Solid-Liquid Separation of Lanthanide/Lanthanide and Lanthanide/Actinide Using Ionic Imprinted Polymer Based on a DTPA Derivative

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Competitive extraction of Gd/La, Gd/Nd, Gd/Eu, Gd/Lu and Am/Eu with a gadolinium-imprinted polymer leads to improvement of the selectivity compare to the corresponding blank material.

Nowadays, lanthanides (Ln) separation still remains a difficult task due to the pronounced chemical and physical similarities between the elements. Some soluble complexing agents exhibit high differentiation between the range of lanthanides such as diethylene triamine pentaacetic acid (DTPA). Moreover a liquid-solid process could be much more convenient as the final separation of the different species can be performed by adapting washing of the resin. Using the concept of ionic imprinting effect developed by Nishide[1] et al. in 1976, we prepared a gadolinium-imprinted polymer based on a DTPA derivative (H_3L) which showed higher selectivity of Gd towards La compared to the corresponding blank material.[2] Moreover, DTPA-like compounds used as chelating agents to form neutral lanthanide complexes and as contrast enhancement agents for magnetic resonance imaging (MRI)[3] and crystals of DTPA-like lanthanide complexes[4] suitable for X-ray were described. We now report on the use of the imprinted resin for the separation of different lanthanides as well as lanthanide/actinide.

The functionalized monomer H_3L was copolymerized with commercialy available divinylbenzene (DVB) containing 45% ethylstyrene (EtSty) in the presence of Gd^{3+} salt.[5] The resin was washed with HCl (1N) to remove the guest cation and then with H_2O until pH 5-6. An untemplated polymer was synthesized in the presence of sodium nitrate to evaluate the influence of imprinting effect. At least two batches of polymers were prepared to check the reproducibility of the synthesis. Moreover, a polymer can be used over a long period without significant change in the selectivity.

These polymers were previously tested in Gd/La separation and it was shown that the Gd-imprinted material was more selective to Gd ($S_{Gd/La} > 20$) than the untemplated one (6.3). The selectivity was determined in other Gd/Ln competitive extraction. Having this aim, equimolar solutions of $Gd(NO_3)_3 \cdot 6H_2O$ and a second lanthanide nitrate salt (Nd, Eu or Lu) were shaken in the presence of resin. These elements were chosen because they are representative of the all range of lanthanide as well for their size as for their coordination constant with DTPA in aqueous solution as reported in Table 1.

Table 1. Hydrated ionic radii and coordination constant of selected lanthanide[a]

La	Nd	Eu	Gd	Lu	
r_{ionic}/Å	4.61	4.62	4.64	4.69	4.75
log K_{DTPA}	19.5	21.6	22.4	22.5	22.4

[a]See Ref. 6.

Whatever the second lanthanide salt is, the initial pH of solutions was 6.7 and after 24 h it decreased to 3.5 due to the release of three moles of H^+ for one mole of Ln^{3+} complexed. But in order not to interfere with the extraction phenomenon by adding high salt concentration no buffer was added. Selectivities in competitive extraction of Gd/Nd, Gd/Eu and Gd/Lu were summarized in Table 2. Results achieved with Gd/La were reported for comparison.

In the case of Gd/La, Gd/Nd and Gd/Lu, untemplated and Gd-

Table 2. Percentages extraction of lanthanides by imprinted and blank polymers and selectivity[a]

Polymer	$\%E_{Gd}$[b]	$\%E_{Ln}$[b]	$S_{Gd/Ln}$[c]	S_{rel}[d]	
Gd/La	Blank	58	18	6.3	>3.2
	Gd-imp.	22	<1.5	>20	
Gd/Nd	Blank	51	37	1.8	1.5
	Gd-imp.	20	9	2.5	
Gd/Eu	Blank	31	36	0.8	0.6
	Gd-imp.	8	16	0.5	
Gd/Lu	Blank	37	28	1.5	1.3
	Gd-imp.	12	7	2.0	

[a]The extraction was performed with 20 mg (blank polymer) or 390 mg (imprinted polymer) shaking with 10 ml equimolar lanthanide solution (10^{-4} mol) for 24 h. Initial and final concentration of each element was determined by ICP-analysis. [b]$\%E = ((C_i - C_f)/C_i) \times 100$. [c]$S_{Ln1/Ln2} = D_{Ln1}/D_{Ln2}$ with $D_{Ln} = ((C_i - C_f)/C_f) \times m/V$ (m = mass of resin, V = volume of solution). [d]$S_{rel} = S_{imp}/S_{blank}$.

