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Effect of polyvinyl alcohol on rare earths (Gd and Tb) separation by extraction resin

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Abstract

Small amounts of polyvinyl alcohol (PVA; 0.5–1.5 wt.%) added to extraction resin was synthesized by suspension polymerization. Their effects on the separation of rare earths (RE) were then investigated by conducting a relative comparison with the performance of pure extraction resin. The supporter and extractant of extraction resin were styrene–divinyl benzene copolymer and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEH[EHP]), respectively. The size of PVA added extraction resin was reduced by 40% particle size of pure extraction resin. Furthermore, a higher level of PVA addition, shorter effluent range and smaller resolution values were shown in the extraction. In constant PVA added extraction resin, more diluted effluent concentration, longer effluent range and bigger resolution values were shown in the extraction. This could be the result of the bonding force between the rare earths and the extraction resin due to the nature of the interaction between the OH^- group in PVA and the OH^- group in extractants such as HEH[EHP]. Thus, the bonding force between the RE and extractants was determined by the level of PVA in the resins and the acidity of the effluent solution became another important factor in the extraction performance of the rare earths. As a result, the optimal level of PVA addition and the concentration of effluent for RE (Gd and Tb) separation were determined to be 0.5 wt.% of PVA and 0.05 M HCl of effluent, respectively.

Keywords: Surfaces; Polyvinyl alcohol; Extraction resin; Rare earths; Suspension polymerization; Solid phase extraction

1. Introduction

The rare earth (RE) separation and purification technology using the extraction resin has the advantages of high selectivity of solvent extraction and high efficiencies of chromatographic separation [1–10]. Therefore, the RE can be separated with high purity by the extraction resin synthesized with extractant and supporter of the resin [10]. When the 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester, HEH[EHP], was used as extractant, the RE was extracted and stripped as expressed in Eqs. (1) and (2).

$$\text{Extraction}: RE^{3+} + 3(HA)_2 \rightarrow RE(HA_2)_3 + 3H^+ \quad (1)$$

$$\text{Stripping}: RE(HA_2)_3 + 3H^+ \rightarrow RE^{3+} + 3(HA)_2 \quad (2)$$

Here, $(HA)_2$ means the dimmer form of the HEH[EHP]. The state of bonding form with RE and three dimmers of the HEH[EHP] is denoted as $RE(HA_2)_3$, shown in Fig. 1(a) [10].

Various kinds of organophosphorus acids have been widely used as extractant of the extraction resin [8–19]. The polymer, including styrene–divinyl benzene [10], its derivatives [20] and modified silica-gels have been used as supporters [7].

In the previous papers [4], we have studied the extraction resin of styrene–divinyl benzene copolymer as the supporter and HEH[EHP] as the extractant in the suspension polymerization. The studies investigated its optimum condition, including stirring speed and level of progenic agent addition on synthesized resin, and its performance in separating rare earths, such as gadolinium and terbium.

The polyvinyl alcohol (PVA), generally used as suspension stabilizer, exhibits the effect of reducing particle size of

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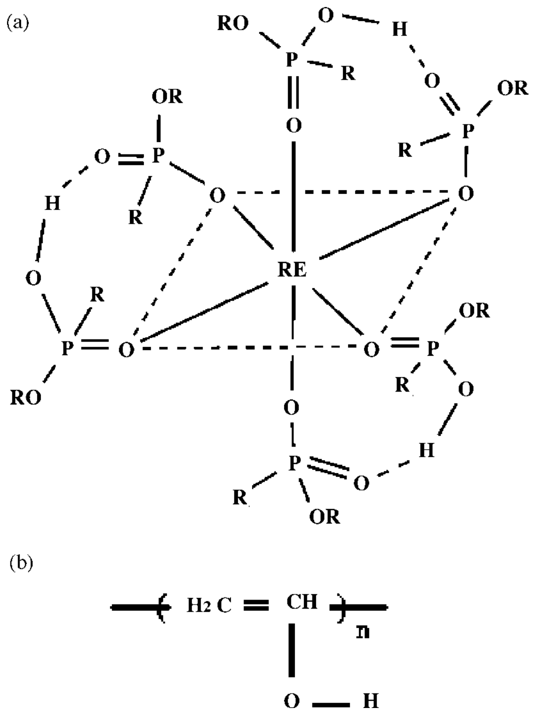

Fig. 1. (a) The bonding form with RE and three dimmers of the HEH[EHP] and (b) the structure formula of PVA.

the polymer by decreasing the surface tension and by improving the dispersion of the reactants during the polymerization reaction [21–23].

