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Ionic imprinting effect in gadolinium/lanthanum separation

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Abstract : A new method based on the use of cation imprinted polymers to separate lanthanum and gadolinium cations is proposed. Using a styrene-DTPA monomer specific of one of these elements, an improvement in separation selectivity is observed when a tailor-made gadolinium imprinted polymer is compared to a non-imprinted or blank polymer. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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Metal-imprinted polymers have received less attention than molecule-imprinted analogues.[1] This technique consists in mixing a metal cation with a functionnalized monomer to form a complex (isolated or not).This is then copolymerised with a crosslinking agent in order to form a rigid matrix. The template (the cation) is removed by acidic washing, so that the prepared solid can be reacted with a mixture of cations. The imprinting cation should be thus preferentially extracted from the solution. One of the first ionic template effect in the synthesis of chelating polymers was reported by Nishide et al. in the seventies.[2] More recently, Kuchen and Schram,[3] prepared resins by copolymerisation of ethylene glycol dimethacrylate with a well-defined Cu(II) complex containing 4-vinylpyridine and methacrylate ligands. Competitive extraction of Cu^{2+} and other bivalent cations (Zn, Cd or Pb) was performed with the imprinted and the blank resins (prepared similarly but without copper). The imprinted polymer was 3 times more selective in favor of the cuprate cation than the blank polymer in the case of the separation Cu^{2+}/Zn^{2+}, in addition the extraction of Cu^{2+} was also increased with the imprinted resin for the Cu^{2+}/Pb^{2+} couple. We have applied this procedure to separate two lanthanide ions (Gd^{3+} and La^{3+}) having similar chemical and physical properties, in particular : the same ionic charge (Ln^{3+}) and similar hydrated ionic radii ($r_{Gd^{3+}} = 4.69$ Å; $r_{La^{3+}} = 4.61$ Å).[4] Like all the rare earths, Gd^{3+} and La^{3+} have coordination numbers between 6 and 12.[5] Such a lack of defined geometry makes

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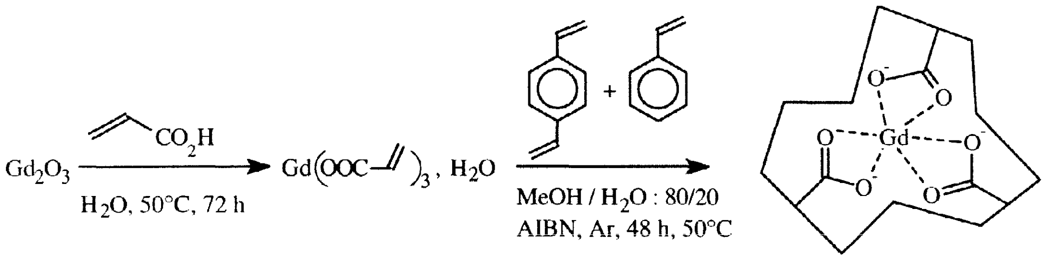
it difficult to separate these types of ions. We report our preliminary results on the preparation of Gd^{3+}-imprinted polymers and their use in La^{3+}/Gd^{3+}ions separation.

Different blank polymers were first prepared. Whatever the monomers mixtures (4-vinylpyridine, 2-hydroxyethyl methacrylate, acrylic acid...) and crosslinking agent (divinylbenzene, ethylene glycol dimethacrylate...), the average extraction selectivity (AES) was 2.4 ± 0.3.[6] This selectivity, which was achieved for non specific materials, can be mainly ascribed to the desolvatation energy, since the hydration enthalpies values[7] (ΔH_S) are -3278 and -3519 kJ.mol^{-1} for La(III) and Gd(III) respectively. In other words, an imprinted effect will occur only if AES < 2.1 or AES > 2.7. Furthermore, in order to avoid a large discrepancy on the selectivity resulting from the measurement, we considered only results when $10\% < E < 85\%$ (see table 1). This interval is evaluated by determination of the incertitude of each experimental parameter (extraction, distribution and selectivity coefficients).

Scheme 1 shows how gadolinium triacrylate[8] was copolymerised with divinylbenzene and styrene.



Scheme 1 : Synthesis of ionic imprinted polymers.

The influence of crosslinkage was studied by modifying the respective amount of divinylbenzene and styrene. The polymers were crushed, sieved (< 200 µm) and washed with acidic (HCl 1N) and basic (NaOH 0,1N) solutions and finally with H_2O until neutrality. The resins were dried and isolated with yields > 95%. Blank polymers, without gadolinium but with acrylic acid, were synthesised and treated similarly. All the materials contained about 15% of acrylic functions (Table 1).

Table 1 : Extraction percentages and Gd/La selectivity's with blank and imprinted polymers.

Polymers	**% Divinylbenzene**	**% Styrene**	**% CH_2=CH-COOH**	**$\%E_{La}$[(a)]**	**$\%E_{Gd}$[(a)]**	**$S_{Gd/La}$[(b)]**
Blank	31	55	14	0	0	-
Blank	86	0	14	0	0	-
Gd^{3+} imprinted	24	62	14	25	46	2.5
Gd^{3+} imprinted	45	40	15	57	79	2.7
Gd^{3+} imprinted	65	21	14	53	77	3.0
Gd^{3+} imprinted	85	0	15	29	58	3.5

