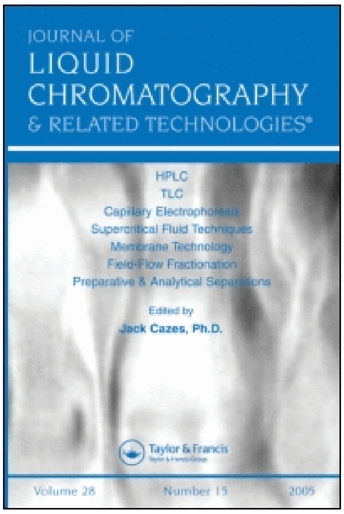

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CHARACTERISTICS OF CENTRIFUGAL PARTITION CHROMATOGRAPHY FOR LANTHANOID SEPARATION IN HDEHP EXTRACTION SYSTEM

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ABSTRACT

Separation of light lanthanoids with centrifugal partition chromatography (CPC) was investigated in extraction system of 30% HDEHP/CCl_4/n-paraffin and HNO_3. Since separation factors between lanthanoids, Ce, Nd, Pr, Sm, Eu and Gd, were independent of volume ratio of CCl_4 and n-paraffin diluents, difference in the density between the mobile phase and the stationary phase was controlled by varying the volume ratio of two diluents in order to operate at reasonable pump-pressure. The effects of volume of the stationary phase and rotational speed on the separation characteristics of CPC were examined to find the optimum operation conditions. The effect of chain length of n-paraffin (number of carbon atoms: 6 - 15) as diluents was also examined. The best separation efficiency was obtained with the longest, n-pentadecane. On the basis of the above results, mutual separation of lanthanoids was successfully performed in 30% HDEHP/15% CCl_4/55% n-pentadecane and 0.5 mol/dm^3 HNO_3 extraction system at a low pump pressure of 4.5 kgf/cm^2.

INTRODUCTION

Centrifugal partition chromatography (CPC) is a new liquid-liquid separation method, in which the centrifugal force enables retention of a stationary phase in the partition cells, dispersion of a mobile phase in the stationary phase and rapid phase separation (1). The method was first developed for separation of organic substances. Recently it has been also applied to separation of inorganic substances (2)(3)(4). The authors reported separation of light lanthanoids with CPC in 30% TBP extraction system using lithium nitrate as a salting-out reagent (5)(6). Difference in density between the aqueous and organic phases could be controlled by using carbon tetrachloride (CCl_4: 1.6 g/cm^3 density) as a heavy diluent and n-dodecane (0.75 g/cm^3) as a light diluent, and then the CPC apparatus was operated at low pump pressure.

In order to achieve effective separation with CPC apparatus, it is important to get both large separation factor and high theoretical plate number. The separation factor depends on the extraction conditions such as acidity of aqueous phase and concentration of extractant. The theoretical plate number is affected by the operation conditions of CPC apparatus such as rotational speed and volume of the stationary phase, and by the physical properties of the two phases such as interfacial tension and viscosity.

Di-2-ethylhexyl phosphoric acid (HDEHP) has been widely used for mutual separation of lanthanoids and actinoids. Separation of lanthanoids in extraction system of HDEHP and hydrochloric acid by using CPC apparatus was also reported (7)(8). This paper deals with the separation characteristics of light lanthanoids with CPC apparatus in extraction system of HDEHP/CCl_4/n-paraffin and nitric acid (HNO_3). To obtain the optimum extraction conditions, distribution coefficients were determined by batch experiments. Then, to find the operation conditions of CPC apparatus giving high theoretical plate number, the effects of volume of the stationary phase, rotational speed and the physical properties were examined. For the effect of the physical properties of the two phases, n-paraffin with different number of carbon atoms (C: 6 - 15) was used as a diluent because their chemical properties seem similar to each other. After that, the separation of lanthanoids with CPC apparatus was demonstrated.

