Novel Template Sorbents for Separation of Americium(III) from Nitric Acid Solutions: Search of Optimal Ion-Imitator of Am^{III}

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A series of new template sorbents that enable selective and effective sorption of Am^{III} from 0.5 to 4M HNO_3 solutions containing high concentrations of Fe^{III} and Zr^{IV} was synthesized from (ethenyl)(diphenyl)phosphine oxide. La^{III}, Ce^{III}, and Pr^{III} were used as template elements imitating the properties of Am^{III}. The highest efficiency of separation of Am^{III} from high amounts of Fe^{III} and Zr^{IV} was displayed by the Ce^{III}-based sorbent.

Introduction. – Since late 1970s [1] [2], new methods of metal ion sorption are being developed, including those based on the use of ion-imprinted (template) polymers (IIPs) or sorbents with memory effects. Such sorbents enable recognition and effective sorption of the cations in the presence of high concentrations of competing ions. Historically, IIPs appeared at the same time as molecularly imprinted polymers (MIPs) [3–5] that enable separating organic molecules based on their size, shape, and specific interactions with the matrix. In the IIP-based methods, cation size, its coordination number, and the local geometry of the complex predetermine the successful recognition and sorption of the cation [6–8].

IIPs are synthesized in three steps:

i) Synthesis of the complex of the template cation with the ligand containing functional groups that are able to polymerize.

ii) Copolymerization of the complex with monomers capable of forming hard 3D matrix, *e.g.*, divinylbenzene (DVB), to tightly fix the ligand and the entire complex, minimizing their conformational changes. This stage ensures the formation of a cavity in the matrix corresponding to the size of the cation, surrounded by the ensemble of tightly fixed complexation groups allocated according to the initial geometry of the complex, *i.e.*, at the distance corresponding to the cation–ligand bond lengths.

iii) Desorption of the template cation.

It was shown that template sorbents could be used for the sorption of U^{VI} and Th^{IV}, and trivalent lanthanides from acid solutions with high salt background, including those with high concentration of d-metals [9]. However, the studies of IIP for the separation of minor actinides, mostly Am^{III}, from acidic nuclear waste are at their initial stage [10]. A new series of template sorbents containing chemically bound preorganized groups of monodentate (ethenyl)(diphenyl)phosphine oxide ($Ph_2P(O)(CH{=}CH_2)$; L) was

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synthesized for selective sorption of $\mathrm{Am^{III}}$ from $\mathrm{HNO_3}$ solutions with high salt concentration [10].

Due to the high specific radioactivity and technical problems of working with high amounts of $^{241}\mathrm{Am}$, the synthesis of $\mathrm{Am(NO_3)_3}$ complex with L and its copolymerization is not possible. Therefore, in this work we have used as templates the trivalent lanthanides with ionic radius (R_I) close to the ionic radius of $\mathrm{Am^{III}}$. However, the ionic radii published in the literature significantly differ. For example, for $\mathrm{Ce^{III}}$ the R_I value was reported to be 107 pm [11], 119 pm [12], or 114 pm [13] (all data are given for the coordination number of 9). Therefore, to find the optimum analog for $\mathrm{Am^{III}}$, we investigated the light lanthanides ($\mathrm{Ln^{III}}$), *i.e.*, $\mathrm{Ce^{III}}$, $\mathrm{Pr^{III}}$, and $\mathrm{La^{III}}$, with ionic radii close to that of $\mathrm{Am^{III}}$: $^{\mathrm{I}}R_{\mathrm{La^{III}}} = 122$ pm, $R_{\mathrm{Pr^{III}}} = 106$ pm, $R_{\mathrm{Am^{III}}} = 107$ pm [11]. It was assumed *a priori* that complexes of $\mathrm{Ln^{III}}$ with L have the same composition and geometry as the complex of $\mathrm{Am^{III}}$.

