Article

The Hybrid Liquid-solid Extraction of Lanthanides by Using Poly(*N*-isopropyl acrylamide-*co*-mono(2-hydroxyethyl)methacrylatephosphate) as a Solid Adsorbent

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Abstract

By utilizing a thermally reversible liquid-solid variation of poly(*N*-isopropylacrylamide-*co*-mono(2-hydroxyethyl)methacrylatephosphate), about 3-fold concentration of neodymium(III) and dysprosium(III) from 25 cm³ of aqueous solution into 5 cm³ of 0.05 mol dm⁻³ EDTA aqueous solution was accomplished without using organic solvent at all.

1 Introduction

Recently, concentration method by utilizing a thermally reversible liquid-solid variation of poly(*N*-isopropylacrylamide)(poly(NIPAM)) has been applied to various compounds.[1] However, poly(NIPAM) becomes less soluble in water once it precipitated from water and it makes difficult to redissolve copolymer in water and consequently to back-extract an analyte from copolymer phase to aqueous phase. Therefore, many researchers used organic solvent to dissolve poly(NIPAM) containing an analyte. The present authors improved this defect inherent in poly(NIPAM) by copolymerizing *N*-isopropylacrylamide(NIPAM) with basic monomer, 4-vinylpyridine. Poly(*N*-isopropylacrylamide-*co*-4-vinylpyridine)(copoly(NIPAM/4VP)) could successfully extract not only ion-associate complexes(e.g., ferriox complex such as tris(1,10-phenanthroline) iron(II) perchlorate)[2] but also chelate complexes such as pyrrolidinedithiocarbamate complex of Zn²⁺, Cd²⁺, and Pb²⁺. [3] Especially in the latter system, pyrrolidinedithiocarbamate complexes extracted into a copolymer phase could be back-extracted into 0.01 mol dm⁻³ EDTA solution with recovery of 40 - 70%.

In the copoly(NIPAM/4VP) system, concentration of metals from aqueous solution to 0.01 *M* EDTA solution could be achieved without using any organic solvents, however, chelate extractant was still necessary to extract metals into a copolymer phase. Here, if it is possible to polymerize NIPAM with a monomer having a functional group to be able to bond to metals, extraction of metals into a copolymer phase can be fulfilled without using chelate extractants. From this point of view, poly(*N*-isopropylacrylamide-*co*-mono(2-hydroxyethyl)methacrylate phosphate)(copoly(NIPAM/MHEMP)) was newly synthesized and its extractability to rare earth elements was examined in this study. Here, the present method was named hybrid liquid-solid extraction method since it has combined characteristics of liquid-liquid and liquid-solid extraction. That is, chelate complex formation is

occurred in the homogeneous solution so that reaction takes place rapidly and shaking for equilibration was unnecessary, and at the phase separation step the copolymer phase containing extracted species transforms to the solid phase so that phases can be simply separated by decantation.

2 Experimental

2.1 Preparation of copoly(NIPAM/MHEMP)

NIPAM was generously donated by Kohjin Co., Ltd. and was used after recrystallization from acetone. Mono(2-hydroxyethyl)methacrylatephosphate(MHEMP) was generously donated by Johoku Chemical Co., Ltd. and was used without further purification. The preparation and purification of copolymer was the same to the previous study. Structural formula of the obtained copolymer is shown in Fig. 1.

2.2 Reagents and apparatus

Neodymium(III) and dysprosium(III) were arbitrarily selected as the representative element of light and heavy rare earth elements, respectively. The other reagents and apparatuses were same as those used in the previous study.

2.3 Extraction procedure

Twenty five milliliter of 0.1 mM ($M = \text{mol dm}^{-3}$) lanthanides solution containing 1wt/v% copolymer was adjusted pH appropriately with 8 M KOH and/or 6 M HNO₃ and was centrifuged at 40°C and 3000 rpm for 60 min. The supernatant solution was separated by decantation and was subjected to the determination of metal ion concentration by ArsenazoIII spectrophotometry. The percent extraction ($EX(\%)$) was obtained by dividing the calculated metal ion concentration in the copolymer phase by the known total concentration in the aqueous solution. The remaining copolymer in the extraction vial was redissolved in 5 cm³ of 0.05 M EDTA solution by vigorously shaking at the room temperature for 1 h. The resulted solution was centrifuged at 40°C and 3000 rpm for 60 min again and the supernatant solution obtained by decantation was subjected to the determination of metal ion concentration by GFAAS method. The recovery of metal ion($R(\%)$) was determined by the following equation.

Fig.1 Structural formula of copolymer.

$$R(\%) = \frac{[\text{Metal ion}]_{\text{supernatant soln.}}}{[\text{Metal ion}]_{\text{total}} \times EX(\%) \times 25 \text{ cm}^3 / 5 \text{ cm}^3} \times 100$$

3 Results and Discussion

3.1 Characterization of copolymer

The monomeric composition of MHEMP determined by organic elemental analysis and viscosity average molecular weight of copolymer determined by use of Ubbelohde viscosimeter were summarized in Table 1. Disagreement between mixing ratio of MHEMP and determined monomeric composition was considered to be ascribed to the difference of monomer reactivity ratio of NIPAM and MHEMP. As increment of the monomeric composition of MHEMP, the precipitation of copolymer due to warmed centrifuge became imperfect and on the contrarily the extractability of metal increased(Fig. 2). Finally, 20% MHEMP containing copolymer, having the highest monomeric composition among the tested copolymers of which reversible liquid-solid variation was stable, was mainly used in this study. For 20% MHEMP containing copolymers synthesized 6 times separately, the viscosity average molecular weight and monomeric composition of MHEMP were $4.6 \times 10^4 \pm 2.6 \times 10^4$ and $20 \pm$