EXPERIMENTAL

Reagents

An extractant of HDEHP (98.2%) and diluents of CCl_4 (97.8%), n-hexane (95 - 97%) and other n-paraffin (99.0%) were used without further purification.

As solutes, Li and Ce nitrates and Pr, Nd, Sm, Eu and Gd oxides of reagent grade were used by dissolving them in HNO_3 solution. Lithium was an unextractable spike to evaluate a dead volume of CPC chromatogram.

Apparatus

Two types of CPC apparatus, Model-LLN and Model-LLB, were supplied by Sanki Engineering Co. Ltd. The former apparatus was used in order to study the effect of the stationary phase volume on the separation efficiency of CPC. The apparatus was equipped with different number of partition-cell cartridges, Model 250W, which consisted of 400 microcells. The volume of each cartridge was 20.8 cm^3. The latter apparatus, Model-LLB, was used for the other experiments because the latter is superior to the former in the pressure-stability. The apparatus was equipped with 6 rotors, in which 720 micro-cells per rotor were molded. The total volume was 135 cm^3.

An inductively coupled plasma (ICP) spectrometer was used for determining the concentration of lanthanoids.

Procedures

In batch experiments, the initial concentration of each solute in the aqueous phase was 500 mg/dm^3. Both aqueous and organic phases of 10 cm^3 were shaken at 25 °C for 5 h. Since the solutes could not be back-extracted quantitatively, the concentration of the solutes in the organic phase was determined by subtracting concentration of the remained solutes in the aqueous phase from that in the initial aqueous phase.

In CPC experiments, at first, the stationary and mobile phases were balanced in the partition cells with the same method previously described (6). Then, sample solution of 1.1 cm^3 was injected through a sample loop to the partition cells by a pump. Each solute was eluted at the flow rate of 1.5 cm^3/min and 25 °C.

Analysis of the chromatogram

Distribution coefficient (K_d), separation factor (α) and resolution between two peaks (R_s) were calculated from chromatograms with the same equations (6). For estimation of the separation efficiency of CPC, relative peak width (W_p) was used instead of the theoretical plate number because of too large dead volume;

$$W_p = V_{wh}/V_R'$$

where V_{wh} in cm^3 is peak width at half height and V_R' in cm^3 is corrected retention volume which was obtained by subtracting retention volume of Li.

RESULTS AND DISCUSSION

Determination of the K_d and α values by batch method

Effect of HNO_3 and CCl_4: TABLE 1 shows the K_d values of lanthanoids obtained by the batch experiments. It was confirmed that Li was not extracted in all experimental conditions. The effect of the concentration of HNO_3 on the K_d values in 30% HDEHP/ 70% n-dodecane is shown in FIGURE 1. The K_d values decreased with increasing concentration of HNO_3. This decrease with the slope of −3 indicates that extraction of lanthanoids with HDEHP is due to cation exchange reaction as follows (9);

$$M^{3+}_{aq} + 3(HY)_{2\,org} \longrightarrow M(HY_2)_{3\,org} + 3H^+_{aq}$$

where M^{3+} is a lanthanoid ion (III) and HY is a HDEHP. On the other hand, the α values between lanthanoids were almost independent of the concentration of HNO_3.

FIGURE 2 shows the effect of concentration of CCl_4 on the K_d values in 30% HDEHP/n-dodecane and 0.5 mol/dm^3 (M) HNO_3. The values decreased with increasing concentration of CCl_4 in analogy with the TBP extraction system. This seems a result of the decrease of the activity of HDEHP in the organic phase with increasing concentration of CCl_4 because CCl_4 has a larger acceptor number than n-dodecane (10). On the other hand, the α values were almost independent of the concentration of CCl_4.

From these results, it was found that the K_d value for adequate retention volume and the difference in density for reasonable pump pressure in CPC operation could be set without decrease of the α value.

Effect of number of carbon atoms of n-paraffin: FIGURE 3 shows effect of number of carbon atoms of n-paraffin on the K_d values in 30% HDEHP/70% n-paraffin and 0.7M HNO_3. The K_d values increased with increasing the number and the α values were almost independent of the number.

