Sulfur Donating Extractants for the Separation of Trivalent Actinides and Lanthanides

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Abstract:

The effective separation of trivalent actinides and lanthanides is capable of reducing the long term radiation hazard associated with used nuclear fuel. This class of separation exploits the tendency of ligands containing large and polarizable soft donor atoms to preferentially bind to the trivalent actinides instead of the lanthanides. Among the soft donors, nitrogen and sulfur based ligands have received the most attention with sulfur donors generally having greater selectivity for the actinides. Herein, the speciation, mechanism, and selectivity for the extraction of lanthanides and actinides from aqueous media into an organic phase by various sulfur containing extractants is reviewed.

Graphical Abstract

Keywords: Solvent extraction, Lanthanide, Actinide, Soft donors, Separations, Sulfur

Highlights:

- Synthesis and extraction mechanisms of sulfur donating extractants.
- Speciation of actinide and lanthanide complexes in solvent extraction.
- Collection of Am/Eu separation factors for assorted dithiophosphinic acids.

Abbreviations:

SF, separation factor; D, distribution ratio; CMPO, carbamoylmethylphosphine oxide; TRUEX, transuranic extraction; CMPS, carbamoylmethylphosphine sulfide; XRD, x-ray diffraction; HDEHP, bis-(2-ethylhexyl)phosphoric acid; HDEHTP, bis-(2-ethylhexyl)monothiophosphoric acid; HDEHDTP, bis-(2-ethylhexyl)dithiophosphoric acid; TBP, tributyl phosphate; HC302, bis(2,4,4-trimethylpentyl)monothiophosphinic acid HC301, bis(2,4,4-trimethylpentyl)dithiophosphinic acid; FS-13, phenyltrifluoromethylsulfone; DFT, density functional theory; HC302, bis-(2,4,4-trimethylpentyl)monothiophosphinic acid; HC272, bis-(2,4,4-trimthylpentyl)phosphinic acid; SANS, small angle neutron scattering; XAFS, extended x-ray absorption fine structure; TPP, triphenylphosphate; DPSO, diphenylsulfoxide; T*t*BP, tri-*tert*-butyl phosphate; TOPO, trioctylphosphine oxide; HTTA, thenoyltrifluoroacetone; TBPS, tri-*iso*-butylphosphine sulfide; HSTTA, thiothenoyltrifluoroacetone.

Contents

1. Introduction

The significant and scalable approach for actinide/lanthanide group separations centers on the principle that actinides may be able to interact more strongly with soft donors, such as chloride, nitrogen and sulfur, relative to lanthanides of comparable charge density. This is most broadly explained on the basis of Pearson's Hard Soft Acid Base chemistry, where softer, more polarizable metals interact preferentially with softer, more polarizable ligand donors [1]. This stronger interaction with soft donors was first discovered by Street and Seaborg by examining the preferential interaction of chloride and americium relative to lanthanides, such as promethium [2]. The stronger interaction between actinides and soft donors relative to the lanthanides is generally thought to be caused by the actinides increased ability to interact more covalently with soft donors [3]. Although heavy actinides were long thought to lack any covalency due relativistic effects encouraging the contraction of the 5f orbitals within the core electronic structure, [4] recent work with berkelium, californium and einsteinium show their ability to bond with some degree of covalency with dipicolinic acid [5–8] and borates [7,9–11].

The origins of the actinide covalency in the literature are frequently debated, as is the extent to which covalency is responsible for controlling trivalent actinide/lanthanide group separations. An emerging idea is that, due to the multiplicity of available orbitals and varying orbital energies across the actinide series, the specifics of actinide-ligand covalency are likely dependent on the given actinide and ligand involved [5-9,11]. This idea more closely mirrors transition metal chemistry, where a given metal-ligand pairing can show unique chemistry across a series of 5f elements. A general class of separations that has limited review in the literature are those based on sulfur-actinide interactions.

