

# Hydroxypyridinone Derivatives: A Low-pH Alternative to Polyaminocarboxylates for TALSPEAK-like Separation of Trivalent Actinides from Lanthanides

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Cite This: *ACS Omega* 2020, 5, 12996–13005



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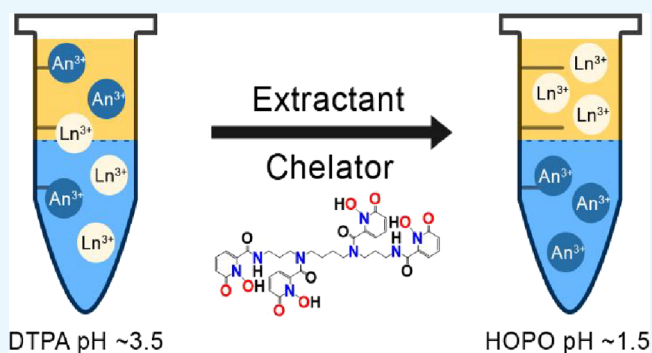


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**ABSTRACT:** Separation of lanthanides (Ln) from actinides (An) is unanimously challenging in reprocessing used nuclear fuel despite of much dedicated efforts over the past several decades. The TALSPEAK process is the current reference method in the United States for  $\text{Ln}^{3+}/\text{An}^{3+}$  separation but suffers from several limitations, such as a narrow working pH window (3.5–4.0), costly pH buffers, and slow extraction kinetics. Studies aiming at improving TALSPEAK have so far focused on polyaminocarboxylates hold-back reagents. Here, a new class of water-soluble ligands comprising hydroxypyridinone metal-binding units are evaluated for  $\text{Ln}^{3+}/\text{An}^{3+}$  separation. The model octadentate chelator 3,4,3-LI(1,2-HOPO) (abbreviated as HOPO) was used in combination with several industry-relevant organic extractants to separate Gd from four transplutonium elements (Am, Cm, Bk, and Cf). Cyanex 301 GN and HDEHP worked best in combination with HOPO, whereas HEH[EHP], Cyanex 572, and ACORGA M5640 did not yield practical  $\text{Ln}^{3+}/\text{An}^{3+}$  separation. Separation factors between  $\text{Gd}^{3+}$  and  $\text{Am}^{3+}$  reach about 50 with the HOPO/Cyanex 301 GN system and 30 with the HOPO/HDEHP system. The results using HDEHP ( $\text{SF}_{\text{Gd}/\text{Am}} = 30$ ,  $\text{SF}_{\text{Gd}/\text{Cm}} = 8.5$ , and  $\text{SF}_{\text{Gd}/\text{Cf}} = 773$ ) are high enough for industrial applications, and the proposed system works at pH values as low as 1.5, which simplifies the process by eliminating the need for pH buffers. In contrast to previously proposed methods, the HOPO-based process is also highly selective at separating Bk from  $\text{Ln}^{3+}$  ( $\text{SF}_{\text{Gd}/\text{Bk}} = 273$ ) owing to *in situ*, spontaneous oxidation of Bk(III) to Bk(IV) by HOPO. The optimal pH in the case of HOPO/Cyanex 301 GN is 3.6 ( $\text{SF}_{\text{Am}/\text{Gd}} = 50$ ,  $\text{SF}_{\text{Cm}/\text{Gd}} = 23$ ,  $\text{SF}_{\text{Bk}/\text{Gd}} = 1.4$ , and  $\text{SF}_{\text{Cf}/\text{Gd}} = 3.2$ ), but this system has the advantage of extracting An ions into the organic phase while keeping Ln ions in the aqueous phase, which is opposite to the conventional TALSPEAK process. This study represents the first optimization of a TALSPEAK-like Ln/An separation method using a HOPO chelator and paves the avenue for further developments of analytical science and reprocessing of used nuclear fuel.



## INTRODUCTION

High-level liquid waste (HLLW), such as PUREX (plutonium uranium redox extraction) raffinate, generates much heat and remains highly radiotoxic for thousands of years mainly due to the presence of long-lived fission products (some of which are lanthanides, Ln) and minor actinides (minor An, mainly consisting of Np, Am, and Cm).<sup>1</sup> On the one hand, partitioning and transmutation of minor An can effectively reduce the heat load,<sup>2</sup> long-term radiotoxicity, and consequently the vitrified volume for HLLW repositories. On the other hand, some Ln isotopes have higher neutron capture cross sections than minor An and are problematic for transmutation and closing the nuclear fuel cycle. Therefore, among many different groups of radionuclides existing in used nuclear fuel, separation of Ln from minor An is of particular interest. The separation of  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  from  $\text{Ln}^{3+}$  is very challenging because they typically exhibit same oxidation state, comparable charge densities, and similar hydrated ionic radii

and, as a consequence, very similar solution chemistry behaviors.<sup>3,4</sup> Discrimination primarily relies on  $\text{Ln}^{3+}$  ions being slightly harder than  $\text{An}^{3+}$  ions. One approach for separating  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  from  $\text{Ln}^{3+}$  is using water-soluble soft donor chelators to preferentially hold back  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  in the aqueous phase, while  $\text{Ln}^{3+}$  ions are selectively extracted into the organic phase by hard donor extractants. A different approach consists of using soft donor extractants to selectively extract  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  while leaving  $\text{Ln}^{3+}$  in the aqueous phase.

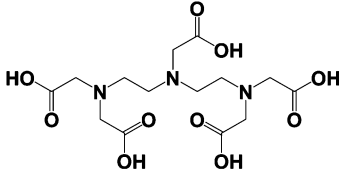
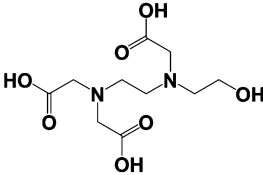
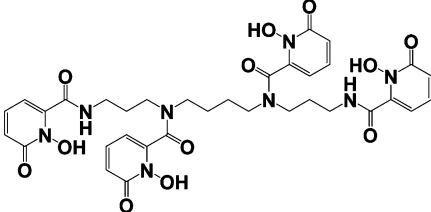
Received: February 27, 2020

Accepted: May 8, 2020

Published: May 28, 2020



**Table 1. Molecular Structures and Solution Thermodynamic Parameters of TALSPEAK-Relevant DTPA, HEDTA, and Proposed Alternative HOPO<sup>4,14,17,20,26–31</sup>**

	pKa	log $\beta_{101}^a$	Molecular structure of the protonated ligand
DTPA	2.3(5) 2.6(2) 4.2(1) 8.3(1) 9.5(1) $\Sigma pK_a = 26.9$ (1 M NaNO <sub>3</sub> ) <sup>27</sup>	[AmDTPA] <sup>2-</sup> 22.9 (0.1 M NH <sub>4</sub> ClO <sub>4</sub> ) <sup>28</sup> [GdDTPA] <sup>2-</sup> 22.5 (0.1 M KNO <sub>3</sub> ) <sup>4</sup>	
HEDTA	3.6(4) 1.6(5) 5.7(2) 9.8(1) $\Sigma pK_a = 20.7$ (1 M NaNO <sub>3</sub> ) [17]	[AmHEDTA] 15.7 (0.1 M NaClO <sub>4</sub> ) <sup>14</sup> [GdHEDTA] 15.1 (0.1 M KNO <sub>3</sub> ) <sup>29</sup>	
HOPO	3.87(1) 5.01(1) 5.68(1) 6.64(1) $\Sigma pK_a = 21.2$ (0.1 M KCl) <sup>20,30</sup>	[AmHOPO] <sup>-</sup> 20.4(2) (in 0.1 M KCl) <sup>26</sup> [GdHOPO] <sup>-</sup> 20.5(1) (in 0.1 M KCl) <sup>31</sup>	

