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COMMUNICATION

Extraction of Lanthanides Using 1-hydroxy-6-N-octylcarboxamido-2(1H)-pyridinone as an Extractant via Competitive Ligand Complexations Between Aqueous and Organic Phases

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The ability to selectively extract lanthanides is crucial in hydrometallurgy and the nuclear fuel cycle. The capabilities of 1-hydroxy-6-N-octylcarboxamido-2(1H)-pyridinone (octyl-HOPO) as an extractant for the separation of lanthanides and actinides was studied for the first time. Octyl-HOPO greatly outperformed the traditional ligand di-2-ethylhexyl phosphoric acid (DEHPA).

Lanthanides are ubiquitous and indispensable in many modern-day scientific applications.^{1,2} They are used extensively in green energy technologies, modern electronics, and advanced weapon systems. With continuous implementation and integration of new technologies in modern society, the demand for lanthanides will continue growing, making it necessary to develop more efficient means of producing and enriching large quantities of lanthanides.³⁻⁵ The development of new methods for the selective separation of the lanthanides (Ln) from other metal ions as well as specific lanthanides has been a topic of great interest in the separation sciences.⁶⁻¹² The ability to selectively separate lanthanides from other metals has additional application in the nuclear fuel cycle as it could further improve the separation of trivalent Ln from trivalent actinides (An), specifically americium(III). The separation processes for the lanthanide fission products from trivalent actinides are arduous due to the similarities in their charge state and size. Traditional solvent extraction (SX) methods are not highly selective for lanthanides, meaning numerous extraction stages are necessary to effectively extract Ln, making processes very inefficient and cost-prohibitive.

The trivalent actinide–lanthanide separations by phosphorous-reagent extraction from aqueous complexes (TALSPEAK) process was developed 50 years ago.^{13,14} The aim of the TALSPEAK process was to enhance the selectivity toward lanthanides over transuranics present in the post TRUEx waste stream.¹⁵⁻¹⁸ The essence of

TALSPEAK lies in utilizing a common ligand, diethylenetriamine pentaacetic acid (DTPA), as a holdback reagent to complex more favourably with actinides over lanthanides. The selectivity of DTPA for actinides in the presence of lanthanides makes it possible to separate Ln from An by extracting the Ln using solvent extraction in combination with high concentrations of organophosphate ligand DEHPA present in the organic solvent diisopropylbenzene (DIPB). This competitive complexation by DTPA in the aqueous phase and by DEHPA in the organic phase is the key to breaking the linear dependence of the extraction efficiency on $1/r(\text{REE radius})$ and achieving the selective extraction of Ln over An. Some of the major disadvantages associated with the TALSPEAK process are (a) low extraction efficiency, (b) high concentrations of DEHPA, (c) susceptibility to a third phase formation, and (d) loss of buffering reagents to the organic phase. All of these drawbacks in the TALSPEAK process are interconnected. For example, the low extraction efficiency demands the use of the higher DEHPA concentrations in the solvent. The increased concentrations of DEHPA can lead to the formation of a third phase during extraction. Within the past decade researchers have looked into replacing DEHPA with other phosphate based extractants (e.g. HEH[EHP]) which is a weaker extractant.¹⁹⁻²¹ HEH[EHP] has more versatility as it can function over wider pH ranges and is not limited to traditional pH range of the TALSPEAK process (pH 3–4.5).¹⁷ Due to HEH[EHP] being a weaker extractant a larger concentration of it would be needed to increase the separation between Ln and An. To overcome these drawbacks that have become associated with traditional TALSPEAK based on phosphate extractants, we herein report a new variant of the TALSPEAK process which utilizes the highly selective ligand 1-hydroxy-6-N-octylcarboxamido-2(1H)-pyridinone (octyl-HOPO), which serves as a replacement for DEHPA. The core of octyl-HOPO, 1,2-HOPO has been studied extensively over the course of the past two decades.²²⁻²⁵ However, much of this research was focused on its use in chelation therapy for the removal of uranium and other actinides from biological systems.²⁵⁻²⁷ More complex ligands utilizing multiple 1,2-HOPO cores that have been linked together have been synthesized for possible MRI imaging agents and sequestering agents.²⁷⁻³¹ Octyl-HOPO has many advantages over DEHPA, some of which include an increased selectivity and stronger binding to Ln. The increase in binding strength allows for a marked decrease in the concentration of the extractant needed to achieve the desired separation, making the

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new TALSPEAK process more effective for the separation of the Ln and An.