Since HDEHP is polar, the association among themselves takes place through the dissolving water in the organic phase. Solubility of water in n-paraf-

TABLE 1
The K_d Values of Lanthanoids Obtained by Batch Experiments (30% HDEHP)

CCl_4: 0%, n-dodecane: 70%

$[HNO_3]$ M	Ce	Pr	Nd	Sm	Eu	Gd
0.25	2.8	3.9	4.9	28	67	123
0.50	0.56	0.72	0.77	4.2	9.1	16
0.75	0.22	0.21	0.24	1.2	2.4	4.3
1.00	0.15	0.11	0.13	0.56	1.0	1.7

CCl_4: 10%, n-dodecane: 60%

$[HNO_3]$ M	Ce	Pr	Nd	Sm	Eu	Gd
0.25	1.9	2.6	3.4	20	45	82
0.50	0.38	0.46	0.53	3.0	6.2	11
0.75	0.15	0.16	0.17	0.88	1.7	3.0
1.00	0.12	0.093	0.12	0.38	0.74	1.2

CCl_4: 20%, n-dodecane: 50%

$[HNO_3]$ M	Ce	Pr	Nd	Sm	Eu	Gd
0.25	1.3	1.8	2.4	15	34	61
0.50	0.26	0.34	0.31	2.1	4.2	7.7
0.75	0.10	0.10	0.12	0.61	1.2	2.2
1.00	0.085	0.056	0.083	0.25	0.50	0.82

CCl_4: 30%, n-dodecane: 40%

$[HNO_3]$ M	Ce	Pr	Nd	Sm	Eu	Gd
0.25	0.87	1.2	1.7	10	25	45
0.50	0.18	0.23	0.22	1.5	3.0	5.5
0.75	0.084	0.066	0.062	0.40	0.84	1.4
1.00	0.077	0.033	0.054	0.17	0.36	0.58

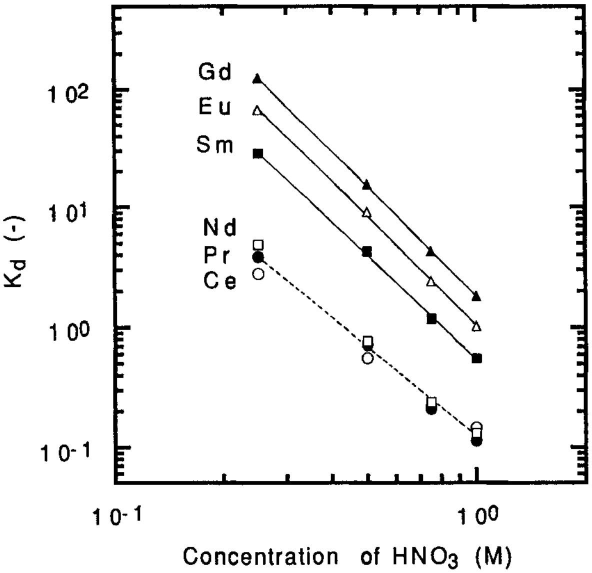

FIGURE 1. Effect of HNO_3 on the K_d values of lanthanoids. Organic phase: 30% HDEHP/70% n-dodecane.