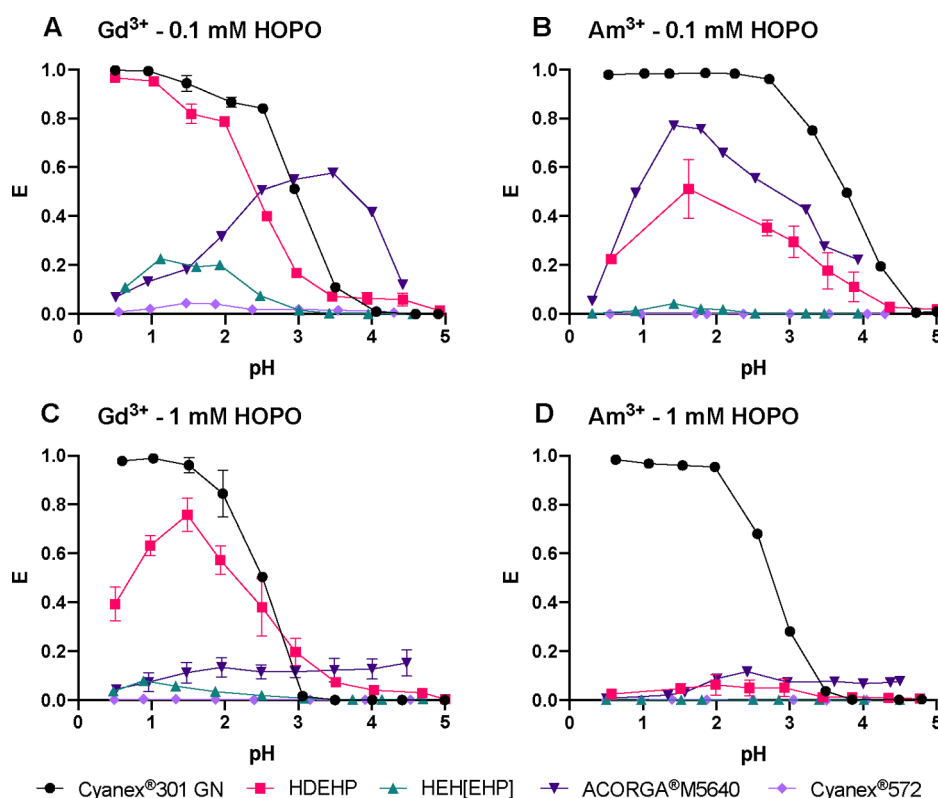
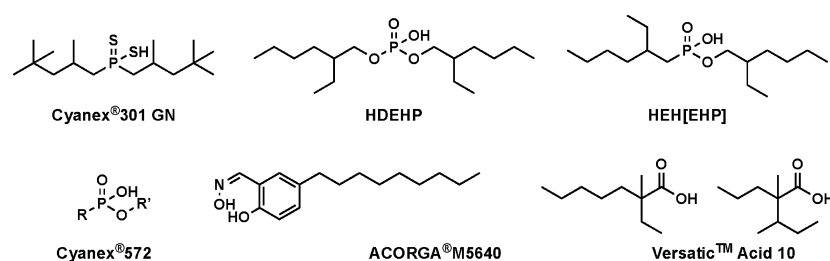
<sup>a</sup> $\beta_{mhl}$  is the stability constant for the reaction  $mM + hH + lL \leftrightarrow M_m H_h L_l$ ,  $\beta_{mhl} = \frac{[M_m H_h L_l]}{[M]^m [H]^h [L]^l}$ .

Many separation processes have been studied based on the first approach. One of the most studied processes in the United States is the so-called trivalent actinide lanthanide separation with phosphorus-reagent extraction from aqueous complexes (TALSPEAK) process.<sup>4</sup> In its standard version, it adopts di-(2-ethylhexyl)phosphoric acid (HDEHP) as the extractant, 1,4-diisopropylbenzene or *n*-dodecane as the diluent, lactic acid/lactate as the pH buffer, and diethylenetriaminepentaacetic acid (DTPA) as the An<sup>3+</sup> hold-back reagent. The working pH range lies between 3.0 and 4.5.<sup>4</sup> It suffers from two major flaws, slow phase-transfer kinetics and high pH dependence due to the pH sensitivity of DTPA and lactate species. Other limitations also include the expensive lactate buffer and lack of compatibility with the acidic feed solutions requiring a pH-adjustment step prior to the actual separation. Below pH 3, DTPA does not bind trivalent metal ions M<sup>3+</sup>, and above pH 4, the extraction fraction decreases for all M<sup>3+</sup> ions as the apparent chelating strength of DTPA becomes stronger and the extraction of lactate by HDEHP starts competing with the extraction of the metal ions. Many studies have been dedicated to the modification of TALSPEAK, especially in improving the separation of Eu<sup>3+</sup> and Gd<sup>3+</sup> from Am<sup>3+</sup> and Cm<sup>3+</sup>. For instance, extensive work by Shafer et al. proposed the replacement of HDEHP by 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]), and as a consequence, DTPA had to be replaced by the lower strength chelator, ethylenediaminetetraacetic acid (HEDTA). The HEH[EHP]/HEDTA combination limits undesirable extraction of water and lactate and exhibits faster phase-transfer kinetics.<sup>3</sup> The separation factors (SF) of Eu<sup>3+</sup> versus Am<sup>3+</sup> (SF<sub>Eu/Am</sub>) and Gd<sup>3+</sup> versus Am<sup>3+</sup> (SF<sub>Gd/Am</sub>) increased from 30–60 in the

conventional TALSPEAK process to 50–100 using the HEH[EHP]/HEDTA combination at pH 3.6.<sup>3</sup>

Combinations of extractants have also been investigated. For example, in the minor actinide lanthanide separation process (ALSEP), a synergistic mixture of HEH[EHP] and *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) or *N,N,N',N'*-tetra-2-ethylhexyl diglycolamide (T2EHDGA) has been proposed by Lumetta et al., and the SF<sub>Gd/Am</sub> values at pH 2–4 reached 120–400 using DTPA as the chelator<sup>5</sup> and 70–140 using HEDTA as the chelator.<sup>6</sup> The SF<sub>Eu/Am</sub> values decrease slightly, about 50–70 at pH 3.4–4.2, using the same extractant mixture and chelator.<sup>7</sup> Gelis et al. used mixed extractants of HEH[EHP] and T2EHDGA and increased the SF<sub>Eu/Am</sub> values to nearly 100 at pH 2 and 3, respectively, using DTPA and HEDTA.<sup>8</sup> Another option of extractant mixture is HEH[EHP] and Cyanex 923. The working pH range was 2.0–3.5, and the SF<sub>Eu/Am</sub> values reached respective maxima of ~65 and ~50 using triethylenetetraminehexaacetic acid (TTHA) and HEDTA as the chelator.<sup>2</sup> Although HDEHP mixed with TODGA or T2EHDGA has also been studied, corresponding separations are not as efficient as those using HEH[EHP].<sup>7,9</sup> All these studies focusing on HEH[EHP] in combination with HEDTA have shown results that surpassed the conventional TALSPEAK process; however, a relatively high pH range is still needed (between 3 and 4), which requires a pH buffer and poses implementation challenges in industrial settings, where the upstream acidity is very high (on the order of molar HNO<sub>3</sub>) and downstream salts are undesirable. More recently, several structural modifications of acetic acid derivatives have been made to explore their applicability to more acidic conditions;<sup>10–12</sup> resulting separation factors decreased considerably from 50–80 at pH 3–4 to <30 at pH < 2. However, in

