of CCl_4 because CCl_4 has the larger acceptor number than n·paraffins such as n·dodecane (10). On the other hand, the α values were almost constant.

TABLE 1
Distribution Ratio of Lanthanoids obtained by a Batch Method (30% TBP, 1M HNO_3)

CCl_4: 0%, n·dodecane:70%

[$LiNO_3$](M)	Ce	Pr	Nd	Sm	Eu
0	2.00E-2	1.89E-2	2.12E-2	2.70E-2	2.60E-2
2	1.70E-1	1.88E-1	2.38E-1	3.62E-1	3.45E-1
4	4.70E-1	6.55E-1	9.12E-1	1.73E 0	1.88E 0
6	1.04E 0	1.63E 0	2.59E 0	6.04E 0	6.91E 0

CCl_4:10%, n·dodecane:60%

[$LiNO_3$](M)	Ce	Pr	Nd	Sm	Eu
0	1.55E-2	1.56E-2	1.58E-2	2.28E-2	2.20E-2
2	1.38E-1	1.57E-1	2.00E-1	3.10E-1	3.08E-1
4	4.10E-1	5.87E-1	8.27E-1	1.59E 0	1.71E 0
6	9.37E-1	1.47E 0	2.53E 0	5.79E 0	6.47E 0

CCl_4:20%, n·dodecane:50%

[$LiNO_3$](M)	Ce	Pr	Nd	Sm	Eu
0	1.18E-2	1.21E-2	1.30E-2	1.99E-2	1.80E-2
2	1.18E-1	1.32E-1	1.83E-1	2.86E-1	2.79E-1
4	3.43E-1	5.17E-1	7.30E-1	1.43E 0	1.54E 0
6	8.40E-1	1.32E 0	2.33E 0	5.35E 0	5.88E 0

CCl_4:30%, n·dodecane:40%

[$LiNO_3$](M)	Ce	Pr	Nd	Sm	Eu
0	9.19E-3	9.08E-3	1.09E-2	1.80E-2	1.50E-2
2	9.43E-2	1.11E-1	1.56E-1	2.56E-1	2.52E-1
4	3.03E-1	4.72E-1	6.44E-1	1.24E 0	1.34E 0
6	7.50E-1	1.19E 0	2.05E 0	5.00E 0	5.41E 0

CCl_4:40%, n·dodecane:30%

[$LiNO_3$](M)	Ce	Pr	Nd	Sm	Eu
0	8.84E-3	7.64E-3	1.08E-2	1.45E-2	1.30E-2
2	8.77E-2	1.04E-1	1.41E-1	2.40E-1	2.44E-1
4	2.68E-1	4.37E-1	6.00E-1	1.13E 0	1.22E 0
6	6.76E-1	1.11E 0	1.98E 0	4.60E 0	5.26E 0

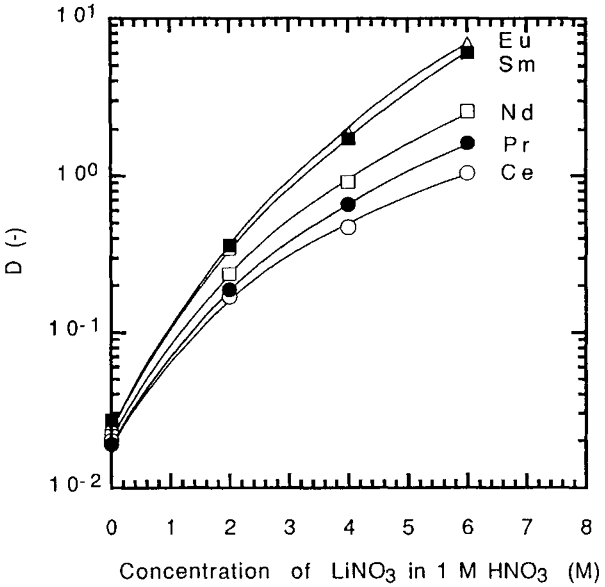

FIGURE 1. Salting-out effect of $LiNO_3$ on the D values of lanthanoids. Organic phase: 30% TBP, 70% n-dodecane.