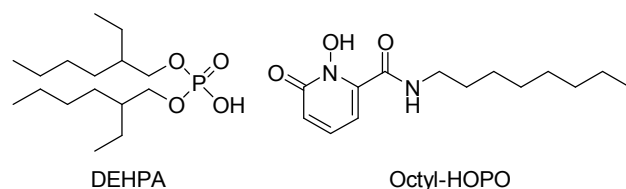


Fig. 1. Structure of DEHPA and its proposed replacement octyl-HOPO.

Octyl-HOPO has been demonstrated as an effective ligand and extractant for the selective complexation of lanthanides in traditional solvent extraction processes.^{29, 31, 32} Herein we report the first investigation and use of octyl-HOPO as a replacement for DEHPA in a TALSPEAK system for the separation of lanthanides. Non-TALSPEAK conditions (e.g. both with and without holdback reagents and/or buffers) were used to directly compare the extraction properties of octyl-HOPO across the lanthanide series.

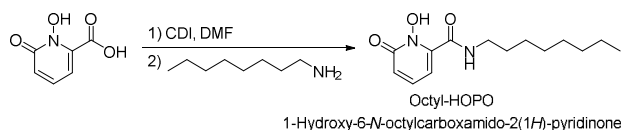


Fig. 2. Reaction scheme for 1-Hydroxy-6-N-octylcarboxamido-2(1H)-pyridinone (Octyl-HOPO).

Octyl-HOPO (Fig. 2.) was synthesized according to the modified literature procedure^{31, 32} and characterized by nuclear magnetic resonance (NMR) and mass spectrometry (MS) (see Supporting Information).

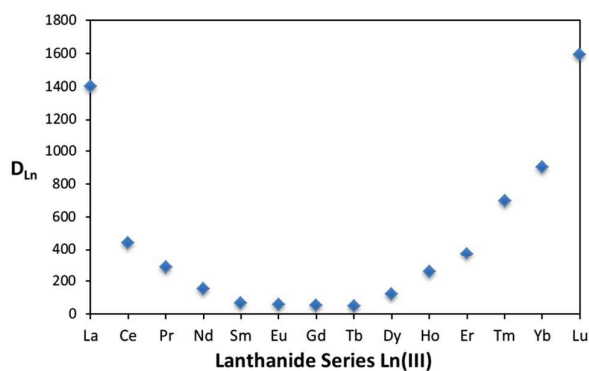


Fig. 3. Extraction results of the solvent extractions under TALSPEAK conditions (DTPA holdback and citric acid buffer). For extraction 20 mmol of octyl-HOPO was dissolved in diisopropylbenzene (DIPB). An organic-to-aqueous phase ratio (O:A) of 1 was used and the samples were mixed for 3 hrs. at 25 °C.

The results shown in Figure 3 and Table 1 confirm that octyl-HOPO is a stronger complexant for lanthanides compared to DEHPA. From the large distribution ratios for the lanthanides shown in Table 1, it is possible to stipulate that only a very small quantity of the ligand is needed to efficiently extract the lanthanides in a process. This

extraction behavior will minimize the extraction stages needed to achieve the desired separation, possibly lowering the costs of a process dramatically. Decreasing the concentration of the ligand will have additional benefits such as lowering the probability of forming a third-phase. The solubility of the ligand at lower concentrations also removes the need for a modifier, improving the hydraulics of the system and simplifying the system.

Table 1. Comparison of distribution ratios for octyl-HOPO (HOPO) and DEHPA utilizing TALSPEAK conditions.

Ln(III)	HOPO $D(\text{Ln})$	DEHPA $D(\text{Ln})$
La	1399.3	0.0444
Ce	441.8	0.0702
Pr	286.9	0.0980
Nd	152.8	0.1109
Sm	67.8	0.1131
Eu	56.9	0.1144
Gd	53.6	0.1062
Tb	46.3	0.1077
Dy	121.2	0.0980
Ho	258.3	0.0716
Er	371.5	0.0540
Tm	699.0	0.5439
Yb	904.6	3.8942
Lu	1592.3	7.3946

When non-TALSPEAK conditions (no holdback reagent) were used, the previous trend seen in Figure 3 for octyl-HOPO was no longer observed. Extraction of Ln(III) using the ligand develops a trend typical of extractants for the Ln(III), which is directly related to the size and acidity of the metal. The increased extraction efficiency of Ln with the octyl-HOPO over DEHPA can clearly be observed in Fig. 4.