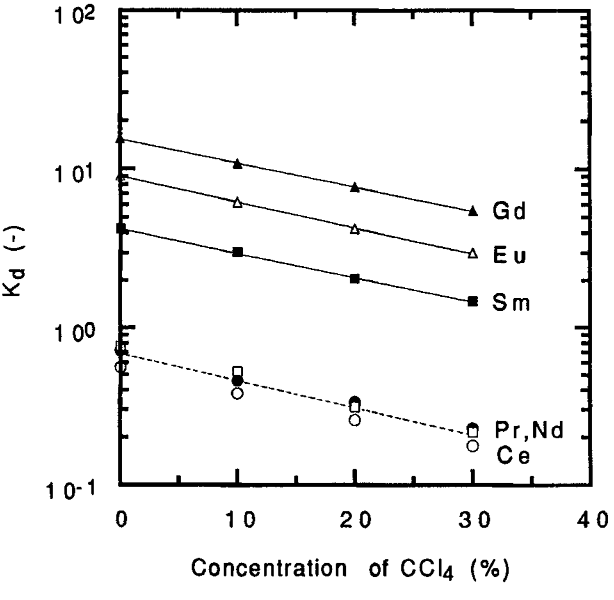

FIGURE 2. Effect of CCl_4 on the K_d values of lanthanoids. Aqueous phase: 0.5 M HNO_3, Organic phase: 30% HDEHP/CCl_4/n-dodecane

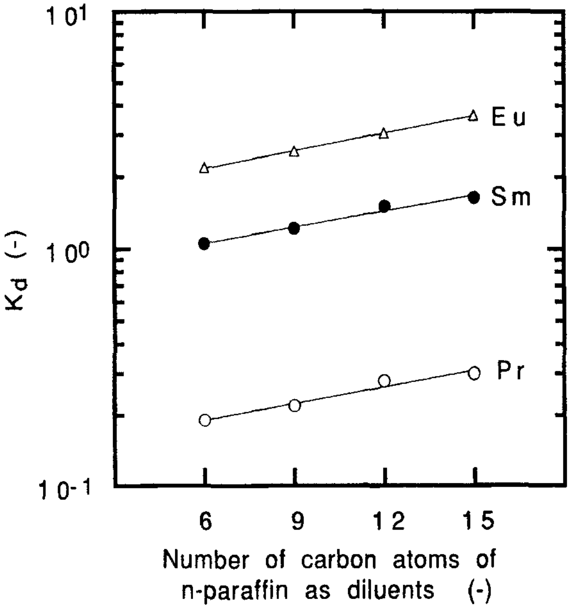

FIGURE 3. Effect of number of carbon atoms of n-paraffin as diluents on the K_d values of lanthanoids. Aqueous phase: 0.7 M HNO_3, Organic phase: 30% HDEHP/ 70%n-paraffin.

fin decreases with increasing the number (11). Therefore, the authors interpret the increase of the K_d values as the increase of the HDEHP activity in the organic phase.

Measurement of the separation efficiency of CPC

Effect of the stationary phase volume: FIGURE 4 shows the effect of volume of the stationary phase on the separation efficiency of CPC, which was examined by changing number of the partition cell cartridges. The relative peak width of Pr and Eu decreased and the resolution between them increased with increasing volume of the stationary phase.

It was observed that the maximum volume of the stationary phase being retained in the partition cells varied with the experimental conditions of CPC. Therefore, the effects of rotational speed and difference in the density on the

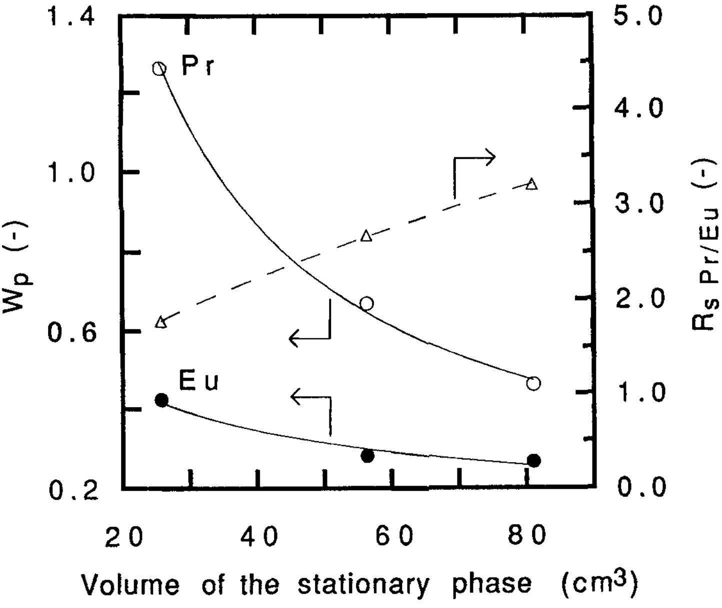

FIGURE 4. Effect of volume of the stationary phase on the separation efficiency of CPC. Mobile phase: 0.5 M HNO_3, Stationary phase: 30% HDEHP/15% CCl_4/ 55% n-dodecane, Rotational speed: 800 rpm.