Results and Discussion. – *Comparison of the Sorption of* $\mathrm{Am^{III}}$ *by Sorbents* **1a**–**1c** (*Scheme*) *and Control Sorbent* **2**. For comparison of the sorption of $\mathrm{Am^{III}}$, the control sorbent **2** (1.01% P) [10] that did not contain any preorganized $\mathrm{Ph_2P(O)(CH{=}CH_2)}$ groups, was used. P Contents corresponding to the amount of the complex-forming groups L in all synthesized sorbents **1a**, **1b**, and **1c** determined by elemental analysis differ insignificantly (*Table 1*). This enables the direct comparison of the sorbents **1a**–**1c** with respect to $\mathrm{Am^{III}}$. To find the best sorbent for $\mathrm{Am^{III}}$ separation from $\mathrm{HNO_3}$ solutions, sorbents **1a**–**1c** were tested for $\mathrm{Am^{III}}$ sorption from 0.5 and 2M $\mathrm{HNO_3}$.

Scheme. *Synthesis of Template Sorbents* **1a**–**1c**

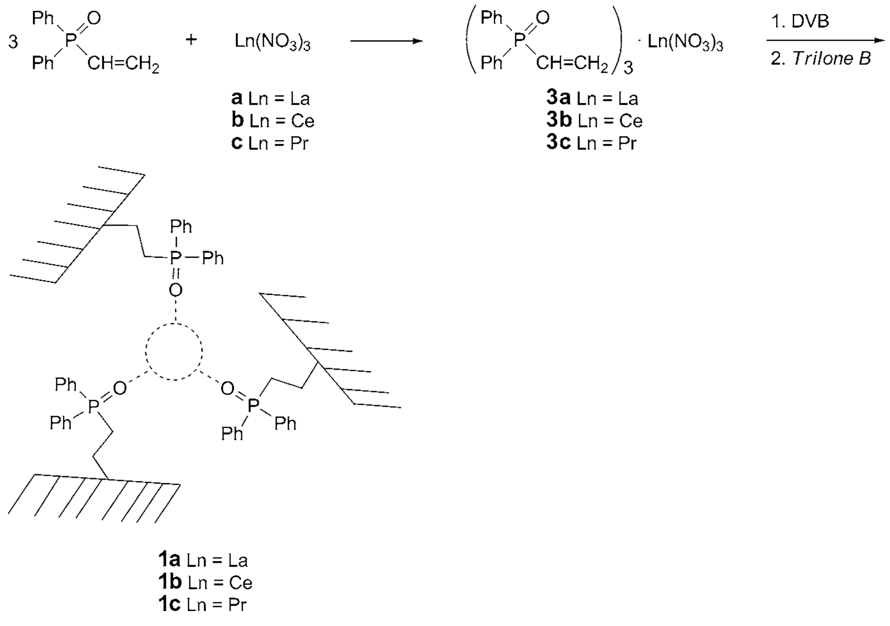

Table 1. *Sorption* (*S*, [%]) *of* Am^{III} *from 0.5 and 2*M HNO_3 *by Template Sorbents* **1a**–**1c** *and Control Sorbent* **2** (20°; $[Am^{III}] = 10^{-6}$M; $[Fe^{III}] = 2$ g/l; $[Zr^{IV}] = 2$ g/l; *V*/*m* = 500 ml/g; contact time, 15 min)

Separation system	0.5M HNO_3	2M HNO_3
1a (La-template), 0.82% P		
Am^{III}	91	92
Am^{III} in the presence of Fe^{III}	89	81
Am^{III} in the presence of Zr^{IV}	86	83
1b (Ce-template), 0.73% P		
Am^{III}	**98**	**97**
Am^{III} in the presence of Fe^{III}	99	94
Am^{III} in the presence of Zr^{IV}	90	90
1c (Pr-template), 0.73% P		
Am^{III}	90	89
Am^{III} in the presence of Fe^{III}	88	90
Am^{III} in the presence of Zr^{IV}	80	83
2 (control sorbent), 1.01% P [10]		
Am^{III}	96	97
Am^{III} in the presence of Fe^{III}	79	87
Am^{III} in the presence of Zr^{IV}	30	15