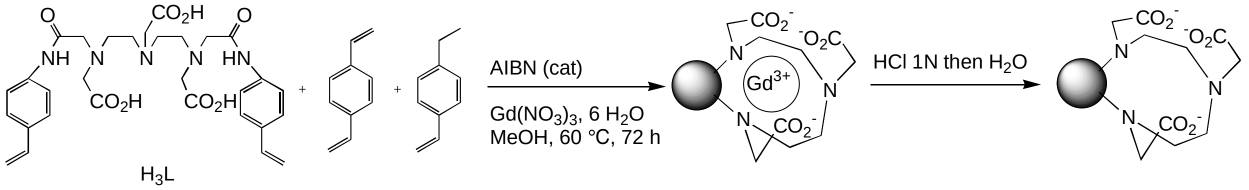

Figure 1.

imprinted polymers extracted preferentially Gd^{3+} with respect to La^{3+}, Nd^{3+} or Lu^{3+}. However, for Gd/Eu competitive extraction, this selectivity was reversed since more Eu^{3+} was extracted compared to Gd^{3+}, whatever the polymer is used. Preorganization of the carboxylate groups due to the presence of gadolinium during the polymerization affected significantly the selectivity of the resin. Indeed, the imprinted polymer enhanced the selectivity towards the metal which was already preferentially extracted with the blank polymer. That is to say that with La, Nd or Lu, the selectivity towards the Gd is increased while in the case of Eu a stronger adsorption of this latter one compare to Gd is observed.

As described by Fish,[6] selectivity is a consequence of the ionic radius of the original metallic ion template. But it can be governed also by other parameters such as the affinity between the host matrix and the guest substance. The highest selectivity is obtained with the pair Gd/La which corresponds to the two elements having the most important differences in term of coordination constant with DTPA or hydrated radii. As far as Nd, Eu and Lu cations were concerned, lower differentiation towards Gd was achieved and this can be attributed to the fact that they have similar physicochemical properties. However, the Eu has a specific behavior as it is stronger extracted than Gd despite the higher coordination constant of Gd with DTPA than Eu in homogenous solution. Two aspects can explain this phenomenon. In one hand, we do not use a pentaacid but a triacid, which can affect dramatically the coordination and so the relative coordination constants $Ln{\cdot}H_3L$ can be modified compared to Ln·DTPA and the thermodynamic stability could favor the Eu^{3+} selectivity. In the second hand, the polymerization was achieved in methanol in order to solubilize all the species present while the extraction was performed in aqueous solution. So the coordination sphere around the cation was different in both cases. More specifically, the size of the gadolinium cation in methanol and of europium cation in aqueous solution could be very close and so the corresponding size and arrangement of the functional groups in the cavity fit better with the europium. A phenomenon of synergy involving the templating factor and the thermodynamic stability led to an improvement of Gd^{3+} selectivity over La^{3+}, Nd^{3+}, Lu^{3+} and an increase of Eu^{3+} selectivity over Gd^{3+} when Gd-imprinted polymer was used.

The blank and Gd-imprinted resins were used in Am/Eu separation as representatives of the actinides and early lanthanides. Solid-liquid extraction experiments were carried out by shaking polymer with a nitric solution containing $[^{241}Am] = 2.3\ 10^{-7}$ mol/l, $[^{152}Eu] = 9.7\ 10^{-9}$ mol/l (pH = 3.5). In order to avoid a complete extraction of both tracers, a macroconcentration of europium nitrate $[Eu(NO_3)_3]{\cdot}6H_2O = 10^{-4}$ mol/l was added. The evolution of the concentration of active ions was followed by γ-Ray spectroscopic measurements of the solution after centrifugation. The weight of polymer and the volume of the solution were adjusted in order to get efficient extraction.

Table 3. Percentages extraction of Am and Eu by imprinted and blank polymers and selectivity

polymer	m_{resin}/mg	V_{sol}/ml	$\%E_{Am}$	$\%E_{Eu}$	$S_{Am/Eu}$
Blank	4	1.5	68	51	2[a]
Gd-imp	40	1	55	30	3

[a] 6 different experiments were performed in order to evaluated the accuracy.

It was checked that after 4 h shaking, the equilibrium was reached and the level of extraction did not increase anymore. As observed for the lanthanide separation,[3] the capacity of the templated polymer was lower compared to the blank one and 10 times more material have to be engaged to achieve significant extraction. Moderate selectivity in favor of americium was achieved with the blank polymer. A significant improvement was observed while the Gd-imprinted polymer was tested. As for lanthanides separation, the preorganization of the functionalized monomer, due to the presence of gadolinium during the polymerization step, enhanced the selectivity towards the ion which was better extracted with the blank polymer and so $S_{Am/Eu} = 3$. Such material allowed extraction of traces of americium into a large excess of europium (Am/Eu *ca* 1/1000).

Further experiments are under progress in order to improve the actinide/lanthanide selectivity.

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