maximum volume were examined. The results are shown in FIGURE 5. The maximum volume increased with increasing the rotational speed and the difference in density. Since the volume of the stationary phase affects the separation efficiency of CPC as described above, the volume of the stationary phase was attempted to keep constant in the CPC experiments below.

Effect of the rotational speed: FIGURE 6 shows the effect of the rotational speed of the partition cells in the region of 800 – 1400 rpm on the separation efficiency of CPC. The operation conditions and the analytical results of chromatograms are shown in TABLE 2 (Serial No.1). The pump pressure increased with increasing the rotational speed. The best separation efficiency was observed at 800 rpm. It was reported that the separation efficiency was improved with increasing the rotational speed because the dropsize of the mobile phase decreased with increasing gravity resulting from rotation (2). In this experimental condi-

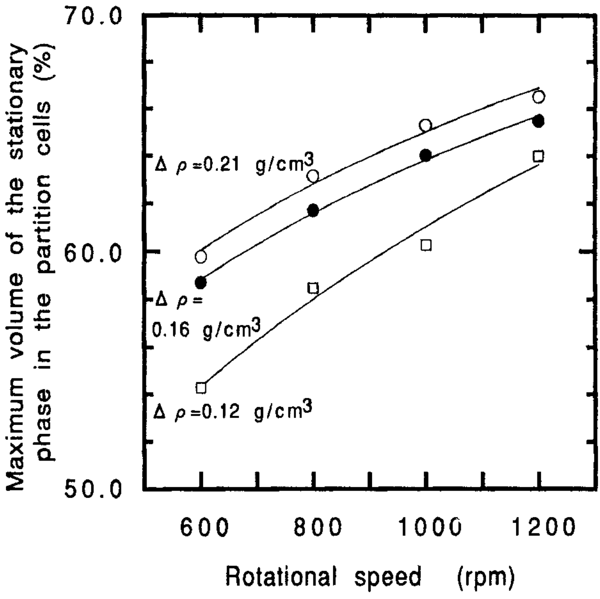

FIGURE 5. Effects of rotational speed and difference in density (Δρ) on the maximum volume of the stationary phase in the partition cells. Mobile phase: H_2O, Stationary phase: CCl_4/n-dodecane.

tions, however, this tendency was not observed. It might be necessary to examine the effect of the rotational speed under other experimental conditions such as another flow rate.

Effect of number of carbon atoms of n–paraffin: FIGURE 7 shows the effect of chain length of n–paraffin (number of carbon atoms: 6 – 15) as diluents on the separation efficiency of CPC. The operation conditions and the analytical results of chromatograms are shown in TABLE 2 (Serial No.2). The relative peak width of Sm and Eu decreased and the resolution increased with increasing the number. Since the α values were not affected by the difference of the number, the net improvement of the resolution between them is ascribed to the decrease in the peak width.

In CPC, the dropsize of the dispersed mobile phase is presumed one of the important parameters affecting the separation efficiency. It is predicted that the