The synthesized template sorbents **1a**–**1c**, as well as the control sorbent **2** were found to effectively and rapidly adsorb Am^{III} from HNO_3 solution. The sorption, *S*, was in all cases higher than 90% (*Table 1*). Sorption by sorbents **1a** and **1c** was lower than that by the control sorbent **2**, which may be due to lower P content and, correspondingly, lower quantity of complexation groups L. Sorption of Am^{III} by **1b**, despite lower concentration of P, does not differ from the sorption by the control sorbent **2**. However, in the presence of high concentrations (2 g/l) of competing ions, Fe^{III} and Zr^{IV}, sorbents **1a**–**1c** are significantly more effective than the control sorbent **2**. In the presence of Fe^{III}, S_{Am} is almost constant for sorbents **1a**–**1c**, while, for the control sorbent, it falls to 79% from 0.5M HNO_3 and 87% from 2M HNO_3. The competing effect of Zr^{IV} on the sorption of Am^{III} by sorbents **1a**–**1c** and **2** is stronger compared to Fe^{III}: in the presence of Zr^{IV}, the sorption of Am^{III} by the control sorbent **2** decreases to 30% from 0.5M HNO_3 and 15% from 2M HNO_3. The decrease of the sorption by sorbents **1a**–**1c** is significantly smaller (*Table 1*).

The strong increase of sorption of Am^{III} by sorbents **1a**–**1c** as compared to control sorbent **2** in the presence of Fe^{III} and Zr^{IV} could be explained by the template effect of La^{III}, Ce^{III}, and Pr^{III} ions. These sorbents contain preorganized ensembles of complexing groups of ligand that enable selective Am^{III} sorption by sorbents **1a**–**1c** in the presence of high concentrations of competing cations despite the lower content of complexing groups compared to sorbent **2**.

From the sorption data of Am^{III} in the presence of Zr^{IV}, one may conclude that the most effective sorbent is **1b**, for whose synthesis Ce^{III} was used as templating cation (*Table 1*). This means that Ce^{III} is the most effective lanthanide imitator for Am^{III}. The efficiency and selectivity of Am^{III} sorption in the presence of Zr^{IV} decreases with both increase (La^{III} template, sorbent **1a**) and decrease of Ln^{III} ionic radius (Pr^{III} template, sorbent **1c**). Therefore, one may conclude that the template ionic radius is the main factor in the design of selective sorbents for the extraction of Am^{III} (and probably, other actinides) from acidic solutions.

Sorption properties of the most effective sorbent **1b** (Ce-template) with respect to Am^{III} were studied in detail.

Sorption of Am^{III} from HNO_3 Solutions by Sorbent **1b**. The results of study of Am^{III} sorption from 0.25 to 5.0M HNO_3 revealed that the dependence of S_{Am} by **1b** on HNO_3 concentration is nonlinear (*Fig. 1*).

Sorption from 0.5 to 2.0M HNO_3 is almost quantitative (97–98%). From 3M HNO_3, the sorption is lower (92%). Upon increase of HNO_3 concentration, sorption further decreases (to 3% from 5M HNO_3) due to competitive complexation of L with the acid through phosphinoyl groups [14]. Similarly, upon the decrease of HNO_3 concentration from 0.5 to 0.25M, the S_{Am} also decreases to 28%, which could be explained by the decreased amount of the adsorbed neutral complex $Am(NO_3)_3$ with L [15]. In the presence of Fe^{III} and Zr^{IV}, the trend of the dependence of S_{Am} on $[HNO_3]$ does not change. No competition effect of Fe^{III} and only a slight effect of Zr^{IV} have been found for Am^{III} sorption. Therefore, one may conclude that the sorption percentage of Am^{III} by sorbent **1b** (Ce-template) is almost constant from 0.5 to 3.0M solutions of HNO_3.

Sorption Isotherm of Am^{III} by Sorbent **1b**. The sorption isotherm of Am^{III} from 2M HNO_3 (*Fig. 2*) by sorbent **1b** is a standard type curve with a plateau.