**Scheme 1. Names and Molecular Structures of Commercial Extractants Used in This Study (Detailed Compositions of Certain Extractants Are Considered as Trade Secrets and Thus Not Revealed)**



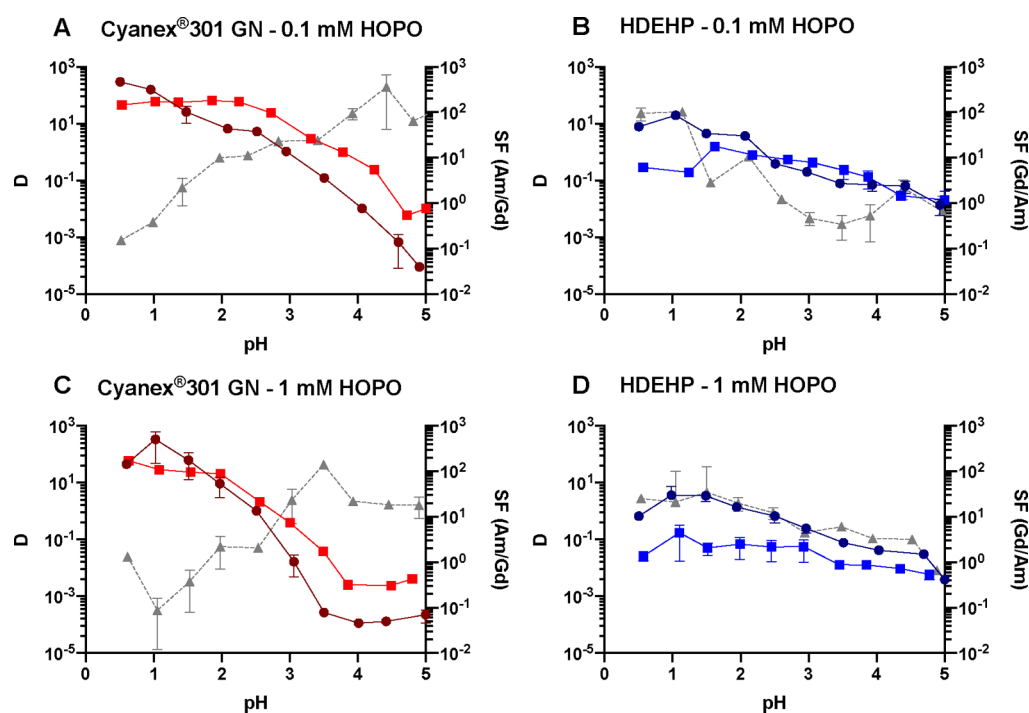
**Figure 1.** Extraction of (A, C) Gd<sup>3+</sup> and (B, D) Am<sup>3+</sup> into a kerosene organic phase as a function of pH in the aqueous phase, with two different HOPO concentrations (0.1 mM in panels (A) and (B) or 1 mM in panels (C) and (D)) and five different extractants (Cyanex 301 GN (black circles), HDEHP (pink squares), HEH[EHP] (cyan upward triangles), ACORGA M5640 (dark purple downward triangles), or Cyanex 572 (light purple diamonds)). [Extractant] = 0.5 M in kerosene;  $V_o/V_a = 1$ ;  $I = 1$  M.

the past 50 years, nearly all efforts have concentrated on only one class of hold-back reagents, the polyaminocarboxylates, especially DTPA,<sup>3,4,7,13</sup> HEDTA,<sup>2,3</sup> TTHA,<sup>2</sup> or DPA (dipicolinic acid).<sup>14</sup>

While all these TALSPEAK-related studies are based on extracting Ln ions, the reverse TALSPEAK approach should be stressed. Ln are predominant over minor An in used nuclear fuel; it might be more tempting, from the engineering standpoint, to extract minor An into the organic phase for transmutation while keeping Ln in the aqueous phase. Many studies of direct An extraction have been accomplished primarily in Europe, with the diamide extraction (DIAMEX) process that aims at trivalent Ln and An co-extraction,<sup>15</sup> the selective actinide extraction (SANEX) process that aims at trivalent Ln/An separation,<sup>16,17</sup> and the group actinide extraction (GANEX) process that aims at Pu and minor An separation.<sup>18,19</sup> Remarkably, SANEX uses either dithiophosphinic acids (cation exchangers) or 2,6-bis(1,2,4-triazin-3-

yl)pyridine (BTP) derivatives (neutral solvating agents) as the extractants.<sup>13</sup> A notable BTP derivative, *n*-propyl-BTP, has been hot-tested on genuine HLLW by the French Atomic Energy Commission (CEA) and the German Institute for Transuranium Elements (ITU), with resulting separation factors comparable to those obtained through the TALSPEAK process. However, BTP derivatives have not yet been adopted in larger-scale industrial processes, in part due to their extreme susceptibility toward radiolysis attributed to the relatively polarizable molecular orbitals encountered in pyridine-based reagents.<sup>13</sup>

The present study evaluates an alternative family of aqueous chelators, the hydroxypyridinones, for potential use in Ln<sup>3+</sup>/An<sup>3+</sup> separation processes, in lieu of common chelators such as the polyaminocarboxylates. The model compound for this family, 3,4,3-LI(1,2-HOPO) (referred to as HOPO; Table 1), was originally developed for the decorporation of radionuclides from contaminated human bodies owing to its low toxicity and



**Figure 2.** Distribution ratio for  $\text{Gd}^{3+}$  (round solid line) and  $\text{Am}^{3+}$  (square solid line) and corresponding separation factors (triangle dashed line) as a function of pH in the aqueous phase, with two different HOPO concentrations (0.1 mM in panels (A) and (B) or 1 mM in panels (C) and (D)) and two different extractants (Cyanex 301 GN (panels (A) and (C)) or HDEHP (panels (B) and (D))). [Extractant] = 0.5 M in kerosene;  $V_o/V_a = 1$ ;  $I = 1$  M.

high affinity for An elements.<sup>20</sup> The coordination chemistry of this bio-inspired chelator has been studied with several f-elements (e.g.,  $\text{Ce}^{4+/3+}$ ,<sup>20</sup>  $\text{Th}^{4+}$ ,<sup>20,21</sup>  $\text{UO}_2^{2+}$ ,  $\text{Pu}^{4+}$ ,<sup>22</sup>  $\text{Am}^{3+}$ ,  $\text{Cm}^{3+}$ ,  $\text{Bk}^{4+}$ ,  $\text{Cf}^{3+}$ , and  $\text{Es}^{3+23}$ ), toxic heavy transition metals (e.g.,  $\text{Pd}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Sn}^{4+}$ ),<sup>24</sup> and other transition metals relevant to nuclear medical applications (e.g.,  $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$ , and  $\text{Hf}^{4+}$ ).<sup>25</sup> Solution thermodynamic data on HOPO show that it has a higher affinity for trivalent An relative to the trivalent Ln.<sup>20,21,26</sup> However, its use in Ln<sup>3+</sup>/An<sup>3+</sup> separation has not yet been investigated thoroughly. Because HOPO is more acidic than DTPA (Table 1), it is expected to yield a viable TALSPEAK-like process at a lower pH, making it a promising hold-back chelator that warrants investigation. Meanwhile, several extractants were also studied to narrow down an optimal combination with HOPO. To that end, we sought to test a wide variety of commercially available structures offering different chemical functionalities (phosphoric acid, thiophosphorous acid, oxime, and beta-diketone) that may play a role in extraction capability (Scheme 1). Hence, the main goal of this study was to determine the promise of HOPO-type chelators for efficient trivalent Ln/An separation processes.