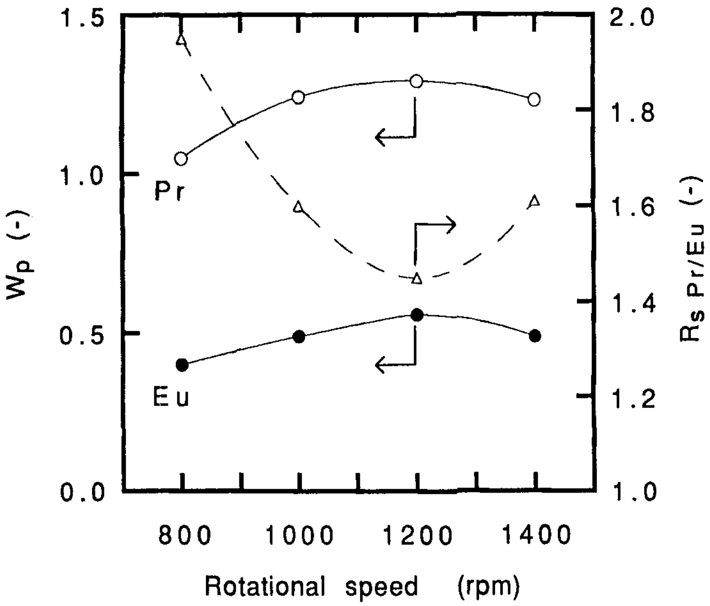

FIGURE 6. Effect of the rotational speed on the separation efficiency of CPC. Mobile phase: 0.5 M HNO_3, Stationary phase: 30% HDEHP/15% CCl_4/55% n-dodecane.

dropsize is reduced with decreasing interfacial tension and viscosity of the stationary phase (12).

The measured values of some physical properties of 30% HDEHP/70% n-paraffin and 0.7 M HNO_3 are shown in TABLE 3. The interfacial tension and the difference in density decreased and the viscosity increased with increasing the number. Since the peak width decreased with increasing the number, the interfacial tension seems to affect strongly the dropsize. However, it is difficult to discuss the effect of the difference in density on the dropsize. The quantitative evaluation of the effect of other physical properties on the dropsize must be necessary for investigation of the separation efficiency of CPC.

Mutual separation of lanthanoids with CPC apparatus

On the basis of the results of determination of the K_d values and measurement of the separation efficiency of CPC, mutual separation of light lanthanoids

TABLE 2
Operation Conditions and Analytical Results of Chromatograms in CPC experiments

Serial number		1				2				3
Mobile phase [HNO_3] M		0.5				0.7				0.5
Stationary phase	[HDEHP] %	30				30	30	30	30	30
	[CCl_4] %	15				—	—	—	—	15
	[n-paraffin] %	55(C12)				70 (C6)	70 (C9)	70(C12)	70(C15)	55(C15)
Stationary phase volume cm^3		53.6	54.1	53.1	55.1	64.6	65.1	65.6	66.0	55.6
Rotational speed rpm		800	1000	1200	1400	900				800
K_d	Pr	0.35	0.36	0.34	0.37	—	—	—	—	0.45
	Sm	—	—	—	—	0.88	1.1_3	1.2_7	1.6_6	2.7_9
	Eu	5.0_6	5.1_8	5.1_2	5.3_4	1.9_1	2.5_3	2.8_7	3.5_9	5.8_3
	Gd	—	—	—	—	—	—	—	—	8.8_0
α	Pr/Sm	—	—	—	—	—	—	—	—	6.2_4
	Pr/Eu	$14._4$	$14._4$	$15._0$	$14._5$	—	—	—	—	$13._1$
	Sm/Eu	—	—	—	—	2.1_7	2.2_4	2.2_6	2.1_6	2.0_9
	Eu/Gd	—	—	—	—	—	—	—	—	1.5_1
W_p	Pr	1.0_5	1.2_4	1.2_9	1.2_3	—	—	—	—	0.73
	Sm	—	—	—	—	0.91	0.81	0.77	0.62	0.40
	Eu	0.40	0.49	0.56	0.49	0.77	0.69	0.64	0.55	0.31
	Gd	—	—	—	—	—	—	—	—	0.30
R_s	Pr/Sm	—	—	—	—	—	—	—	—	1.6_3
	Pr/Eu	1.9_5	1.6_0	1.4_5	1.6_1	—	—	—	—	2.5_5
	Sm/Eu	—	—	—	—	0.46	0.52	0.57	0.63	1.0_5
	Eu/Gd	—	—	—	—	—	—	—	—	0.68
Pump pressure kgf/cm^2		7	11	15	20	32	29	27	25	4.5

1: Effect of rotational speed, 2: Effect of number of carbon atoms as diluents, 3: Demonstration of mutual lanthanoids separation.