While separations centering on selective sulfur-actinide interactions are demonstrated to be the most efficient single-stage trivalent lanthanide-actinide separations, sulfur has generally received little attention relative to nitrogen donating ligands [5,12–20]. Some of this lack of attention is due to complications arising from sulfur contamination in high-level waste streams, [21] the poor radiation resistance of sulfur ligands, [22,23] and the difficulty of extractant synthesis and purification [24–26]. Despite these potential issues, sulfur containing ligands provide remarkably high separation factors that could be utilized in more efficient separation processes than nitrogen based separations [25–28]. Bis(2,4,4-trimethylpenthy)dithiophosphinic acid, Cyanex 301 (HC301) in Figure 1, has reported separation factors between Am and Eu, $\mathrm{SF}^{\mathrm{Am}}_{\mathrm{Eu}} = \mathrm{D}_{\mathrm{Am}}/\mathrm{D}_{\mathrm{org}}$ where $\mathrm{D}_{\mathrm{M}} = [\mathrm{M}]_{\mathrm{org}}/[\mathrm{M}]_{\mathrm{aq}}$, of greater than 5,000 [28]. See Section 3 for a more complete description. Trifluoromethyl substituted aryl dithiophosphinates have the highest $\mathrm{SF}^{\mathrm{Am}}_{\mathrm{Eu}}$ever reported using any approach at greater than 100,000 [25]. More explanation regarding separation factors and distribution ratios, D, is provided in Section 3 (*vide infra*). The purpose of this review is to summarize the work done with various sulfur containing ligands for the separation of actinides from lanthanides.

2. Origin of Selectivity

The preference that soft donors have for actinides over lanthanides is thought to stem from greater covalency encouraging shorter and stronger actinide-soft donor bonds, though reports exist that suggest some covalent actinide-ligand interactions have longer, weaker bonds [29]. It has been shown that U(III) and Pu(III) both form shorter bonds with sulfur than with lanthanides of nearly the same ionic radii, La(III) and Ce(III) when using thiophosphorylphosphinothioic amides, $N(SPR_2)_2$, (R = Ph, *i*Ph, and H) [13] and arylthiolate ligands [30]. In computational modelling of the same complexes, the shorter bond lengths were also observed an interpreted to indicate increased covalency [13,30]. Although complexes of thiophosphorylphosphinothioic amides with both U(III) and Pu(III) showed shorter bond lengths than with similar lanthanides, the Pu-S bond length, although shorter than the U-S bond, was not a short as expected based on the different crystallographic radii of U and Pu. Therefore, it was concluded that the Pu-S interactions had a degree of covalence intermediate between that of the U-S bonds and the lanthanide-S bonds [13]. This lead Gaunt et al. to conclude that the light actinides bond more covalently with sulfur, but this effect decreases along the series, possibly terminating at Am or Cm [13].

This hypothesis has been difficult to test as only small amounts of the actinides heavier than Pu are available and their high specific activities make them challenging to handle. Another consequence of the high specific activity of transuranic actinides is the damage to crystal structures by self-irradiation. Despite the associated challenges, single crystals of $(NBu_4)Am[S_2P(t\mathrm{Bu}_2C_{12}H_6)]_4$ have been synthesized and analyzed along with the analogous Nd and Eu crystals [31]. Single crystal XRD has shown that the Am-S bond (2.921(9) Å) is shorter than with Nd (2.941(8) Å), a lanthanide with a similar ionic radius [31]. Although the uncertainty at the 68% confidence interval associated with these measurements makes it difficult to say with confidence that Am and Nd have different metal-sulfur bond lengths, UV-vis spectroscopy and luminescence spectra of the same crystals show that for Am, the ligand field has a far greater influence on the metal's electronic structure, as reflected in the f-f electronic transitions, than for either Nd or Eu [31]. In crystals of Am, Cm, and Cf dithiocarbamates, the heavier actinides showed shorter metal-sulfur bonds than the similarly sized lanthanides when accounting for changes in the metal's ionic radii [32]. This suggests Am and heavier actinides have greater interactions with soft, sulfur donating ligands than lanthanides. The greater interactions of sulfur donating ligands with the actinides may manifest as stronger bonds and different speciation that may enable an effective method of separating lanthanides and actinides.

The selectivity that the above sulfur donors display towards actinides is thought to be due to the ability of actinides to bond more covalently than lanthanides. The source of this greater covalency is thought to arise from energy degeneracy or orbital overlap between the metal and ligand or some combination of both [33]. Density functional theory (DFT) experiments have shown that the 5f orbitals of Am overlap with orbitals in dithiophosphinic acids in a bonding manner while the same ligand orbitals are antibonding to the 4f orbitals of Eu [34,35]. Across the heavy actinides, covalency was found to increase as due to greater energy degeneracy between the actinides and dithiophosphinic acid [36]. Additional DFT studies have shown that the bonding of a dithiophosphinic acid to Am is energetically more favorable than bonding with Eu [37,38].

The more favorable bonding of dithiophosphinic acid to Am than Eu has not only suggests the formation of stronger bonds, but also brings the possibility of different speciation for lanthanides and actinides. Bhattacharyya et al. found that with HC301, Am would form complexes of the form $Am(C301)_3$ whereas Eu could form two complexes $Eu(C301)_3$ and $Eu(C301)_2(NO_3)$ [38]. These differences between lanthanides and actinides can cause selectivity in an extraction system due to the greater extractability of the actinide [36,37] or differences in the speciation of the metals that have different extractabilities in the organic phase [38].