Table 1 Monomeric composition and viscosity average molecular weight of copolymer¹

MHEMP monomeric composition		Viscosity average molecular weight
Mixing ratio of MHEMP	Determined monomeric composition	
99:1(1%)	11%	6.3×10^3
19:1(5%)	15%	1.8×10^4
9:1(10%)	20%	4.6×10^4
4:1(20%)	27%	1.4×10^4

¹ Only as for 20% MHEMP containing copolymer, values are the average of copolymers synthesized 6 times separately, others are data obtained with those synthesized 1 time.

3.7%, respectively. However, the variation of the viscosity average molecular weight was not considered in this study, since it did not affect on the extractability to lanthanides. In order to determine a lower critical solution temperature(LCST) of copolymer, turbidities of 1% copolymer aqueous solutions adjusted at pH 2 and 12, respectively, were observed at 660 nm by changing the temperature in a cell holder room at a rate of 0.2°C/min. LCSTs of copolymer solutions adjusted at pH 12 were higher(33-35°C) than those at pH 2 in all monomeric compositions(32-33°C) and LCST increased as the increment of MHEMP monomeric composition. Taking into consideration the fact that pK_{a1} and pK_{a2} values of MHEMP determined by the potentiometric method were 2.57 and 6.60, respectively, these phenomenon can be understood as follows: For the copolymer solutions adjusted at pH 12 or for high MHEMP content copolymer, dissociated phosphate ions in a molecule disturbed a coil-globule transition of copolymer molecule due to the electrostatic repulsion.

3.2 Effects of pH and the monomeric composition

The effect of MHEMP monomeric composition on the extractability of Nd^{3+} was examined by changing the pH in the range of 1 to 12. Figure 2 shows that the extractability of Nd^{3+} increased along with the increment of MHEMP monomeric composition. However, the increment of MHEMP monomeric composition brought not only the better extractability but also the worse solubility in water and 27% MHEMP containing copolymer could not be dissolved in water rapidly. 20% MHEMP containing copolymer gave the next best extractability to 27% one and could be easily dissolved in water, therefore, it was mainly used in this study.

3.3 Recovery of metal ion

In order to find out the optimum condition for back-extraction of lanthanides from copolymer to aqueous solution, Nd^{3+} and Dy^{3+} were extracted in the acidic region of 1-6 M HCl. However, the experimental results of unsatisfactory extractabilities for both elements implied that back-extraction of

Fig. 2 The effects of pH and the monomeric composition of copolymer on the extraction of Nd^{3+} . [copoly(NIPAM/MHEMP)]=1.0wt/v%. MHEMP content: 11%, (◇); 15%, (△); 20%, (○); 27%, (□).

lanthanides from copolymer by HCl solution would be difficult. Next, Nd^{3+} and Dy^{3+} were extracted in the presence of EDTA. As can be seen from Fig. 3, both elements could not be extracted in the pH range 4-13 when EDTA coexisted. Finally, Nd^{3+} and Dy^{3+} were extracted into copolymer from 25 cm^3 aqueous solution and were back-extracted by 5 cm^3 of 0.05 M EDTA aqueous solution (Table 2) and around 3-fold concentration was attained without using any organic solvents. The stability constants and extraction ones of heavy rare earths with di(2-ethylhexyl)phosphoric acid (HDEHP), which is the analogue to MHEMP, are greater than those of light rare earths[4], however, in the present system extractabilities of Dy^{3+} were worse than those of Nd^{3+} in all the pH regions (Fig. 3). The inconsistency between the ordinary HDEHP extraction system and the present copoly(NIPAM/MHEMP) extraction system was remained unexplained. At least, it is obvious that the uptake of Nd^{3+} into copolymer phase was not due to the absorption of hydroxide formed by the hydrolysis, since very low extractabilities less than 15% were obtained in all pH regions when poly(NIPAM) was used to extract Nd^{3+} instead of copoly(NIPAM/MHEMP) under the same extraction condition.

Fig. 3 Effect of EDTA on the extraction. $[\text{Nd}^{3+}] = [\text{Dy}^{3+}] = 0.1 \text{ mM}$, [20% MHEMP containing copolymer] = 1 wt/v%, [EDTA] = 0.05 M. Extraction was carried out without EDTA; $\diamond$, Nd^{3+} ; $\circ$, Dy^{3+} ; and with EDTA; $\blacklozenge$, Nd^{3+} ; $\bullet$, Dy^{3+} .

Table 2 Concentration of lanthanides¹

pH at extraction — pH at back-extraction	Nd^{3+}			Dy^{3+}		
	EX (%)	R (%)	Concentration	EX (%)	R (%)	Concentration
PH 5.1 — pH 4.1	95%	76%	3.6-fold	52%	104%	2.7-fold
PH 5.1 — pH 9.0	97%	60%	2.9-fold	55%	96%	2.6-fold

¹ Theoretical concentration due to volume ratio (25 $\text{cm}^3/5 \text{ cm}^3$) is 5-fold. $[\text{Ln}^{3+}] = 0.1 \text{ mM}$, [EDTA] = 0.05 M, [20% MHEMP containing copolymer] = 1 wt/v%.

References

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