According to the literature data, an isotherm of this type corresponds to the formation of a complex with constant composition [16]. It is possible to calculate the maximum loading capacity of the sorbent that was equal to $1.09 \cdot 10^{-4}$ mol of Am^{III} per

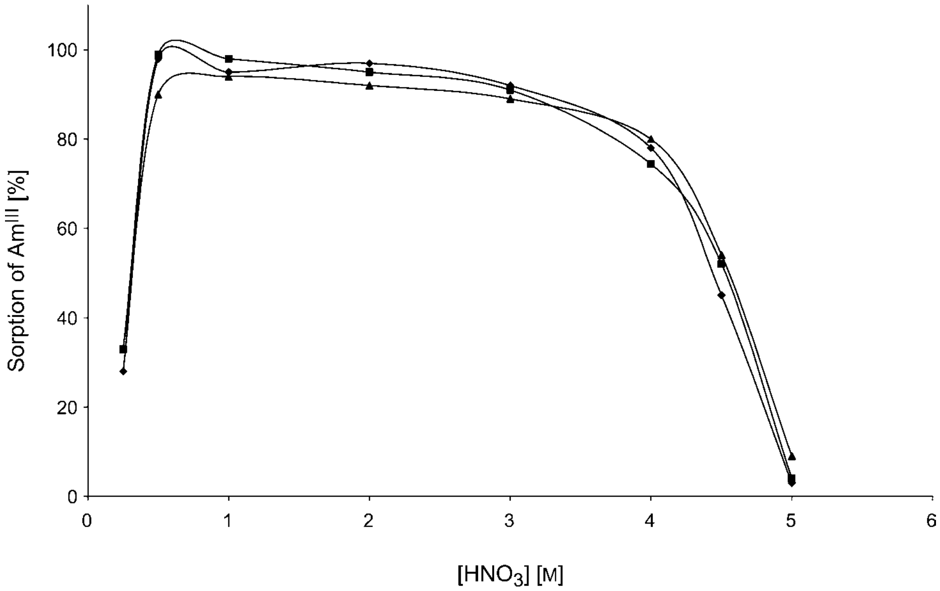

Fig. 1. *Sorption of Am^{III} by sorbent* **1b** *as a function of HNO_3 concentration without foreign cations* (◆), *and in the presence of Fe^{III}* (■) *and Zr^{IV}* (▲) *at 20°*

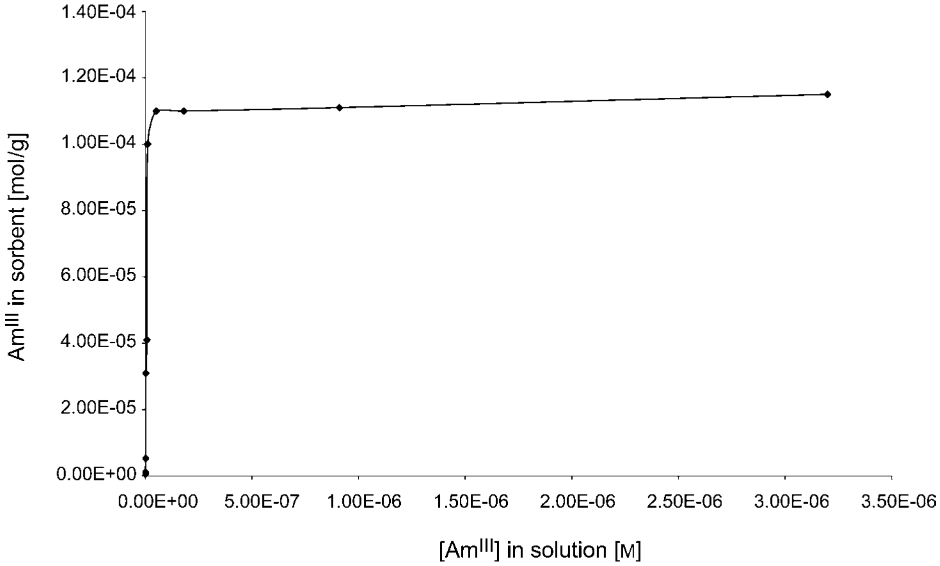

Fig. 2. *Sorption isotherm of* Am^{III} *by sorbent* **1b** *from* 2 M HNO_3 *at* 20°

1 g of the sorbent, or 26.5 mg/g Am^{III}. The calculation of the ratio of sorbent capacity to the P content of the sorbent that corresponds to complexing groups expressed in mmol/g gives the value of 1:2.2, which is close to the theoretically expected ratio 1:3. The difference could be explained by the fact that partial dissociation of complex **1b** takes place upon sorbent synthesis, which results in the formation of free ligand groups in the sorbent matrix, also complexing with Am^{III}. This leads to an increase in the sorption capacity of the sorbent over the theoretical value of 19 mg/g Am^{III} calculated from the 1:3 complex stoichiometry.