3. Sulfur Donating Extractants

Many different types of sulfur containing extractants have been studied for their application in the organic phase of a liquid-liquid extraction system. Sulfur containing extractants would preferentially extract actinides to the organic phase while the lanthanides primarily remain in the aqueous phase. Systems that use sulfur containing extractants are already used industrially for the separation of cobalt and nickel from magnesium and manganese [39]. These extractants have yet to be developed into a technologically feasible means for the separation of lanthanides and actinides. Lab scale experiments have shown great promise regarding the selectivity of sulfur donor extractants in actinide/lanthanide separation, but barriers to their implementation due to the limited chemical and radiolytic stability of the extractants and the impact of sulfate, a decomposition product, on waste processing remain [21].

Two main mechanisms exist by which these extractants function, solvation and cation exchange. Solvating extractants are neutral, polar molecules that solvate metal ions in the organic phase when the metal is bound by the appropriate anions to maintain a neutral charge [40]. Solvating extractants usually extract most efficiently at higher acid concentrations and metals can be stripped from them at low acid concentrations [40]. Cation exchange extractants have acidic functional groups capable of exchanging a hydrogen ion initially bound to the extractant in the organic phase with a metal ion from the aqueous phase [40]. Unlike solvating extractants, cation exchange extractants extract most strongly at low acid conditions and can be stripped at high acid concentrations [40].

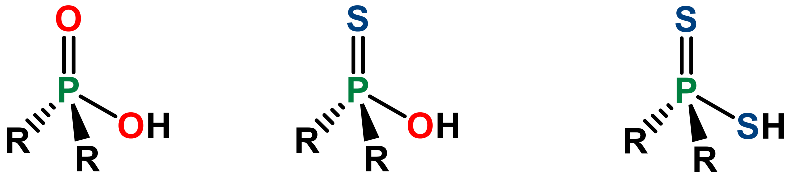
Synergism can occur when a mixture of extractants is used and the resulting extraction of the metal is greater than the summed metal recovery by each individual extractant, at the same concentration. Although synergism is a complex process, several mechanisms exist through which synergistic extraction can occur [41,42]. Synergism can be caused by the opening of a chelate ring and the addition of a lipophilic adduct on the newly vacant site, the replacement of coordinated waters with a more lipophilic group, or an increase in the coordination number of the metal ion allowing additional lipophilic molecules to bond to the complex [41,42]. Additionally, the addition of a synergic agent can alter other aspects of the extraction system by causing changes in interfacial properties, or effecting aggregation and micelle formation [41].

In liquid-liquid extractions, the amount of metal extracted is quantified by the distribution ratio (D). The distribution ratio is defined as the concentration of analyte in the organic phase divided by the concentration of analyte in the aqueous phase, as shown in Equation 1. When extracting radioactive materials, the radioactivity of each phase is often substituted for the concentration as radioactivity is proportional to the concentration and is typically easier to measure than the concentration. To quantify the efficacy of a separation using liquid-liquid extraction, the separation factor (SF) is evaluated. The separation factor is the ratio of the distribution ratios of the species being separated as shown in Equation 2. In this paper, the distribution ratio of the actinide is the numerator while the ratio for the lanthanide is the denominator. Therefore, a SF greater than unity indicates that actinides are extracted more readily than lanthanides and a separation factor of one indicates no separation.

$$D = \frac{[M]_{org}}{[M]_{aq}} = \frac{A_{org}}{A_{aq}} \tag{1}$$

$$SF_{An/Ln} = \frac{D_{An}}{D_{Ln}} \tag{2}$$

Among the many types of sulfur bearing extractants, a general trend is found. When comparing phosphinic, monothiophosphinic, and dithiophosphinic acids, the extraction strength decreases with increasing sulfur in the extractant, but the separation factor increases in the same order. This is true for phosphoric and phosphonic acids as well [43–45].



phosphinic acid (1) monothiophosphinic acid (2) dithiophosphinic acid (3)

Figure 1: Phosphinic (1), monothiophosphinic (2), and dithiophosphinic acid (3) functional groups [45].

3.1 Carbamoylmethylphosphine sulfide

Carbamoylmethylphosphine oxides (CMPO) have been widely studied for their ability to non-selectively extract the trivalent lanthanides and actinides from highly acidic media as in the transuranic extraction (TRUEX) process. Since the actinides show a preference for soft donors, Matloka et al. studied softer, sulfide versions of CMPO, carbamoylmethylphosphine sulfide (CMPS) for the separation of lanthanides and actinides [46].