In spite of many studies on these effects of PVA in polymerization and sol–gel process [24–26], there have been no papers that focus on the effect of PVA on RE separation in the extraction resin.

In this work, small amounts of PVA (0.5–1.5 wt.%) were added to extraction resin as suspension stabilizer. Its effect on their performance for the separation of RE was investigated by conducting a relative comparison with the performance of no PVA added extraction resin. The physical effect of the PVA on the size of extraction resin and its chemical interaction due to their hydroxyl group existence with the extractant were explained. In addition, the effect of the effluent solution acidity on the extraction ranges and resolution values of each PVA added resin was also investigated.

2. Experimental

2.1. Materials

PVA (DC chemicals, degree of hydrolysis; 87.5 mol%) were used as received in this study without further purification. Styrene monomer (Kanto chemical, 99%) and divinyl benzene (Fluka Chemika, 50%) were pretreated by 10% NaOH and benzoyl peroxide (Acros organics, 99%) were used as the initiators of polymerization. Octanoic acid (Junsei, 99%) and methylcellulose (Showa chemical, 99%) were used as dispersion agents. Toluene (Oriental Chemical, 99%) and *n*-heptane (Oriental Chemical, 99%) were used as the porogenic-agents. The extractant in this work is the HEH[EHP]. Stock solutions of RE, 50:50 wt.% of Gd and Tb were prepared by dissolving the rare earth oxides, Gd_2O_3 (Sigma, >99.9%) and Tb_4O_7 (Sigma, >99.9%) in hydrochloric acid.

2.2. Resin synthesis by suspension polymerization

The procedures for the suspension–polymerization method for resin synthesis were shown in Fig. 2. The suspension–polymerization reaction were carried out in a batch reactor with the reactant mixtures including styrene, divinyl benzene, benzoyl peroxide, toluene, *n*-heptane, octanoic acid, methylcellulose and HEH[EHP] in deionized water. At the same time, a small amount of PVA (0.5, 1 and 1.5 wt.%) was added to the suspension solution. At 80 °C, the suspension–polymerization reaction was conducted for 24 h at the stirring speed of 3000 rpm [4].

Three kinds of extraction resins synthesized after the copolymerization reaction were washed with ethanol and acetone and were filtered to eliminate remaining solvent. The particle size and its shape were measured by the SEM (Hitachi S-3000H).

2.3. Extraction chromatography experiment

The experimental apparatus for the separation of synthesized resin was shown in Fig. 3.

The Pyrex chromatography column ($\varphi = 46$ mm, $h = 150$ mm) was employed for the separation of the RE at a constant temperature of 50 °C by water jacket. The operating conditions were listed in Table 1.

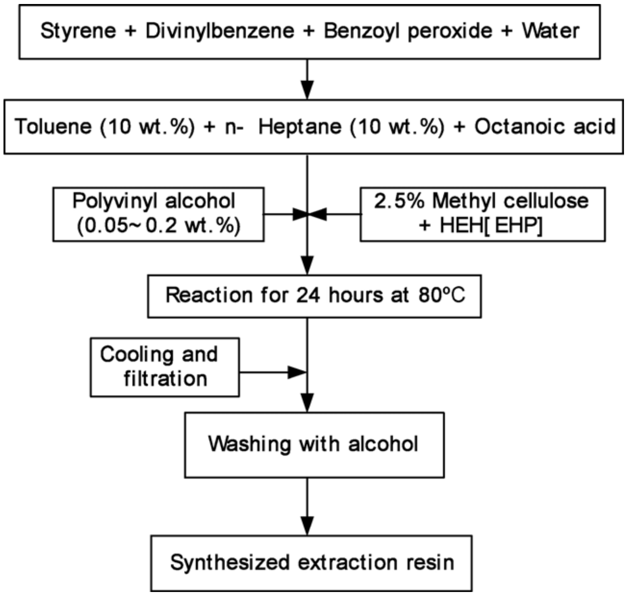

Fig. 2. Synthesis procedure of extraction resin by the suspension-polymerization method.