Sorption of Eu^{III} *and* Pu^{IV} *by Sorbent* **1b**. The sorption of Eu^{III} was also studied, as it is a chemical analog of Am^{III}. Since the ionic radius of Eu^{III} is slightly smaller than that of Am^{III} ($R_{Eu^{III}} = 98$ pm [11]), it could be expected that sorption of Eu^{III} would be also lower than Am^{III}. Indeed, experimentally determined values for S_{Eu} are lower than Am^{III} (*Table 2*). In the presence of Fe^{III}, the sorption of Eu^{III} is not depressed as in the case of Am^{III}. However, the competing effect of Zr^{IV} on the sorption of Eu^{III} is higher compared to Am^{III}: the sorption of Eu^{III} is decreased to 12–22%.

Table 2. *Sorption* (*S*, [%]) *of* Eu^{III} *and* Pu^{IV} *from* HNO_3 *by Template Sorbent* **1b** (20°; $[Eu^{III}] = [Pu^{IV}] = 10^{-6}$ M; $[Fe^{III}] = 2$ g/l; $[Zr^{IV}] = 2$ g/l; $V/m = 500$ mg/g; contact time, 15 min)

Separation system	0.5M HNO_3	2M HNO_3	4M HNO_3
Eu^{III}	72	91	89
Eu^{III} in the presence of Fe^{III}	68	92	90
Eu^{III} in the presence of Zr^{IV}	12	22	18
Pu^{IV}	82	89	91
Pu^{IV} in the presence of Fe^{III}	78	90	88
Pu^{IV} in the presence of Zr^{IV}	10	11	8

As in the case of Eu^{III}, the sorption of Pu^{IV}, the ionic radius of which (93 pm [11]) is shorter than that of Am^{III} [11], is less effective, compared to Am^{III}, and is not depressed by Fe^{III}, similar to Am^{III} and Eu^{III} (*Table 2*). As in the case of Eu^{III}, the competing effect of Zr^{IV} on the sorption of Pu^{IV} is higher than on the sorption of Am^{III}: sorption of Pu^{IV} decreases to 8–11%.

Conclusions. – By simple three-stage syntheses, new template sorbents have been obtained, that enable selective, rapid, and effective sorption of Am^{III} from HNO_3 solution. The templating effect is observed upon Am^{III} sorption in the presence of high amounts of Fe^{III} and Zr^{IV}, which enables more effective sorption of Am^{III} compared with the control sorbent without templating properties. Among the studied samples, sorbent **1b** that was synthesized in the presence of Ce^{III} exhibited the highest efficiency towards Am^{III} in the presence of competing cations: Fe^{III} and Zr^{IV}. Taking into the account that Ce^{III} is more abundant than La^{III}, Pr^{III}, and Nd^{III} [10], this is beneficial for industrial-scale synthesis of the sorbents for Am^{III} sorption from HNO_3 solutions.

Significant difference of Am^{III}, Eu^{III}, and Pu^{IV} sorptions especially in the presence of Zr^{IV} enables to recommend sorbent **1b** for sorption separation of Am^{III} from 0.5 to 4.0M HNO_3 solutions that contain high concentrations of d-metal cations.