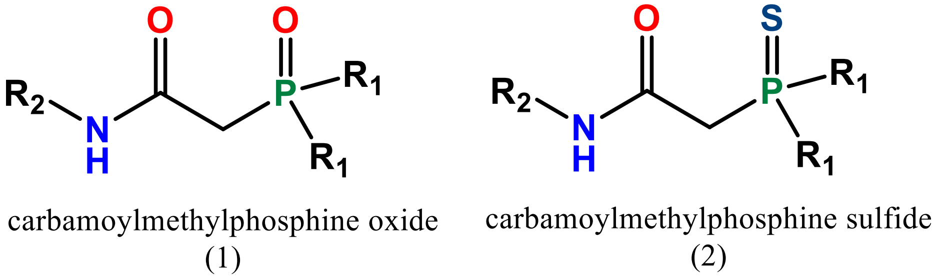
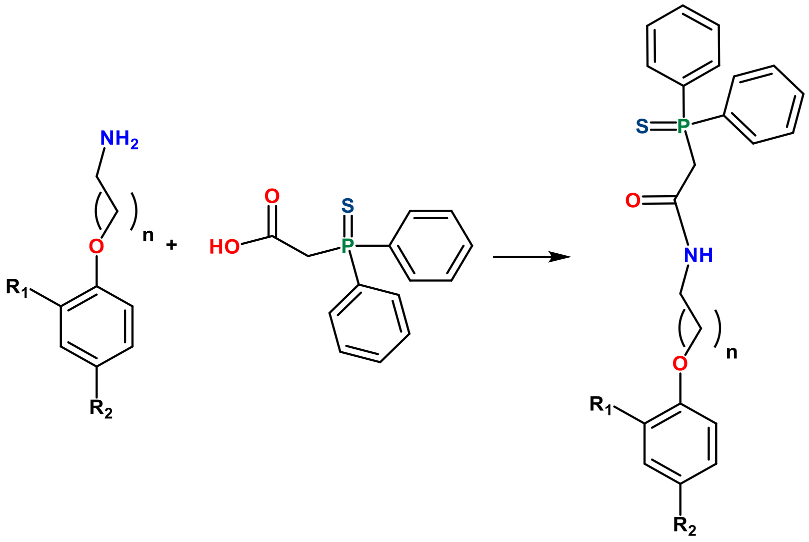


Figure 2: Structures of a generic carbamoylmethylphosphine oxide (1) and carbamoylmethylphosphine sulfide (2). R_1 = methyl, t-butyl, t-pentyl. R_2 = t-butyl, t-pentyl [46].

Matloka et al. prepared the various types of CMPS they used by the condensation of 2-(diphenylphosphorothioyl)acetic acid with the appropriate amine containing substituent as shown in Scheme 1 [46].



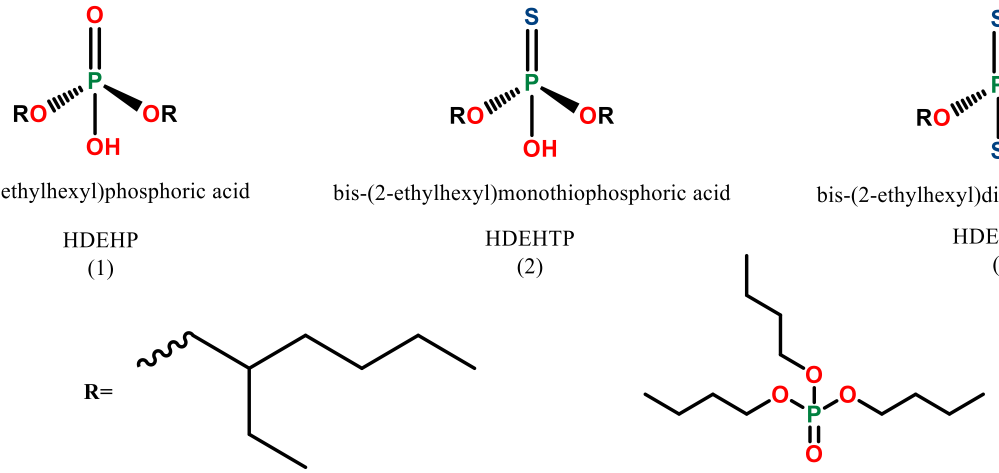
Scheme 1: Synthetic procedure for the preparation of CMPS [46]. As tested, R_1 and R_2 were combinations of methyl, *t*-butyl, and *t*-pentyl groups and n=1,2 [46].