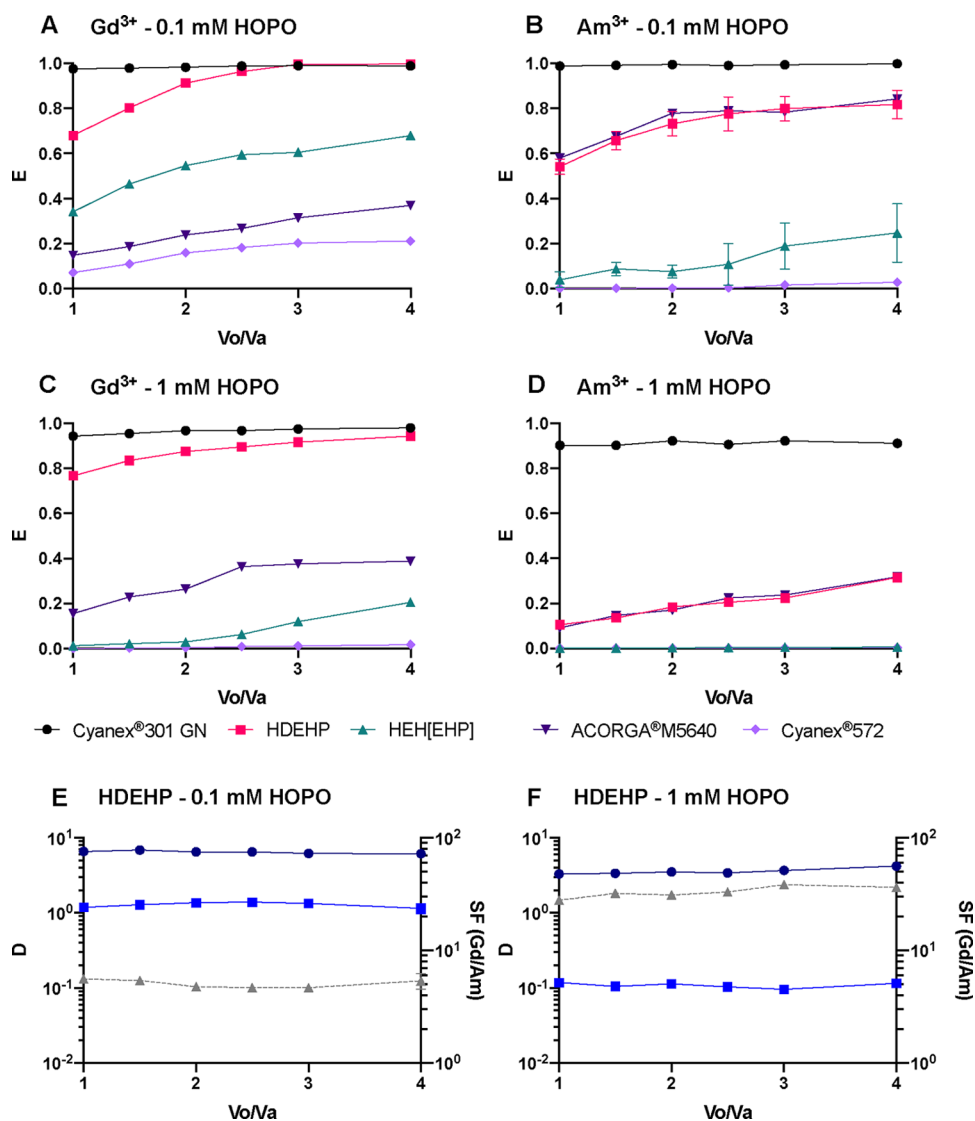
## RESULTS AND DISCUSSION

**Influence of pH.** One of the most important industry-relevant parameters for separation processes is the working pH range. In a first series of experiments illustrated in Figures 1 and 2, the extraction capability of tested extractants in the presence of HOPO, between pH 1 and 5, was determined to follow the order: Cyanex 301 GN > HDEHP  $\approx$  ACORGA M5640 > HEH[EHP] > Cyanex 572. While HDEHP, HEH[EHP], and Cyanex 572 show lower affinities to  $\text{Am}^{3+}$  than  $\text{Gd}^{3+}$ , Cyanex 301 GN and ACORGA M5640 favor extracting  $\text{Am}^{3+}$  over  $\text{Gd}^{3+}$ , as shown in Figure 1. This different

behavior provides the flexibility to extract either Ln<sup>3+</sup> or An<sup>3+</sup> into the organic phase while keeping the other in the aqueous phase. Although ACORGA M5640, HEH[EHP], and Cyanex 572 can differentiate the two radiotracers, their respective extraction power is too low to be applicable for industrial separations. Hence, only Cyanex 301 GN and HDEHP are stressed herein.

Very few results have been reported on the separation of  $\text{Am}^{3+}$  from Ln<sup>3+</sup> by Cyanex 301 GN and mostly focused on  $\text{Eu}^{3+}/\text{Am}^{3+}$ .<sup>32–35</sup> Cyanex 301 GN quantitatively extracts both f-elements at a low pH range but does not discriminate them at high acidity. This extractant therefore seems suitable for Ln-An co-extraction, but it is not selective under these experimental conditions. It is also worth noting that this study was designed to evaluate HOPO as a new aqueous chelator. We therefore focused on using commercially available extractants and did not perform any purification of these extractants prior to extraction experiments. The impurities present in commercial Cyanex 301 GN may have a significant effect on our results, which will need to be investigated further by scaling up metal concentrations. Above pH 2.5, HOPO starts to deprotonate and binds  $\text{Am}^{3+}$  with a slightly higher affinity than that for Ln<sup>3+</sup>.<sup>26</sup> Good separation can be achieved at pH values above 3.5 with Cyanex 301 GN in the presence of 0.1 mM HOPO (Figure 2A). The optimal pH range for the combination HOPO/Cyanex 301 GN is 3.5–4.5, independent of the excess of HOPO (Figure 2A,C).