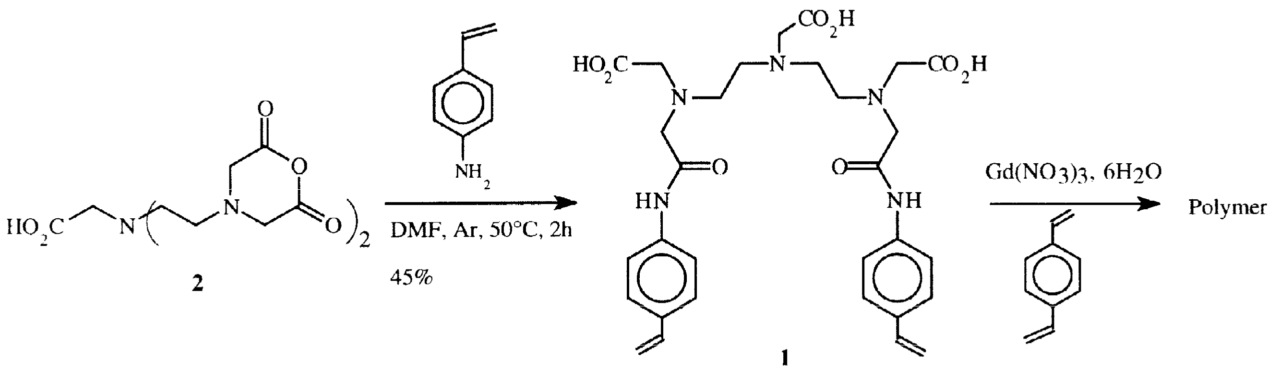
(a) %E = (Ci - Cf) x 100 /Ci ; (b) see ref. 6

The matrixes were tested by competitive extraction of Gd^{3+} and La^{3+} salts.[9] The respective amount of extracted ions were determined by ICP analysis of the filtrate.

Blank polymers were not able to extract any cations from the solution whatever the divinylbenzene/styrene ratio. This is probably due to the inaccessibility of acrylic sites.

The use of template during polymerisation increased the extraction capacity of the resins. An optimum effect was observed by using 45–65% divinylbenzene, the higher the crosslinking ratio was, the higher the selectivity towards the printed cation. The increase in rigidity of the tridimentional network explains this observation and this is consistent with many of the results described previously in the literature for molecular imprinting.[10] The observed selectivities could be explained by an heterogeneous distribution of acrylate functions in the polystyrenic matrix. However, no data concerning the structure of these amorphous solids is yet available.

Since copolymer from divinylbenzene and acrylic acid have been found to be the most efficient (table 1), we made a new functionalized resin based on more specific ligands for lanthanide. Diethylene triamine pentaacetic acid (DTPA) was known to be a highly efficient complexing agent with constants : log K(La^{3+}) = 19.5 and log K(Gd^{3+}) = 22.5.[11]



Scheme 2 : Synthesis and polymerisation of a DTPA derivative.

Therefore, the polymerisable DTPA derivative **1** was thus synthesised by reacting *p*-vinyl aniline with the commercially available dianhydride **2** in 45% yield. This compound was copolymerised with divinylbenzene in presence of gadolinium nitrate.[12] The corresponding blank polymer was also synthesised. The two materials were evaluated in competitive extraction of La^{3+} and Gd^{3+} (Table 2).

Table 2 : Extraction with polymerised DTPA

Polymer	%ELa	%EGd	SGd/La
Blank	10	33	4.4
Gd^{3+} imprinted	34	87	13.6

In contrast to the previous resins (table 1), even the blank material showed higher efficiency in extraction of the Gd^{3+} lanthanide. This improved selectivity (4.4) was due to the highest intrinsic affinity of the ligand for Gd^{3+} compared to La^{3+}.[11]

The introduction of the gadolinium nitrate salt prior to the polymerisation process produced an imprinted material, the extraction capacity of which was remarkably enhanced compared to the blank polymer. Interestingly, the imprinted matrix was 3 times more Gd^{3+}-selective than the blank one.

In conclusion, we have found that imprinting effect can be observed in the case of ions having similar chemical and physical properties. Materials prepared with non specific monomers in the presence of gadolinium salts exhibited already higher efficiency and selectivity than the corresponding blank polymers. Moreover when monomers were specifically designed to interact with the target cation, the improved imprinting effect was similar to that observed in the case of the separation Cu^{2+}/Zn^{2+} and the selectivity factor was increased up to 13.6 in favor of the gadolinium. These resins can be used for example as stationary phases in chromatography as it was done for resolution of racemates.[1] The use of tailor-made copolymers based on DTPA derivative appeared to be the best material for La^{3+}/Gd^{3+}ions separation in solide-liquide extraction.

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9. *Standard extraction procedure :* After polymerisation and removal of metal, the material was evaluated in competition extraction test. In a flask, 240 mg polymer were introduced in 10 ml aqueous solution containing 2.5 mmol $La(NO_3)_3.6H_2O$ and $Gd(NO_3)_3.6H_2O$ in equimolar quantities. The suspension was shaken vigorously by a mechanical horizontal stirring during 24 h, in order to reach thermodynamic equilibrium. The solution was then filtered through a Millipore filter (0,45 mm) and the filtrate was analysed by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectro D apparatus) to determine the ions concentration. Syntheses and measurements were reproduced to confirm the results.
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12. In a polymerization flask, 380 mg (0.84 mmol) $Gd(NO_3)_3.6H_2O$, 500 mg (1 eq.) **1** and 1.9 ml (16 eq.) divinylbenzene were disolved in 4 ml MeOH. 4 mg AIBN were added and the flask was sonicated, flushed with argon and closed. The reaction mixture was heated at 50°C for 24 h. The solid was crushed, sieved and washed as previously described.