Experimental Part

General. The studied sorbents **1a**–**1c** were synthesized in three steps (*Scheme*). It was important to obtain just the compounds resulting from Ln^{III} and L in actual aq. acid solns. Therefore, at the first step, anh. $Ln(L)_3(NO_3)_3$, **3a**–**3c**, were isolated by solvent extraction of $Ln(NO_3)_3$ from 0.1M HNO_3 using L soln. in *o*-1,2-dichlorobenzene (DCB). L was introduced into the extraction system in fourfold excess, since the composition of the extracted complex was not known. At the second step, complexes **3a**–**3c** were copolymerized with divinylbenzene (DVB) to yield the Ln^{III}-containing copolymers **4a**–**4c**. At *Step 3*, Ln^{III} was desorbed from the copolymers using 1% *Trilone B* (Na-EDTA) soln., which gave the final template sorbents **1a**–**1c** (*Table 1*) containing the ensembles of preorganized groups L with optimal composition, arranged in the positions favoring the complexation with Am^{III} (analogously to Ln^{III}), and hence its selective and effective sorption.

The control sorbent **2** was synthesized earlier [10] by copolymerization of DVB with (ethenyl)(diphenyl)phosphine oxide.

The NMR spectra were recorded using *Bruker AV-300* spectrometer with working frequencies of 300.11 (^1H) and 121.50 MHz (^{31}P) in $CDCl_3$, using the signal of residual H-atoms from the solvent as internal standard (^1H) and 85% H_3PO_4 (^{31}P) as external standard; δ in ppm, J in Hz. $Ph_2P(O)(CH{=}CH_2)$ was prepared as described in [17]. Since sorption of Am^{III} was studied from HNO_3 solns., lanthanides were used in the form of nitrates: $La(NO_3)_3 \cdot 6\,H_2O$, $Ce(NO_3)_3 \cdot 6\,H_2O$, and $Pr(NO_3)_3 \cdot 6\,H_2O$. The accuracy of N and P determination in polymers were ±0.4 and ±0.2%, resp.

Syntheses of Complexes of Ln^{III} with (Ethenyl)(diphenyl)phosphine Oxide. Tris[(ethenyl)(diphenyl)phosphine oxide]lanthanum(3+) Nitrate (**3a**). For the synthesis, 4.16 g (20 mmol) of $Ph_2P(O)(CH{=}CH_2)$ dissolved in 20 ml of DCB were added to 2 g (0.46 mmol) of $La(NO_3)_3 \cdot 6\,H_2O$, partly dissolved in 1 ml of 0.1M HNO_3, and mixed at 20° for 2 h. During this stage, the aq. phase turned colorless. The org. phase was separated and dried (Na_2SO_4). The supernatant was filtered, washed twice with 10 ml of DCB, and evaporated *in vacuo* at 40°/12 Torr to *ca.* 5 ml, and then 20 ml of toluene were added. The precipitated oil-like compound was twice re-precipitated from DCB/toluene to afford **3a** (2.70 g, 58%). Mixture of an oil-like substance and pale-yellow crystals. ^1H-NMR: 7.61–7.54 (*m*, 4 H_o); 7.49–7.43 (*m*, 2 H_p); 7.35–7.28 (*m*, 4 H_m); 6.56–6.38 (*m*, =CH); 6.29–6.02 (*m*, =CH_2). ^{31}P-NMR {^1H}: 31.23 (*s*, $\Delta\nu_{1/2} = 28$). Anal. calc. for $C_{42}H_{39}LaN_3O_{12}P_3$ (1009.57): C 49.96, H 3.89, N 4.16, P 9.20; found: C 50.01, H 3.84, N 4.09, P 8.91.

The other lanthanides complexes were prepared similarly.

Tris[(ethenyl)(diphenyl)phosphine oxide]cerium(3+) Nitrate (**3b**). Yield: 67%. Needle-like pale-yellow crystals. M.p. 141–143°. ^{1}H-NMR: 8.68 (*s*, $\Delta\nu_{1/2} = 28$, 4 H_o); 8.23 (*s*, $\Delta\nu_{1/2} = 56$, 1 H, =CH); 7.66 (*t*, 2 H_m); 7.53 (*s*, $\Delta\nu_{1/2} = 17$, 4 H_p); 7.26 (*dd*, ^3J(P,H) = 29, ^3J(H,H) = 7.1, 1 H, =CH$_2$); 6.73 (*dd*, ^3J(P,H) = 45, ^3J(H,H) = 12, 1 H, =CH$_2$). ^{31}P-NMR {^{1}H}: 68.94 (*s*, $\Delta\nu_{1/2} = 130$). Anal. calc. for $C_{42}H_{39}CeN_3O_{12}P_3$ (1010.78): C 49.90, H 3.89, N 4.16, P 9.13; found: C 50.04, H 3.91, N 4.11, P 8.93.