In the presence of HOPO, HDEHP is more suitable than the other three extractants tested (ACORGA M5640, HEH[EHP], and Cyanex 572) to achieve high extraction fractions at a low pH and simultaneous discrimination of  $\text{Gd}^{3+}$  and  $\text{Am}^{3+}$ . This remains true when HOPO increases from 0.1 mM (Figure 2B) to 1 mM (Figure 2D), and the separation improves with a  $\text{SF}_{\text{Gd}/\text{Am}}$  value of  $\sim 70$  (Figure 2D). The

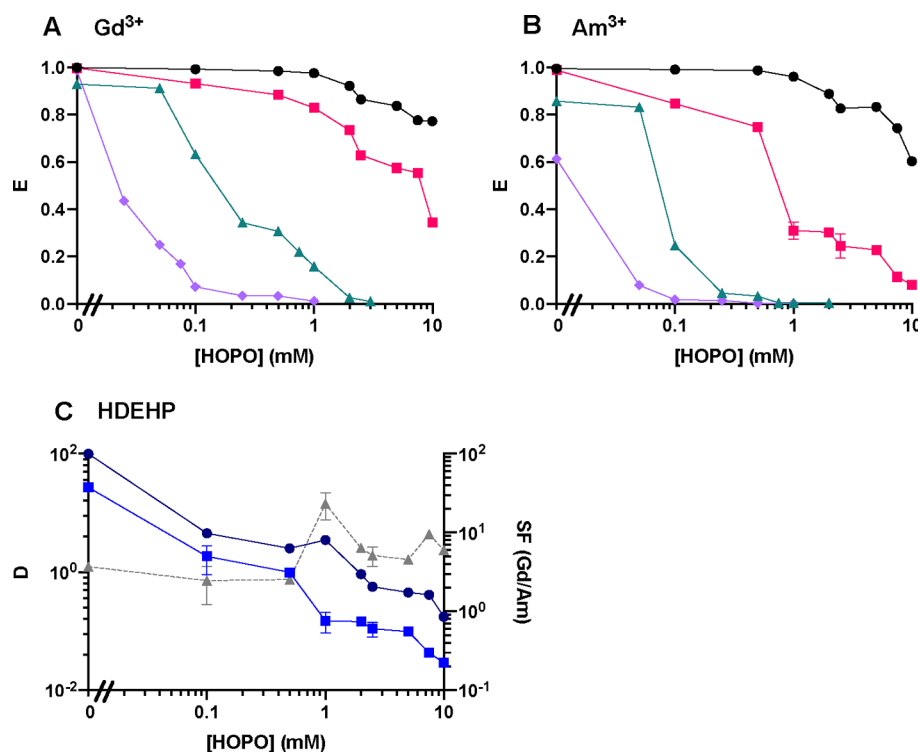


**Figure 3.** Extraction of (A, C)  $Gd^{3+}$  and (B, D)  $Am^{3+}$  into a kerosene organic phase as a function of phase volume ratio, with two different HOPO concentrations (0.1 mM in panels (A) and (B) or 1 mM in panels (C) and (D)) and five different extractants (Cyanex 301 GN (black circles), HDEHP (pink squares), HEH[EHP] (cyan upward triangles), ACORGA M5640 (dark purple downward triangles), or Cyanex 572 (light purple diamonds)). [Extractant] = 0.5 M; pH =  $1.50 \pm 0.02$ ;  $I = 1$  M; corresponding distribution ratios for  $Gd^{3+}$  (round solid line) and  $Am^{3+}$  (square solid line) and separation factors (triangle dashed line) with HDEHP, at (E) 0.1 mM HOPO or (F) 1 mM HOPO.

HOPO/HDEHP combination presents an extraction maximum for  $Gd^{3+}$  at pH 1.5 (Figure 1C) that is likely due to the protonation of HDEHP at a low pH (corresponding to HDEHP's  $pK_a$  value of  $\sim 1.5$ ).<sup>36</sup> At the extractant concentration used in the present study, the extraction of  $Am^{3+}$  by HDEHP is completely suppressed by 1 mM HOPO over the pH range of 1–5, offering a robust  $Gd^{3+}/Am^{3+}$  separation. Above pH 1.5, HOPO starts complexing  $Ln^{3+}$  ions, and their extraction is hindered, thus yielding an extraction maximum peak around pH 1.5 for  $Gd^{3+}$ . A working pH at 1.5 is chosen considering both high extraction and efficient separation. The HOPO/HEH[EHP] combination exhibits a behavior similar to that of HOPO/HDEHP, but the extraction fractions are much lower. Indeed, HOPO seems too strong for HEH[EHP] whose extraction efficiency is known to be lower than that of HDEHP.<sup>3</sup> Thus, other compounds of the HOPO family that are selective but weaker metal binders, such as the hexadentate ligand TREN-HOPO,<sup>37</sup> could be more suitable in combination with HEH[EHP]. A system with a higher HEH[EHP]

concentration relative to HDEHP for a given HOPO concentration is also likely to yield efficient Ln/An separation.

**Influence of Phase Volume Ratio ( $V_o/V_a$ ).** For the sake of comparison, extraction data at various phase volume ratios and at pH 1.5 were collected. The extraction results displayed in Figure 3 are congruous with the results from the pH-dependence studies, and the extractant efficacy follows the order: Cyanex 301 GN > HDEHP > HEH[EHP] > Cyanex 572. The high affinity of HOPO for trivalent f-elements therefore allows comparing the strength of a broad variety of extractants, including the most efficient ones like Cyanex 301 GN (Figures 1 and 3). In combination with 0.1 mM HOPO at pH 1.5, Cyanex 301 GN almost fully extracts both  $Gd^{3+}$  and  $Am^{3+}$  even when the phase volume ratio is as low as 1 (Figure 3). HDEHP also quantitatively extracts  $Gd^{3+}$  (Figure 3A) and more than 50% of  $Am^{3+}$  at  $V_o/V_a \geq 1$  (Figure 3B). ACORGA M5640 and Cyanex 572 exhibit low separation factors or poor extraction capability in the presence of HOPO even at a high  $V_o/V_a$ . All the extraction curves, except those at extremities,