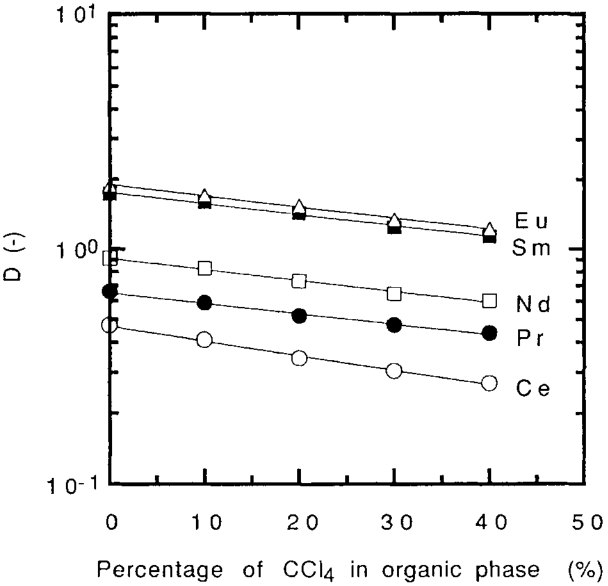

FIGURE 2. Diluent effect of CCl_4 on the D values of lanthanoids. Aqueous phase: 4 M $LiNO_3$, 1 M HNO_3.

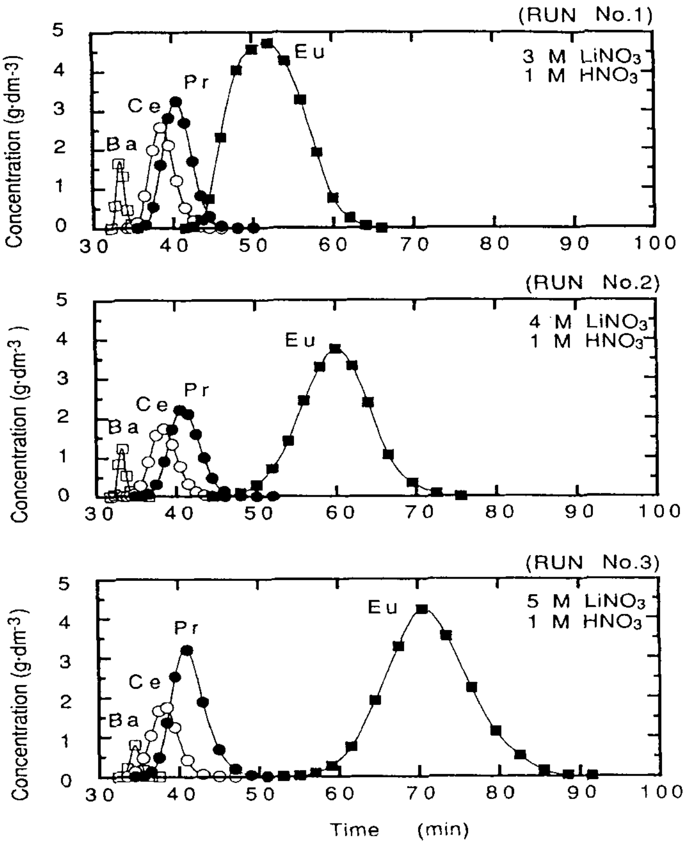

FIGURE 3. Chromatograms of Ba, Ce, Pr and Eu.

Therefore, when using CCl_4 as diluent, the the density difference between the two phases can be controlled without decrease of α values. In addition, the effect of CCl_4 on the D is advantageous for the CPC separations since the CCl_4 diluent makes t_R somewhat smaller in the region where the salting-out is effective.

TABLE 2
Experimental Conditions and Analytical Results for RUN No.1, No.2 and No.3

RUN No.		1	2	3
mobile phase	[$LiNO_3$] (M)	3.0	4.0	5.0
	[HNO_3] (M)	1.0	1.0	1.0
stationary phase	[TBP] (%)	30	30	30
	[n·dodecane] (%)	45	40	35
	[CCl_4] (%)	25	30	35
D	Ce	0.09(0.19)	0.09(0.30)	0.07(0.46)
	Pr	0.13(0.27)	0.14(0.47)	0.12(0.75)
	Eu	0.32(0.61)	0.50(1.4)	0.69(2.8)
α	Pr/Ce	1.4 (1.4)	1.6 (1.6)	1.7 (1.6)
	Eu/Pr	2.5 (2.3)	3.6 (2.9)	5.8 (3.7)
N_{eff}	Ce	11	9.1	4.7
	Pr	16	15	8.9
	Eu	16	39	45
R_s	Pr/Ce	0.29	0.35	0.33
	Eu/Pr	0.84	1.6	2.0
	ρ_{aq} (g·cm^3)	1.15	1.19	1.22
	ρ_{org} (g·cm^3)	1.06	1.10	1.13
	$\Delta\rho$ (g·cm^3)	0.09	0.09	0.09

( ) batch experiment results

Separation of Lanthanoids with CPC

Chromatograms for RUNs No.1, 2 and 3 are shown in FIGURE 3 and the experimental conditions and analytical results are summarized in TABLE 2. The parenthesized values were calculated by interpolating the batch experiment data.