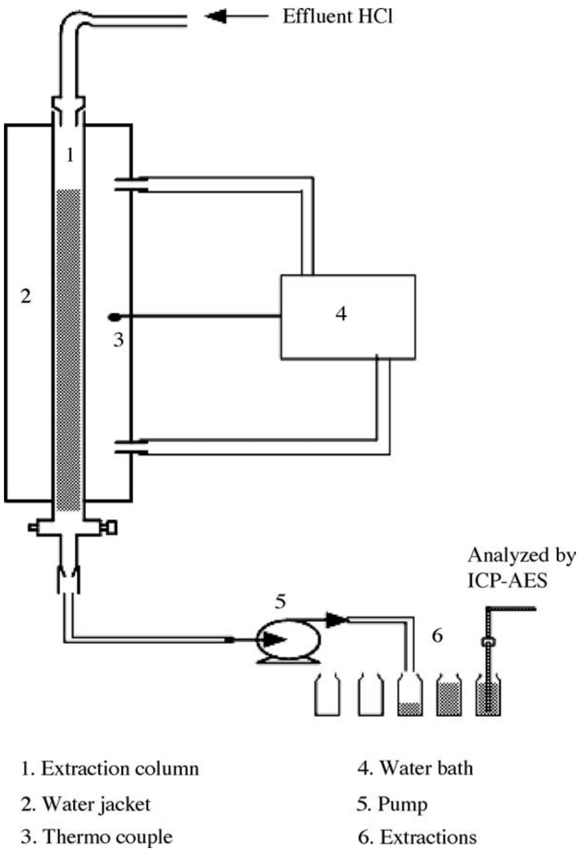

Fig. 3. The experimental apparatus for separation of RE by synthesized extraction resin.

Table 1
The experimental conditions of extraction chromatography

Extraction chromatography	Conditions
Extraction resin	
Packing amount in chromatography column (g)	10
Separation temperature (°C)	50
Stock solution	
Base	Diluted HCl
Concentration (g [RE]/l)	50 (25 for each Gd, Tb)
Acidity (pH)	2
Deposited amount (ml)	1.5
Effluent (diluted HCl)	
Concentration (M)	0.05, 0.1 and 0.2
Flow rate (ml/min)	0.5

1.5 ml of stock solution was deposited on the three kinds of extraction resins in the column, respectively. Afterwards, effluent solution was passed down the column at a rate of 0.5 ml/min, and then drained out from the bottom of the column by a micro pump. To measure the concentration of separated RE in effluent solution; ICP-AES (Jobin yvon emission instrument, JY138 ULTRACE) was used.

3. Results and discussion

3.1. The size of extraction resin

The morphology and the particle size of no PVA added resin and the three kinds of synthesized extraction resins through the SEM were shown in Fig. 4.