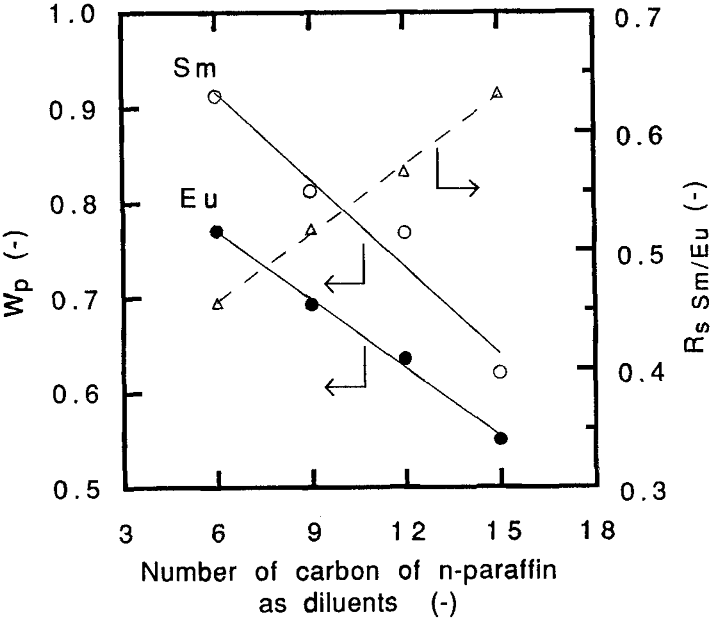

FIGURE 7. Effect of number of carbon atoms of n-paraffin as diluents on the separation efficiency of CPC. Mobile phase: 0.7 M HNO_3, Stationary phase: 30% HDEHP/ 70% n-paraffin, Rotational speed: 900 rpm.

TABLE 3
Some Physical Properties of 30% HDEHP/70% n-Paraffin at 25 °C
(Aqueous phase: 0.7 M HNO_3)

n-Paraffin	Interface tension (10^{-2}N/m)	Viscosity (mPa·s)	Difference in the density (g/cm^3)
n-hexane	5.31	0.56_4	0.41_0
n-nonane	4.94	1.39	0.23_1
n-dodecane	4.70	2.60	0.19_9
n-pentadecane	4.52	4.32	0.18_7

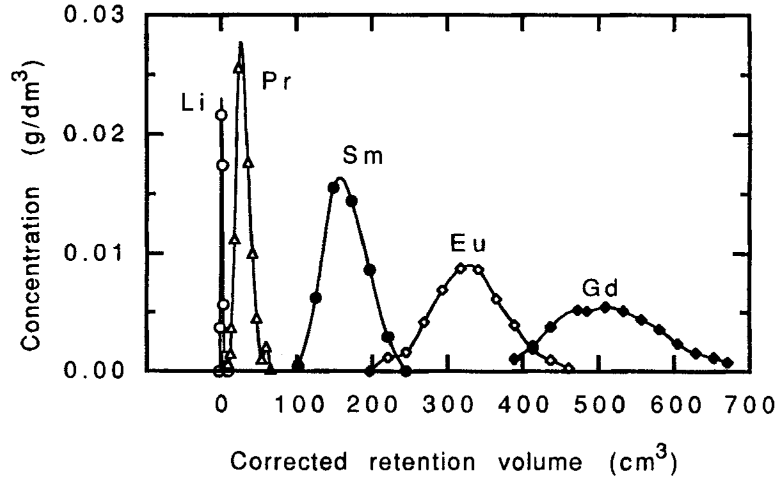

FIGURE 8. Chromatogram of Li, Pr, Sm, Eu and Gd. Mobile phase: 0.5 M HNO_3, Stationary phase: 30% HDEHP/15% CCl_4/55% n-pentadecane, Rotational speed: 800 rpm.