The D values were quite different from those of the batch experiments. The initial concentrations of solutes in the aqueous phase of batch experiments were much lower than those in the sample solutions of CPC

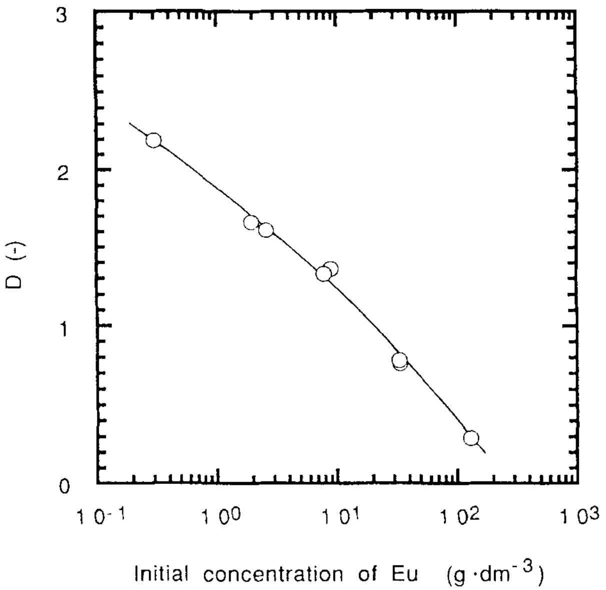

FIGURE 4. Concentration effect on the D values of Eu.

experiments. FIGURE 4 shows the concentration effect on the D values of Eu. The D values decreased with increasing the initial concentration of Eu in aqueous phase. Therefore, the differences between the CPC and the batch data were caused by the concentration effects primarily.

The "bleeding" problem (11) of the stationary phase from the partition cells may be another cause of the differences. The leak rate of the stationary phase up to about 3 cm^3 per hour was observed in some CPC experiments. If the volume of stationary phase in the partition cells decreases, the D values calculated from eq.[2] are underestimated.

Although the D values for Eu increased with increasing $LiNO_3$ concentration, those of Ce and Pr did not increase. Therefore, the α values between Pr and

Eu considerably increased from 2.5 in RUN No.1 to 5.8 in RUN No.3. Since the retention time of Eu was longer than those of Ce and Pr, Eu was more diluted in the mobile phase in partition cells than Ce and Pr. The concentration effect on the D values of Ce and Pr would be larger than that of Eu.

The N_{eff} for Eu increased from 16 in RUN No.1 to 45 in RUN No.3, while that for Ce or Pr decreased. Consequently, R_s between Pr and Eu was improved from 0.84 in RUN No.1 to 2.04 in RUN No.3, while that between Ce and Pr was hardly improved.

The density difference between the two phases could be maintained constant ($\Delta\rho$: 0.09 $g \cdot cm^{-3}$) by substituting n·dodecane with CCl_4 as diluent. Consequently, operation of the CPC apparatus could be carried out at reasonably low pressure (2.0 MPa) without any leak of the mobile phase.

CONCLUSIONS

Separation of light lanthanoids(III) with CPC was studied in 30% TBP-n·dodecane extraction system by the aid of salting-out effect of $LiNO_3$. By substituting n·dodecane with CCl_4 as diluent of TBP, use of $LiNO_3$ up to 5 M was realized. Although the concentration effect of the lanthanoids showed the difference of the apparent D values between the CPC and the batch experiments, it also caused the increase of the α values between Pr and Eu. Therefore, effective separation of Pr and Eu (α: 5.8, R_s: 2.0) was performed under appropriate operational conditions (pump pressure: 2.0 MPa at 800 rpm, 30% TBP-35% n·dodecane-35% CCl_4, and 5 M $LiNO_3$-1 M HNO_3).

If suitable diluents can be selected to control the density difference between the stationary and mobile phases, CPC will serve as an effective separation method for macroamounts of inorganic species.

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