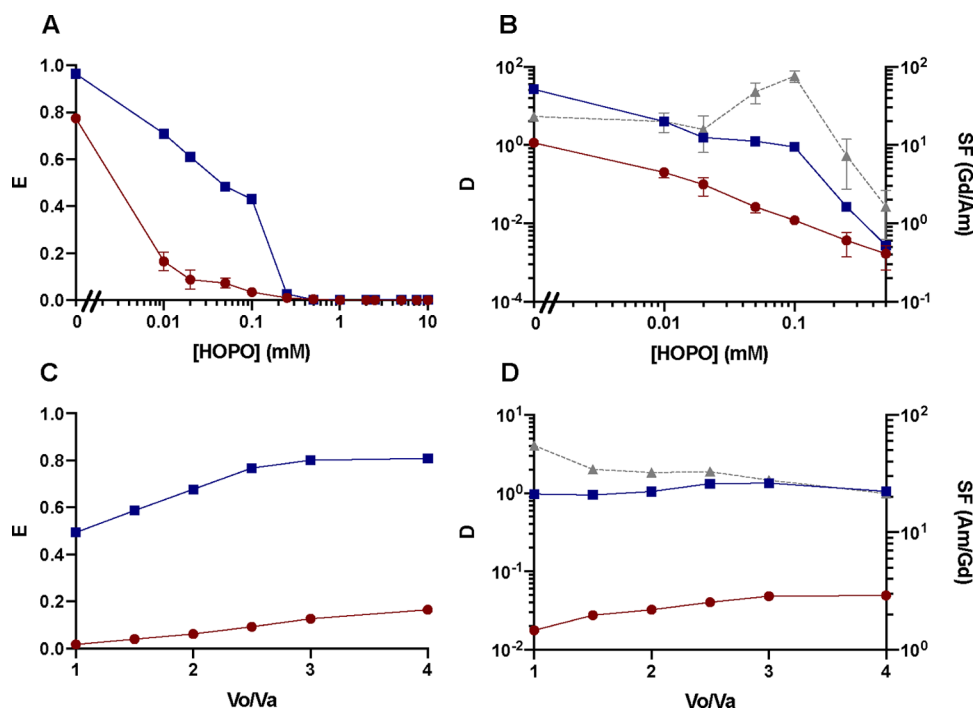


**Figure 4.** Extraction of (A)  $\text{Gd}^{3+}$  and (B)  $\text{Am}^{3+}$  into a kerosene organic phase as a function of HOPO concentration in the aqueous phase, with four different extractants: Cyanex 301 GN (black circles), HDEHP (pink squares), HEH[EHP] (cyan upward triangles), or Cyanex 572 (light purple diamonds). [Extractant] = 0.5 M;  $V_o/V_a = 3$ ; pH =  $1.50 \pm 0.03$ ;  $I = 1$  M; (C) corresponding distribution ratio for  $\text{Gd}^{3+}$  (round solid line) and  $\text{Am}^{3+}$  (square solid line) and separation factors (triangle dashed line).

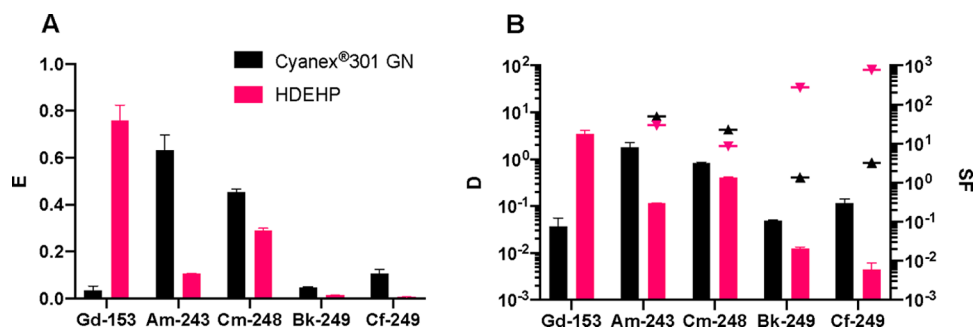
i.e., when  $E$  approaches 0 and 1, increase fast in the beginning and gradually reaches a plateau, which agrees with the mathematical expression of  $E$ . All tested extractants show reduced extraction of  $\text{Am}^{3+}$  relative to  $\text{Gd}^{3+}$  except Cyanex 301 GN that outcompetes HOPO at pH 1.5 (Figure 3). Interestingly, the extraction of  $\text{Gd}^{3+}$  by ACORGA M5640 at pH 1.5 is not influenced by the presence of HOPO (Figures 3A and 3C), whereas the extraction of  $\text{Am}^{3+}$  is hindered as the concentration of HOPO increases (Figure 3B and 3D). This is in line with previous solution thermodynamic studies that demonstrated the higher affinity of HOPO toward Sf elements relative to the 4f series at a low pH.<sup>26,31</sup> Although HEH[EHP] can differentiate  $\text{Gd}^{3+}$  from  $\text{Am}^{3+}$ , the separation is impractical as  $D$  values for both  $\text{M}^{3+}$  ions are much lower than 1 (Supplementary Figure S1) under the studied conditions. For the HDEHP/HOPO combination, a  $V_o/V_a$  value of 1 and a HOPO concentration of 1 mM HOPO are optimal (Figure 3E,F). The optimal  $V_o/V_a$  value for Cyanex 301 GN will be shown later since the data for Cyanex 301 GN at pH 1.5 (Supplementary Figure S1) does not demonstrate good separation. The optimal  $V_o/V_a$  condition at the working pH range will be provided in the **Optimal Conditions for Separation** section.

**Influence of 3,4,3-LI(1,2-HOPO) Concentration.** For the sake of comparison, extraction data at various HOPO concentrations (at pH 1.5 and  $V_o/V_a = 3$ ) were measured for HDEHP, HEH[EHP], Cyanex 301 GN, and Cyanex 572. Figure 4A,B shows that HOPO is a strong chelator for both  $\text{Ln}^{3+}$  and  $\text{An}^{3+}$  ions since the extraction curves of all extractants decrease as the HOPO concentration increases. At pH 1.5, Cyanex 301 GN is the strongest extractant for both  $\text{Gd}^{3+}$  and  $\text{Am}^{3+}$  and is slightly influenced by HOPO complexation with

the metal ions. In contrast, HEH[EHP] and Cyanex 572 are most sensitive to the competing hold-back complexation reactions as extraction fractions plummet even at a low HOPO concentration. Both  $E$  and SF values are low for Cyanex 572, and it appears to be not suitable for  $\text{Ln}^{3+}/\text{An}^{3+}$  separation. Although HEH[EHP] is efficient and exhibits the highest SF of  $\sim 60$  (Supplementary Figure S2), the  $D$  values of both  $\text{M}^{3+}$  ions used to calculate the SF value are very low ( $D_{\text{Gd}} = 0.09$  and  $D_{\text{Am}} = 0.0016$ ) (Supplementary Figure S2), rendering the HOPO/HEH[EHP] combination impractical at this pH. HDEHP is slightly weaker than Cyanex 301 GN in extracting the two elements, being the second least influenced by an excess of HOPO. The extraction capability is congruent with the results from the pH- and  $V_o/V_a$ -dependence studies and follows the order: Cyanex 301 GN > HDEHP > HEH[EHP] > Cyanex 572. Hence, HOPO competition with the extractants follows the order: Cyanex 301 GN < HDEHP < HEH[EHP] < Cyanex 572. The results obtained here show that HOPO has a higher affinity for  $\text{An}^{3+}$  ions than  $\text{Ln}^{3+}$  ions as most extraction fractions of  $\text{Am}^{3+}$  are lower than those of  $\text{Gd}^{3+}$  (except for the Cyanex 301/HOPO combination due to the specificity of this extractant, *vide infra*). In the absence of HOPO, nearly all trivalent ions are extracted by the five tested extractants, and thus no practical separation is observed under the tested conditions (Figure 4). Once HOPO is added to the liquid–liquid extraction system, the SF values increase even for Cyanex 301, while this pH is not optimal for this particular extractant (Supplementary Figure S1). The SF values with HDEHP/HOPO combination gradually increase as the HOPO concentration increases (Figure 4C). A HOPO concentration of 1 mM was selected for HDEHP to ensure



**Figure 5.** Influence of the HOPO concentration in (A) the aqueous phase and (C) the phase volume ratio on Cyanex 301 GN extraction of Gd<sup>3+</sup> (round solid line) and Am<sup>3+</sup> (square solid line); (B, D) corresponding distribution ratios and separation factors (triangle dashed line). [Cyanex 301 GN] = 0.5 M in kerosene;  $V_o/V_a = 1$ ; pH =  $3.55 \pm 0.05$ ;  $I = 1$  M.