Tris[(ethenyl)(diphenyl)phosphine Oxide]praseodymium(3+) Nitrate (**3c**). Yield: 52%. Dense oil-like, bright-green substance. ^{1}H-NMR: 10.90 (*s*, $\Delta\nu_{1/2} = 69$, 4 H_o); 9.47 (*s*, $\Delta\nu_{1/2} = 86$, =CH); 8.02 (*s*, $\Delta\nu_{1/2} = 28$, 6 H, H_m, H_p); 7.51 (*d*, ^3J(P,H) = 41, 1 H, =CH$_2$); 7.32 (*dd*, ^3J(P,H) = 21, ^3J(H,H) = 7, 1 H, =CH$_2$). ^{31}P-NMR {^{1}H}: 122.12 (*s*, $\Delta\nu_{1/2} = 400$). Anal. calc. for $C_{42}H_{39}N_3O_{12}P_3Pr$ (1011.58): C 49.86, H 3.88, N 4.16, P 9.18; found: C 50.09, H 3.96, N 3.84, P 8.78.

Copolymerization of **3a**–**3c** *with DVB. Copolymer of Tris[(ethenyl)(diphenyl)phosphine Oxide)lanthanum(3+) Nitrate with DVB* (**4a**). To 0.35 g (0.5 mmol) of **3a**, dissolved in 15 ml of DCB, 3.2 g of DVB and 4 drops of ^{t}BuOO^{t}Bu were added. The mixture was warmed in a microwave oven at 60° for 6 h. After cooling to 20°, the copolymer was ground, washed five times with 20-ml portions of CHCl$_3$ and air-dried at 20° for 24 h, followed by vacuum drying in a dessiccator: 3.04 g of copolymer **4a** were obtained. Found: N 0.32, P 0.87.

As described above, other compounds were obtained.

Copolymer of Tris[(ethenyl)(diphenyl)phosphine oxide]cerium(3+) Nitrate with DVB (**4b**): found: N 0.78, P 0.77.

Copolymer of Tris[(ethenyl)(diphenyl)phosphine oxide]praseodymium(3+) Nitrate with DVB (**4c**): found: N 0.55, P 0.82.

Desorption of Ln^{III} from Copolymers **4a**–**4c**. Copolymer **4a** (1.30 g) was mixed with 20 ml of 1% *Trilone B* soln. and left for 30 min. The precipitate was filtered to give a pale-yellow filtrate. The procedure was repeated three times, and then the precipitate was washed four times with 100-ml portions of deionized H$_2$O. The product was air-dried at 20° for 48 h and then vacuum-dried in desiccator (1 Torr) over P_2O_5; 1.12 g of template sorbent **1a** (La-sorbent) was obtained; found: N 0.00, P 0.82.

As described above, the following sorbents were obtained: template sorbent **1b** (Ce-sorbent): found: N 0.00, P 0.73; template sorbent **1c** (Pr-sorbent): found: N 0.00, P 0.73.

Sorption of Am^{III}. The sorption of Am^{III}, Eu^{III}, and Pu^{IV} (initial total concentration of 10^{-6} M) was studied under static conditions at the soln./sorbent ratio of 500 ml/g. The phase contact time was 15 min, which was sufficient to reach constant sorption. The concentrations of ^{241}Am and ^{152,154}Eu in soln. before and after sorption were determined by gamma-spectrometry, and of ^{239}Pu by alpha-spectrometry. The percent of adsorbed Am (S_{Am}), Eu (S_{Eu}), and Pu (S_{Pu}) were then calculated. Sorption experiments were performed using sorbent fractions sized 0.05–0.5 mm.

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Received February 27, 2014