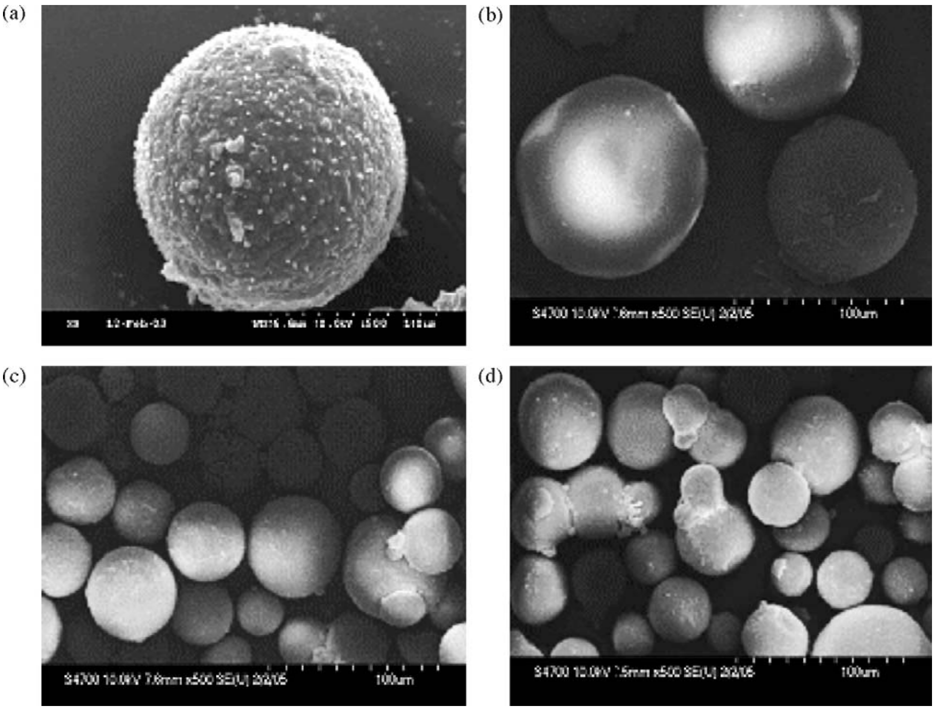

Fig. 4. SEM photographs of synthesized extraction resin: (a) pure extraction resin, (b) PVA (0.5 wt.%) added extraction resin, (c) PVA (1.0 wt.%) added extraction resin and (d) PVA (1.5 wt.%) added extraction resin.

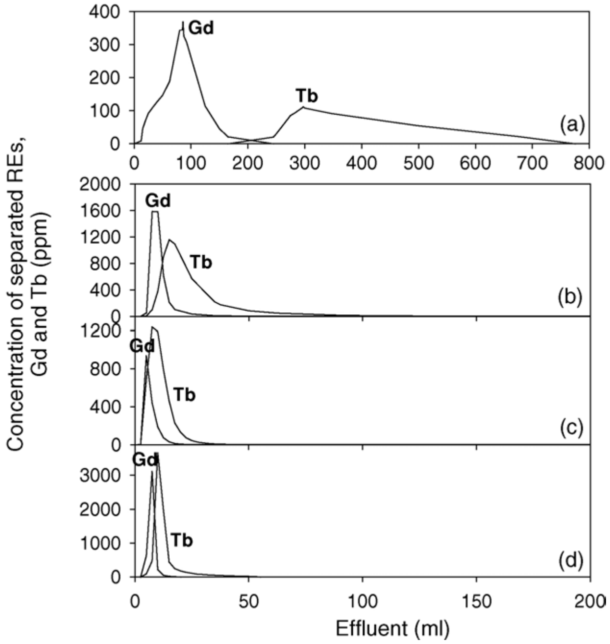

Fig. 5. Chromatogram of Gd–Tb mixture for various concentration of PVA (temperature: 50 °C, effluent: 0.2 M HCl, flow rate: 0.5 ml/min, feed deposit: 1.5 ml). (a) Pure resin, (b) PVA: 0.5 wt.%, (c) PVA: 1 wt.% and (d) PVA: 1.5 wt.%.

The shape of four resins was the same sphere type. The size of no PVA added resin was about 150 μm. However, the size of 0.5 wt.% PVA added resin was about 105 μm, which was a small value of the 70% of the particle size of the pure resin. This is evidence of the effect of PVA as the suspension stabilizer was achieved by reducing the size of extraction resin during the suspension polymerization. Generally, the higher the level of PVA addition in polymerization, the smaller the synthesized polymer became, such that it was recorded as 60 μm diameter at a level of 1 wt.%. However, for levels of PVA over 1 wt.%, the size of the PVA added resins did not change with further addition; this is shown in Fig. 4(d), which displays the size of a 1.5 wt.% PVA added resin. This might have been caused by the fact that the PVA effect on controlling the size of the resins was restricted by the constant level of PVA maintained with the organophosphorus acids during the suspension polymerization.