**Figure 6.** (A) Extraction fraction of Gd<sup>3+</sup> and An<sup>3+</sup> using Cyanex 301 GN (black bars, [Cyanex 301 GN] = 0.5 M in kerosene, pH = 3.6, [HOPO] = 0.1 mM,  $V_o/V_a = 1$ ,  $I = 1$  M) and HDEHP (pink bars, [HDEHP] = 0.5 M in kerosene pH = 1.5, [HOPO] = 1 mM,  $V_o/V_a = 1$ ,  $I = 1$  M); (B) corresponding distribution ratios (bars) and separation factors between Gd<sup>3+</sup> and An<sup>3+</sup> (triangle solid points) using Cyanex 301 GN (black) and HDEHP (pink).

optimal separation, while that of Cyanex 301 GN is discussed hereafter since its optimal pH range is 3.5–4 instead of 1.5.

**Optimal Conditions for Ln<sup>3+</sup>/An<sup>3+</sup> Separation.** For a robust separation process, the SF should be no smaller than  $10^7$  and the results described above show that both Cyanex 301 GN and HDEHP yield SF values greater than 10 in the presence of HOPO. It should be noted that 3,4,3-LI(1,2-HOPO) is just a model compound of the HOPO family, and it was not initially developed for separation purposes; thus, even more selective HOPO derivatives are likely to be developed in the future. For the combination HDEHP/HOPO, as detailed above (Figures 1–4), the best separation performances are obtained at pH 1.5 with 1 mM HOPO and for  $V_o/V_a = 1$ . For Cyanex 301 GN, the Gd<sup>3+</sup>/Am<sup>3+</sup> separation has been optimized at pH 3.6. The influence of the HOPO concentration and the phase volume ratio  $V_o/V_a$  on the extraction of Gd<sup>3+</sup> and Am<sup>3+</sup> in the system HOPO/Cyanex 301 GN are displayed in Figure 5. As mentioned above, this

extraction formulation allows for the preferential extraction of Am<sup>3+</sup> over Gd<sup>3+</sup> under all the conditions tested. The HOPO/Cyanex 301 GN system therefore offers a remarkable opportunity to develop the reverse-TALSPEAK processes. The optimal conditions for this system are 0.1 mM HOPO and  $V_o/V_a = 1$ .

**Separation of Gd from Am, Cm, Bk, and Cf.** The optimized conditions determined above were used to test the performance of the HOPO/Cyanex 301 GN and HOPO/HDEHP extraction systems for the separation of Gd from Am, Cm, Bk, and Cf. As shown in Figure 6, for both HOPO/extractant systems, the extraction trend along the actinide series is as follows: Am  $\approx$  Cm > Bk  $\approx$  Cf. The decrease in extraction fraction from Am<sup>3+</sup> and Cm<sup>3+</sup> to Cf<sup>3+</sup> is consistent with recently reported DFT-calculated free energies of complexation of [AmHOPO]<sup>-</sup>, [CmHOPO]<sup>-</sup>, and [CfHOPO]<sup>-</sup> that showed almost identical stability of the Am<sup>3+</sup> and Cm<sup>3+</sup> complexes and a slightly higher stability of the Cf<sup>3+</sup>

complex.<sup>38</sup> Extraction fractions for Bk were far lower than for Am<sup>3+</sup> and Cm<sup>3+</sup>. This is consistent with oxidation of Bk<sup>3+</sup> to Bk<sup>4+</sup> under the tested conditions and in line with our recent discovery of the HOPO-mediated stabilization of Bk<sup>4+</sup> in aqueous solutions due to the extreme affinity and selectivity of this chelator for tetravalent cations.<sup>23,39</sup> The Cyanex 301 GN/HOPO formulation is selective for Am<sup>3+</sup> and Cm<sup>3+</sup> against Gd<sup>3+</sup> but does not segregate Gd<sup>3+</sup> from Bk<sup>4+</sup> and Cf<sup>3+</sup> because of the low extraction yields for Bk<sup>4+</sup> and Cf<sup>3+</sup>. Of note, the SF values between Am<sup>3+</sup> and Cm<sup>3+</sup> and between Bk<sup>4+</sup> and Cf<sup>3+</sup> are relatively low, highlighting the difficulty of separating adjacent transplutonium elements under those conditions (SF<sub>Am/Cm</sub> = 2.2 and SF<sub>Cf/Bk</sub> = 2.4). The HDEHP/HOPO combination was also found to be selective in Gd<sup>3+</sup>/Am<sup>3+</sup> separation (Figure 6), with a resulting SF<sub>Gd/Am</sub> value slightly lower than that of the TALSPEAK process but at a higher acidity (pH 1.5) and therefore appealing for industrial applications.

## CONCLUSIONS

A new class of water-soluble ligands with hydroxypyridinone binding units have been evaluated for Ln/An separation in TALSPEAK-like configurations. The model compound 3,4,3-LI(1,2-HOPO) was coupled with several industry-relevant organic extractants for the separation of Gd and four transplutonium elements (Am, Cm, Bk, and Cf). Two extractants with the highest separation performance were selected, and three physicochemical parameters (pH, HOPO concentration, and phase volume ratio) were optimized to give the best separation. The Cyanex 301 GN/HOPO and HDEHP/HOPO combinations have opposite separation behaviors. Cyanex 301 GN/HOPO preferentially extracts the actinides into the organic phase, while HDEHP/HOPO preferentially extracts Gd<sup>3+</sup>, providing two different approaches for Ln/An separation. The optimized separation factors attained between Gd<sup>3+</sup> and Am<sup>3+</sup> are 50 and 30, respectively, using Cyanex 301 GN and HDEHP. The results using HDEHP are comparable to those of the TALSPEAK process but at a much lower pH (1.5 instead of 3.0–4.5), which is preferable since it eliminates the need for a pH buffer and is more compatible with the highly acidic upstream steps. The separation factors between other actinides and Gd<sup>3+</sup> have also been measured with SF<sub>Am/Gd</sub> = 50, SF<sub>Cm/Gd</sub> = 23, SF<sub>Bk/Gd</sub> = 1.4, and SF<sub>Cf/Gd</sub> = 3.2 for Cyanex 301 GN and SF<sub>Gd/Am</sub> = 30, SF<sub>Gd/Cm</sub> = 8.5, SF<sub>Gd/Bk</sub> = 273, and SF<sub>Gd/Cf</sub> = 773 for HDEHP. This first investigation shows that HOPO chelators are promising candidates for further developments in actinide/lanthanide separation. Future studies are therefore warranted and will aim at characterizing these systems more in depth by probing a variety of phenomena and parameters such as extraction kinetics, influence of organic extractant concentration and purity, influence of nitrate ion concentration, susceptibility of HOPO ligands toward radiolysis, differences among cations from the whole lanthanide series, system behavior as metal concentrations are increased, etc.

## EXPERIMENTAL METHODS

**Caution!** All isotopes used in this study, <sup>153</sup>Gd ( $t_{1/2}$  = 240.4 d,  $3.5 \times 10^3$  Ci/g), <sup>243</sup>Am ( $t_{1/2}$  = 7388 y, 0.2 Ci/g), <sup>248</sup>Cm ( $t_{1/2}$  =  $3.49 \times 10^5$  y,  $4.2 \times 10^{-3}$  Ci/g), <sup>249</sup>Bk ( $t_{1/2}$  = 330 d,  $1.6 \times 10^3$  Ci/g), and <sup>249</sup>Cf ( $t_{1/2}$  = 351 y, 4.1 Ci/g), are hazardous and radioactive materials with high specific radioactivities and

should be handled only in specifically designated facilities in accordance with appropriate safety controls.

