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# Synthesis of a template sorbent for the extraction of americium(III) from nitric acid solutions

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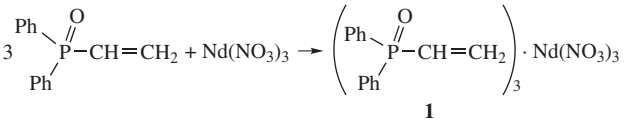
A template sorbent that can rapidly and efficiently uptake americium(III) from nitric acid solutions has been obtained *via* a three-stage synthesis. The sorbent shows high selectivity and retains $Am^{III}$ sorption against a background of $Fe^{III}$.

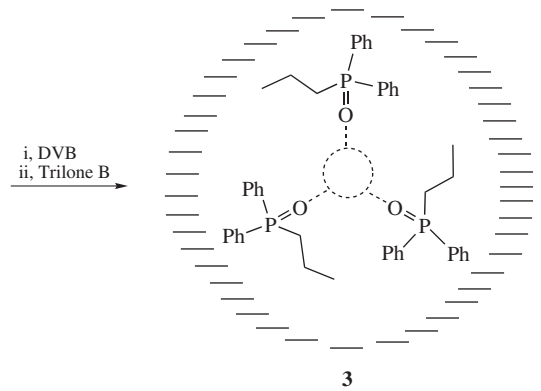
In recent years, there is an intense development of a new research direction in the chemistry of sorption processes based on the use of template sorbents or sorbents possessing memory effect, which can recognize sterically complementary target compounds and extract them with high selectivity. Initially, template sorbents were proposed to recover and concentrate organic compounds, *e.g.*, pesticides, from the environment.[1,2] It was shown later that these sorbents can be used for the selective extraction of prescribed metal cations from solutions;[3–5] in this case, there is no need to use masking agents. Before our work, however, there was no systematic studies on the synthesis and properties of phosphoryl-containing template sorbents promising for the extraction of minor actinides from liquid radioactive wastes, first of all, $Am^{III}$.[6] Therefore, for the selective sorption of $Am^{III}$, we have prepared a new template sorbent containing chemically bound monodentate ethylenediphenylphosphine oxide groups.

The sorbent was obtained in three stages (Scheme 1). We used available vinyldiphenylphosphine oxide $Ph_2P(O)CH{=}CH_2$ (**L**) as a complex-forming molecule. Neodymium(III) was employed as a simulant of americium(III) because the ionic radius ($R_I$) of $Nd^{III}$ is close to that of $Am^{III}$ ($R_{Am^{III}}$ = 107 pm, $R_{Nd^{III}}$ = 104 pm).[7,8]

It was important to obtain just the compound resulting from $Nd^{III}$ and **L** in actual aqueous acid solutions; therefore, complex



**1**




**3**

**Scheme 1**

$Nd(\mathbf{L})_3(NO_3)_3$ (**1**) was obtained at the first stage by liquid–liquid extraction with 0.1 M solution of **L** in $CH_2Cl_2$.† The ligand was intentionally used in extraction as a 4.3-fold excess because complex composition was unknown *a priori*. At the second stage, the complex was copolymerized with divinylbenzene (DVB) in *o*-dichlorobenzene solution in the presence of *tert*-butyl peroxide as an initiator to form copolymer **2**. The final product, template

† The NMR spectra were recorded on a Bruker AV-300 spectrometer operating at 300.11 MHz ($^1$H) and 121.50 MHz ($^{31}$P) in $CDCl_3$ solutions using residual proton signals as internal reference ($^1$H) and 85% $H_3PO_4$ as external reference ($^{31}$P). Vinyldiphenylphosphine oxide was obtained according to a published procedure.[10]

*Tris(vinyldiphenylphosphine oxide)neodymium(3+)* nitrate **1**. A solution of 4.16 g (20 mmol) of vinyldiphenylphosphine oxide in 20 ml of $CH_2Cl_2$ was added to a suspension of 2 g (0.46 mmol) of $Nd(NO_3)_3{\cdot}6H_2O$ in 1 ml of 0.1 M $HNO_3$. The mixture was vigorously stirred at 20 °C for 2 h. In so doing, the aqueous layer gradually became colourless. The organic layer was separated and concentrated to 5 ml, and 20 ml of benzene was added. The precipitate resulted after two days was reprecipitated twice from $CH_2Cl_2$–benzene to give 3.21 g (76%) of complex **1** as pale blue needles, mp 102–104 °C. $^{31}P\{^1H\}$ NMR, $\delta$: 127. $^1$H NMR, $\delta$: 9.07 (s, 4H, $\Delta\nu_{1/2}$ 30 Hz, *o*-$H_{Ph}$), 8.78 (s, 1H, $\Delta\nu_{1/2}$ 66 Hz, =CH), 7.74–7.63 (complex multiplet, 1H, =C$H_2$ and 6H, *m*-$H_{Ph}$, *p*-$H_{Ph}$), 6.76 (dd, 1H, =C$H_2$, $^2J_{HP}$ 45 Hz, $^3J_{HH}$ 10 Hz). Found (%): C, 49.53; H, 3.81; N, 3.99; P, 9.15. Calc. for $C_{42}H_{39}N_3NdO_{12}P_3$ (%): C, 49.69; H, 3.87; N, 4.14; P, 9.15.

*Copolymerization of complex* **1** *with DVB*. Divinylbenzene (3.6 g) and four drops of *tert*-butyl peroxide were added to a solution of 0.5 g (0.5 mmol) of complex **1** in 8 ml of *o*-dichlorobenzene. The mixture was heated on stirring at 60 °C for 20 h. The resultant copolymer was grinded to powder, washed by decantation with chloroform (5×20 ml), dried in air and then in a vacuum dessicator to give 4.04 g of copolymer **2**. Found (%): N, 0.85; P, 1.11.