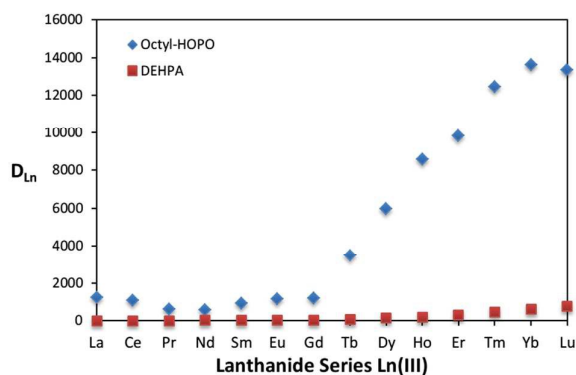


Fig. 4. Extraction results for the lanthanides in a citric acid buffer in the absence of the DTPA holdback reagent. For the extraction experiments 20 mmol of either octyl-HOPO or DEHPA dissolved in DIPB was used. An O:A of 1 was used and samples were mixed for 3 hrs. at 25 °C.

Once the extraction behavior of the lanthanides with octyl-HOPO was determined, the ligand's ability to separate Eu(III) from Am(III) was investigated with a direct comparison to DEHPA. The

concentrations of DEHPA and the ligand used in the experiments were kept equivalent so that a direct comparison could be made. The aqueous phase with four different DTPA concentrations was used respectively during the experiment to study the effect of the holdback reagent (DTPA) would have on the extraction behavior of the octyl-HOPO and DEHPA. The extraction of Eu and Am were monitored using radiotracers Eu-152/154 and Am-241. The results from these experiments are shown in Table 2. The ligand has higher affinity for both Eu and Am compared to DEHPA at all four DTPA concentrations. There is a noticeable decrease in the extraction of the Am(III) by octyl-HOPO as the concentration of DTPA is increased, resulting in a 40-fold decrease in the extraction of Am(III). The dramatic decrease in the extraction of the Am(III) compared to Eu(III) is the main reason for the increased separation factor (SF) between the two. The SF for DEHPA is the inverse of octyl-HOPO with large SFs at low concentrations of holdback reagents that decrease as the DTPA concentration is increased. Although the DEHPA has a large SF at 0.005 M DTPA, this result is most likely due to DEHPA's inability to compete with the holdback reagent. The statement is supported by the fact that the distribution ratios for both Eu and Am decrease dramatically as the DTPA concentration increased.

Table 2. Effects of DTPA on Am/Eu separation under TALSPEAK condition using 0.5 M lactic acid as a buffer.

[DTPA]	Octyl-HOPO			DEHPA		
	D_{Eu}	D_{Am}	$SF_{Eu/Am}$	D_{Eu}	D_{Am}	$SF_{Eu/A}$
M						
0.005	4363.8	507.9	8.59	4.0×10^{-2}	1.2×10^{-3}	34.06
0.01	301.5	21.62	13.95	7.5×10^{-2}	1.4×10^{-3}	55.22
0.05	217.9	10.11	21.55	4.6×10^{-3}	8.0×10^{-4}	5.559
0.1	293.5	12.50	23.48	3.4×10^{-3}	5.0×10^{-4}	7.142

In summary, these results lead us to conclude that octyl-HOPO has great versatility for the separation of lanthanides and is a viable replacement for DEHPA in the TALSPEAK process. The extraction efficiency of octyl-HOPO is considerably higher than that of DEHPA under the TALSPEAK conditions. Presently, we are synthesizing more lipophilic HOPO ligands possessing either longer alkyl groups that are branched or multiple alkyl chains of the amide (e.g. di-*n*-octyl). Further studies are currently underway to determine the extraction properties of octyl-HOPO in less common organic diluents (e.g. ionic liquids). We feel that these experimental results reported and discussed in this work represent class of extractants for REEs that function as cation exchangers and are stronger than DEHPA and other commonly used phosphorous-based extractants.

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