**Chemicals.** HOPO was procured from Ash Stevens, Inc. (Detroit, MI). <sup>153</sup>Gd was acquired as GdCl<sub>3</sub> in 1 M HCl from Eckert and Ziegler Isotope Products (Valencia, CA). An <sup>243</sup>Am<sup>3+</sup> stock solution was prepared by dissolving <sup>243</sup>Am<sub>2</sub>O<sub>3</sub> (Lawrence Berkeley National Laboratory inventory, Berkeley, CA) in 1 M HNO<sub>3</sub>; <sup>248</sup>CmCl<sub>3</sub> (95.78% <sup>248</sup>Cm, 4.12% <sup>246</sup>Cm, 0.06% <sup>245</sup>Cm, and 0.02% <sup>244</sup>Cm/<sup>247</sup>Cm isotopic distribution by atom percentage), <sup>249</sup>BkCl<sub>3</sub>, and <sup>249</sup>CfCl<sub>3</sub> were purchased from the National Isotope Development Center at Oak Ridge National Laboratory (Oak Ridge, TN) and dissolved in 0.1 M HCl. HNO<sub>3</sub> (6 M) was purchased from VWR Chemicals BDH, HNO<sub>3</sub> (0.1 M) from EMD Millipore Corp. (Billerica, MA), HCOOH from Sigma-Aldrich Co. LLC (St. Louis, MO), NaNO<sub>3</sub> with >99% purity from Alfa Aesar (Ward Hill, MA), NaOH with ≥97% purity from Sigma-Aldrich Co. LLC (St. Louis, MO), kerosene from Alfa Aesar (Heysham, U.K.), and Ultima Gold from Perkin Elmer Inc. (Waltham, MA). All extractants detailed below were used as received. HDEHP with ≥95% purity was purchased from EMD Millipore Corp. (Billerica, MA) and HEH[EHP] with 97% purity from Sigma-Aldrich Co. LLC (St. Louis, MO). Cyanex 301 GN (68–72% R<sub>2</sub>PSSH, 18–22% petro distillate, 5–7% R<sub>3</sub>PS, and 1–2% R<sub>2</sub>P(=S)OH), Cyanex 572 (30–60% (2-ethylhexyl)-ester phosphonic acid, and 40–70% organophosphorus), and ACORGA M5640 (50% 5-nonylsalicylaldehyde oxime, modified with 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB)) were kindly supplied as test samples by Cytec Industry Inc. (Princeton, NJ). Two other extractants, Versatic Acid 10 (carboxylic acids) and 2-thenoyltrifluoroacetone (TTA), were also tested. The preliminary results (not shown) indicated that Versatic Acid 10 has virtually no extraction capability at the working pH range and TTA has severe salting-out effects, making them impractical for this study, and thus no further discussion will be presented on them.

**Liquid–Liquid Extraction Procedures.** The following conditions were kept consistent for all experiments except where otherwise noted: (i) all extractants were fixed at 0.5 M in kerosene; (ii) sodium nitrate (1 M) was used to keep the ionic strength constant; (iii) formic acid (50 mM) was used as the buffer for pH 3–4 and acetic acid (50 mM) for pH 4.5–5; (iv) all experiments were performed at ambient temperature (25 °C); (v) contact time was 1 h; and (vi) experiments were done in triplicate. Each extraction consisted of the following three steps: (i) Conditioning: the organic phase was contacted with the aqueous phase (phase volume ratio, defined as the organic-to-aqueous volume ratio,  $V_o/V_a = 1$  for pH-dependence studies and  $V_o/V_a = 0.5$  for the rest studies), which contained every component but metal ions, and shaken to reach equilibrium. (ii) Extraction: a volume of 2 μL (maintained at this level to minimize the possible effects of extractant loading) radiotracer was pipetted into 398 μL of aqueous phase, the pH was determined, and 400 μL of conditioned organic phase was contacted with the aqueous phase and shaken for 60 min. Several tests were performed to investigate the influences of pH, phase volume ratio, and HOPO concentration; and (iii) Counting: the contacted two phases were separated by centrifugation (5 min at 3000 rpm), and a volume of 100 μL was aliquoted out of each phase into a scintillation vial with 10 mL of scintillation cocktail (Ultima Gold, Perkin Elmer, Shelton, CT) for liquid scintillation analysis (Packard Tri-Carb model B4430, Perkin Elmer).



**Data Interpretation.** Three parameters were used to characterize the extraction performance, distribution ratio ( $D$ , eq 1) in terms of radioactivity ( $A$ ) with the unit of counts per minute (cpm), extraction fraction ( $E$ , eq 2) calculated from  $D$  and the phase volume ratio  $V_o/V_a$ , and separation factor (SF, eq 3):

$$D_M = \frac{[M]_{\text{tot,org}}}{[M]_{\text{tot,aq}}} = \frac{\left(\frac{N}{V}\right)_{\text{tot,org}}}{\left(\frac{N}{V}\right)_{\text{tot,aq}}} = \frac{\left(\frac{A}{\lambda V}\right)_{\text{org}}}{\left(\frac{A}{\lambda V}\right)_{\text{aq}}} \xrightarrow[\text{same isotope}]{\text{same isotope}} D_M$$

$$= \frac{A_{\text{org}}}{A_{\text{aq}}} \quad (1)$$

$$E = \frac{D_M}{D_M + V_a/V_o} = \frac{1}{1 + \frac{1}{D_M(V_o/V_a)}} \in [0, 1] \quad (2)$$

$$SF_{M_1/M_2} = \frac{D_{M_1}}{D_{M_2}} \quad (3)$$

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c00873>.

Distribution ratios for  $Gd^{3+}$  and  $Am^{3+}$  and corresponding separation factors as a function of phase volume ratio and HOPO concentration for Cyanex 301 GN and HEH[EHP] extraction (PDF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical

Sciences, Geosciences, and Biosciences Division at the Lawrence Berkeley National Laboratory under Contract DE-AC02-05CH11231. R.J.A. also acknowledges support from the Nuclear Regulatory Commission under Faculty Development Grant NRC-HQ-84-14-G-0052.

## ■ ABBREVIATIONS

An	actinides
ALSEP	minor actinide lanthanide separation process (ALSEP)
BTP	2,6-bis(1,2,4-triazin-3-yl)pyridine
CEA	French Atomic Energy Commission
DIAMEX	diamide extraction
DTPA	diethylenetriaminepentaacetic acid
DPA	dipicolinic acid
GANEX	group actinide extraction
HEDEHP	di-(2-ethylhexyl)phosphoric acid
HEDTA	ethylenediaminetetraacetic acid
HEH[EHP]	2-ethylhexylphosphonic acid mono-2-ethylhexyl ester
HLLW	high-level liquid waste
HOPO	3,4,3-LI(1,2-HOPO)
ITU	Institute for Transuranium Elements
Ln	lanthanides
PUREX	plutonium uranium redox extraction
SANEX	selective actinide extraction
TALSPEAK	trivalent actinide lanthanide separation with phosphorus-reagent extraction from aqueous complexes
TODGA	<i>N,N,N',N'</i> -tetraoctyl diglycolamide
TTHA	triethylenetetraminehexaacetic acid
T2EHDGA	<i>N,N,N',N'</i> -tetra-2-ethylhexyl diglycolamide

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