was demonstrated. Mobile phase of 0.5 M HNO_3 was selected for the adequate retention volume. In order to operate the CPC apparatus under a stable condition, the difference in density between the two phases was adjusted to be 0.054 by use of 15% CCl_4 as a heavy diluent. Since the separation efficiency was improved with increasing number of carbon atoms, n-pentadecane was used as a light diluent. The rotational speed was fixed at 800 rpm.

FIGURE 8 shows a chromatogram of Li, Pr, Sm, Eu and Gd. The analytical results of the chromatogram are also summarized in TABLE 2 (Serial No.3). Since the relative peak width of Pr and Eu was reduced as compared with the n-dodecane diluent system (Serial No.1), the resolution between Pr and Eu increased from 1.9_5 to 2.5_5. The resolution between Eu and Gd (R_s=0.68) was not so good because of small α value (α=1.5), but the others were good ($R_s \geq 1$). Furthermore, the CPC apparatus could be stably operated under very low pressure (4.5 kgf/cm^2).

CONCLUSIONS

The characteristics of CPC for lanthanoid separation were investigated in the extraction system of 30% HDEHP/CCl_4/n–paraffin and HNO_3. The K_d values showed a dependency on concentration of HNO_3 and the diluents but the α values did not. Therefore, the adequate K_d values and difference in the density were obtained without decrease of α values for the reasonable retention volume and pump pressure, respectively.

The separation efficiency of CPC was improved with increasing the number of carbon atoms of the n–paraffin used as a light diluent. It is of interest that the separation efficiency of CPC could be improved not only by the optimization of the operation conditions but also by the selection of diluent. In future, the authors intend to examine the effect of the physical properties of the diluent on the separation efficiency more quantitatively.

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REFERENCES

1. W.Murayama, T.Kobayashi, Y.Kosuge, H.Yano, Y.Nunogaki, K.Nunogaki, J. Chromatogr., 239: 643–649 (1982).

2. K.Akiba, S.Sawai, S.Nakamura, W.Murayama, J.Liq.Chromatogr., 11: 2517–2536 (1988).

3. S.Muralidharan, R.Cai, H.Freiser, J.Liq.Chromatogr., 13: 3651–3672 (1990).

4. Y.Surakitbanharn, S.Muralidharn, H.Freiser, Solv.Extr.Ion.Exch., 9: 45–49 (1991).

5. S.Usuda, H.Abe, S.Tachimori, H.Takeishi, W.Murayama, "Application of Centrifugal Partition Chromatography to Separation of Actinides and

Lanthanides in TBP Extraction System", in Solvent Extraction 1990, Part A, T.Sekine, ed., Elsevier Sci. Pub., Amsterdam, 1992, pp. 717-722.

6. H.Abe, S.Usuda, H.Takeishi, S.Tachimori, J.Liq.Chromatogr., 16: 2661-2672 (1993).

7. T.Araki, T.Okazawa, Y.Kubo, H.Ando, H.Asai, J.Liq.Chromatogr., 11: 267-281 (1988).

8. T.Araki, H.Asai, H.Ando, N.Tanaka, K.Kimata, K.Hosoya, H.Narita, J.Liq. Chromatogr., 13: 3673-3687 (1990).

9. D.F.Peppard, G.W.Mason, G.Giffin, J.Inorg.Nucl.Chem., 27: 1683-1691 (1965).

10. U.Mayer, V.Gytmann, W.Gerger, Monatshefte Für Chemie, 106: 1235-1257 (1975).

11. P.Schatzberg, J.Phys.Chem., 67: 776-779 (1963).

12. C.B.Hayworth, R.E.Treybal, Ind.Eng.Chem., 42: 1174-1181 (1950).

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