3.2. The performance of synthesized resin

Using the relatively concentrated 0.2 M HCl as the effluent solution, the extraction range of synthesized resin without PVA was shown in Fig. 5(a), and the extraction ranges of PVA added resins (0.5, 1 and 1.5 wt.%) were shown in Fig. 5(b–d).

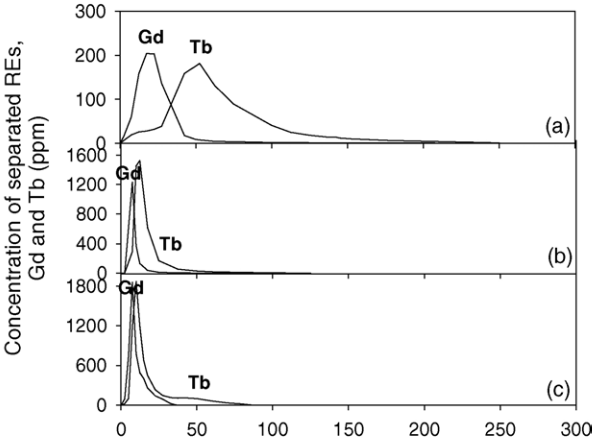

Fig. 6. Chromatogram of Gd–Tb mixture for various concentration of PVA (temperature: 50 °C, effluent: 0.1 M HCl, flow rate: 0.5 ml/min, feed deposit: 1.5 ml). (a) PVA: 0.5 wt.%, (b) PVA: 1 wt.% and (c) PVA: 1.5 wt.%.

It is very clear that the effluent range, together with the resolution value $\alpha_{\mathrm{Gd}}^{\mathrm{Tb}}$ [4] of the PVA added resins, was even shorter than that of the resin without PVA. Furthermore, this range became shorter with an increased level of PVA addition, as demonstrated in Table 2.

Therefore, the 0.2 M HCl was too acidic and inefficient to be used as an effluent for PVA added resins in separation. This means that PVA plays an important role in controlling the bonding state between the RE and the extractant. In other words, PVA weakens the bonding force between the RE and the extractant, thus making stripping easier.

Moreover, the extraction ranges and the resolution values of PVA added resins became even shorter with respect to the level of PVA in resins. This might be because the OH^- group in PVA interacted with the OH^- group in HEH[EHP], as shown in Fig. 1. Thus, at higher levels of PVA added resins, the bonding force between the RE and the extractant was weaker and more dispersed. This weakening effect and its relationship proportional to the level of PVA in resin was further confirmed through the relative extraction performance test conducted on three kinds of resins with a 0.1 M HCl effluent solution; the results are shown in Fig. 6.

The extraction ranges and the resolution values of PVA added resins also became shorter with respect to the level of PVA. However, their overall extraction ranges and resolution values became longer and larger than those derived from using a 0.2 M HCl effluent solution. This could be explained

Table 2
The performance and characteristics of synthesized resin (temperature: 50 °C, effluent: 0.2 M HCl, flow rate: 0.5 ml/min, feed deposit: 1.5 ml)

	Resin without PVA	Resin (PVA) (0.5 wt.%)	Resin (PVA) (1 wt.%)	Resin (PVA) (1.5 wt.%)
Effluent range (ml)				
For Gd	174	47	23	18
For Tb	675	85	40	40
Resolution value ($\alpha_{\mathrm{Gd}}^{\mathrm{Tb}}$)	0.727	0.11	0.09	0.07