*Desorption of* $Nd^{III}$ *from copolymer* **2**. A suspension of 1.3 g of copolymer **2** in 20 ml of 2% solution of Trilon B was stirred for 30 min. The precipitate was separated by filtration to give a light blue filtrate. The manipulation was repeated additionally three times. The precipitate was washed with water in the same manner (4×20 ml), dried in air and then in a vacuum dessicator to give 1.12 g of sorbent **3**. Found (%): N, 0.00; P, 0.93.

*The control sorbent* **4**. 3.7 g of DVB and 4 drops of *tert*-butyl peroxide were added to 0.3 g (1.31 mmol) of vinyldiphenylphosphine oxide dissolved in 8 ml of *o*-dichlorobenzene. The solution was heated and stirred at 60 °C during 20 h. The resultant copolymer was grinded to powder, washed by decantation with chloroform (5×20 ml), dried in air and then in a vacuum desiccator to give 3.84 g of copolymer **4**. Found (%): P, 1.01.

**Table 1** Degree of sorption (%) and Kd (ml $g^{-1}$) (in parentheses) of $Am^{III}$ and $Eu^{III}$ when extracted from nitric acid solutions at 20 °C, $[Am^{III}] = [Eu^{III}] = 10^{-6}$ mol $dm^{-3}$, V/m = 500 ml $g^{-1}$, time of phase contact is 15 min.

| Entry | $[HNO_3]$/mol $dm^{-3}$ | | | | |
|---|---|---|---|---|---|
| | Sorbent **3** | | | Sorbent **4** | |
| | 0.5 | 2.0 | 5.0 | 0.5 | 2.0 |
| $Am^{III}$ | 98 (25000) | 97 (16000) | 5.0 (26) | 96 (12000) | 97 (16000) |
| $Am^{III}$ in the presence of 2 g $dm^{-3}$ $Fe^{III}$ | 91 (5100) | 93 (6600) | 2.7 (14) | 73 (1400) | 86 (3100) |
| $Am^{III}$ in the presence of 2 g $dm^{-3}$ $Zr^{IV}$ | 48 (460) | 19 (120) | > 1 (—) | 30 (210) | 15 (88) |
| $Eu^{III}$ | 92 (5800) | 84 (2600) | > 1 (—) | — | — |

sorbent **3**, was obtained after desorption of $Nd^{III}$ from the copolymer using an aqueous solution of Trilon B.

The sorbent rapidly and efficiently extracts $Am^{III}$ from nitric acid solutions (Table 1).‡ The sorption of $Am^{III}$, $S_{Am}$, by templated (**3**) and control (**4**) sorbents from 0.5 and 2 M $HNO_3$ was quantitative (Table 1). In all cases, sorption is completed within 15 min at room temperature. From 5 M $HNO_3$ the $S_{Am}$ by sorbent **3** achieved 2.7% that could be explained by the monodentate character of the complexes formed with the functional groups of the sorbent.[9] As it was expected, sorbent **3** selectively extracts $Am^{III}$ from solutions with high $Fe^{III}$ concentration (2 g $dm^{-3}$). In the presence of $Fe^{III}$, 91 and 93% of $Am^{III}$ is extracted from 0.5 and 2 M $HNO_3$, respectively; therefore, the sorption is almost constant. For sorbent **4**, the corresponding values are 73% for 0.5 M $HNO_3$ and 86% for 2 M $HNO_3$.

However, for extraction from 2 M $HNO_3$ in the presence of $Zr^{IV}$ (2 g $dm^{-3}$), $S_{Am}$ decreases down to 19%. Possible explanation of this fact is a smaller difference in ionic radii of $Zr^{IV}$ and $Am^{III}$, as compared with that of $Fe^{III}$ and $Am^{III}$, another reason is the known higher extraction efficiency of zirconium(IV) in comparison with that of americium(III). Nonetheless, the sorption degree of $Am^{III}$ increases to 48% in 0.5 M $HNO_3$. (For sorbent **4**, this value is 30% for 0.5 M $HNO_3$ or 15% for 2 M $HNO_3$).

We also studied the sorption of europium(III) as an analogue of americium(III). The ionic radius of $Eu^{III}$ is smaller[8] than that of $Am^{III}$; therefore, as would be expected, the sorption of $Eu^{III}$ in all experiments is lower than that of $Am^{III}$: 92% ($Kd = 5.8\times10^3$ ml $g^{-1}$) from 0.5 M $HNO_3$ and 84% ($Kd = 2.6\times10^3$ ml $g^{-1}$) from 2 M $HNO_3$.

Thus, using the simple three-stage synthesis, we prepared the template sorbent that can rapidly and efficiently extract americium(III) from 0.5 and 2 M nitric acid. The template effect is displayed by the sorption of $Am^{III}$ in the presence of high concentrations of $Fe^{III}$ and $Zr^{IV}$ that result in significant increase in $Am^{III}$ separation. Upon this $Kd_{Am}$ for templated sorbent **3** is more than two times higher than $Kd_{Am}$ for control sorbent **4**.

‡ The sorption of $Am^{III}$ and $Eu^{III}$ (initial concentration $10^{-6}$ mol $dm^{-3}$) was carried out under batch conditions at the ratio of solution volume to sorbent weight (V/m) of 500 ml $g^{-1}$. Phase contact time was 15 min. The contents of $^{241}Am$ and $^{152-155}Eu$ in the solution before and after sorption was determined from $\gamma$ activity. These data were used to calculate the degree of sorption ($S$) in percent and distribution coefficient (Kd) in ml $g^{-1}$.

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