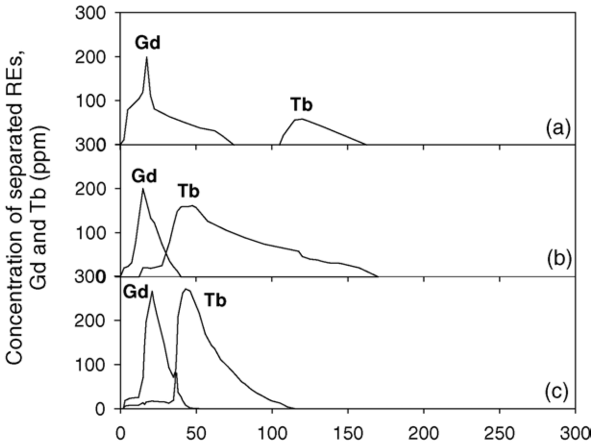

Fig. 7. Chromatogram of Gd–Tb mixture for various concentration of PVA (temperature: 50 °C, effluent: 0.05 M HCl, flow rate: 0.5 ml/min, feed deposit: 1.5 ml). (a) PVA: 0.5 wt.%, (b) PVA: 1 wt.% and (c) PVA: 1.5 wt.%.

by analyzing the acidity of the effluent solution used, indicating the amount of force necessary to strip the adsorbed RE from the extraction resins. Fig. 6 displays the longer extraction ranges and higher resolution values of the three kinds of resins due to the use of relatively lower levels of acidity in the 0.1 M HCl solution of effluent, as compared to the acidity levels of the 0.2 M HCl effluent solution. However, in considering these results, it must be noted that the 0.1 M HCl effluent solution is still too acidic to efficiently strip the RE from the extraction resins.

These trends – a more diluted effluent concentration, longer effluent range and bigger resolution values – were also shown in subsequent extraction performance tests conducted with further diluted effluents, including a 0.05 HCl solution, with the optimum resolution ranges and the biggest resolution value being found under these conditions. Fig. 7 shows the extraction performance test of the three kinds of resins with a 0.05 M HCl effluent solution.

The effluent range and resolution value of the three kinds of resins are listed in Table 3.

For 0.5 wt.% PVA added resins, the effluent ranges of Gd and Tb were 70 and 160 ml, respectively, with the resolution value at 1.145. These figures proved much better than those of our earlier best performance, achieved with no PVA added resins and a 0.2 M HCl effluent solution (Table 2).

The bonding force between the RE and extractant is one of the key factors in the separation of RE using the extraction resin. When the bonding force is very strong, it might be difficult to strip the RE from the extractant resin, causing the concentration of the effluent to become high. Therefore, a larger force is required to properly weaken this bond within the limits of the optimum extractant range and the resolution value of the RE. (The weakening the bonding force between the RE and extractant could be originally attributed to the interaction between the hydroxyl group of PVA and the extractant.) These proper and optimum conditions in our study were shown in the performance test of 0.5 wt.% PVA added resin and using a 0.05 M HCl solution as the effluent.

Table 3
The performance and characteristics of synthesized resin (temperature: 50°C, effluent: 0.05 M HCl, flow rate: 0.5 ml/min, feed deposit: 1.5 ml)

	Resins (PVA composition; wt.%)		
	0.5	1	1.5
Effluent range (ml)			
For Gd	70	40	50
For Tb	160	170	115
Resolution value ($\alpha_{\mathrm{Gd}}^{\mathrm{Tb}}$)	1.145	0.505	0.417

4. Conclusions

The effects of adding PVA to extraction resin to serve as a suspension stabilizer and weakening agent between the RE and extraction resin were verified from the following:

(1) The PVA added to the extraction resin (0.5–1.5 wt.%) in the suspension polymerization reduced the particle size of the pure extraction resin by 60%. However, this effect was restricted at levels of PVA over 0.1 wt.%.
(2) In PVA added extraction resins, a higher level of PVA addition, a shorter effluent range and smaller resolution values were shown in the extraction.
(3) In constant PVA added extraction resins, a more diluted effluent concentration, a longer effluent range and bigger resolution values were shown in the extraction.
(4) The optimal level of PVA addition and effluent concentration for RE (Gd and Tb) separation were 0.5 wt.% PVA and 0.05 M HCl, respectively.

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