All CMPS varieties are solvating extractants. They were found to extract lanthanides and americium poorly from 1 M nitric acid with no measurable separation in distribution experiments with ^{241}Am and ^{152}Eu when CMPS was dissolved in methylene chloride - the only solvent tested [46]. Unlike typical experiments with CMPO, these systems did not include phase modifiers to improve the solubility of the extracted metal-ligand complex [41,47–50]. With CMPO, phase modifiers are used to prevent the formation of a third phase [41]. A third phase occurs when the single organic phase splits into two distinct organic phases, commonly due to a high concentration of metal ions or acid in the organic phase. It remains to be seen if third phases form as readily with CMPS as with CMPO. Additionally, when single crystals of the terbium CMPS complex were studied by XRD, no Tb-S bonding was seen [46]. Assessment of this system with phase modifiers might be appropriate, since these are crucial for metal extraction in the CMPO system.

Although the CMPS sulfide does not seem to interact with the lanthanides or actinides, CMPS has been shown to form metal-sulfur bonds with softer metals. Aleksenko et al. synthesized and studied several different CMPS and CMPO derivatives with Pd(II) and Re(I) [51]. Pd and Re both formed metal-sulfur and metal-oxygen bonds with the CMPS and the expected metal-oxygen bonds with CMPO [51].

3.2 Di- and mono- thiophosphoric acids

Di- and mono- thiophosphoric acids are the sulfur analogs of the widely used cation exchange extractant bis-(2-ethylhexyl)phosphoric acid (HDEHP). For this reason, the extractants bis-(2-ethylhexyl)monothiophosphoric acid (HDEHTP) and bis-(2-ethylhexyl)dithiophosphoric acid (HDEHDTP) have been the most studied extractants in this class.



bis-(2-ethylhexyl)phosphoric acid
HDEHP
(1)

bis-(2-ethylhexyl)monothiophosphoric acid
HDEHTP
(2)

bis-(2-ethylhexyl)dithiophosphoric acid
HDEHDTP
(3)

tributyl phosphate
TBP
(4)

Figure 3: Structure of HDEHP (1), HDEHTP (2), HDEHDTP (3), and TBP (4) [52].

Dithiophosphoric acids are typically synthesized by the reaction of phosphorus pentasulfide with the appropriate anhydrous alcohol [53,54]. Unfortunately, hydrogen sulfide evolves during the course of the reaction. This reaction is sensitive to moisture, as water will cause the formation of the triprotic inorganic acid instead of the desired monoprotic diester [53]. This sensitivity to water does complicate the synthesis, but reasonable yields can be achieved with the proper attention to reaction conditions.

Pattee et al. was one of the first groups to extract lanthanides and trivalent actinides with a thiophosphoric acid. They found that although HDEHDTP extracts Am and Eu far more weakly than HDEHTP, HDEHDTP gives larger separation factors (SF=2.55) than HDEHTP (SF=0.89) in nitric acid [52]. These separation factors were found to be consistent over a range of approximately pH 1.7 to 3.6 for HDEHDTP and 0.8 to 1.9 for HDEHTP [52]. HDEHP gives a separation factor of approximately 0.06 [55]. Xu et al. have confirmed these results in perchloric acid media, by observing the same trend in extractant efficiency and selectivity with HDEHDTP and HDEHTP [44]. They measured similar separation factors of 2.43 (pH 3.13) and 0.68 (pH 2.87) for HDEHDTP and HDEHTP respectively [44]. These separation factors are considerably lower than those for the dithiophosphinic acids discussed in Section 3.3. Small amounts of strongly extracting and non-selective impurities may be present, as was observed with some dithiophosphinic acids [56]. Pattee et al. also considered both fully protonated HDEHDTP in cyclohexane and fully saponified HDEHDTP (i.e. NaDEHDTP) in benzene and observed conventional extraction of Am and Eu in discrete HDEHDTP complexes whereas reverse micelles containing up to 25 water molecules per metal ion were observed for the saponified system [57]. It remains unclear as to whether metal is extracted as discrete complexes, reverse micelles; or some combination of both at intermediate degrees of saponification.

Extracted complex stoichiometry has been found through slope analysis experiments, where the distribution of the metal of interest is measured as a function of extractant concentration and pH. In these studies, one metal atom was found to be extracted by 3 HDEHDTP or HDEHTP molecules according to Equations 3 through 6 [52] and by 6 HDEHP according to Equations 7 and 8 [55]. The authors also suggest that some quantity of water is present in the extracted complex, [52] but do not report an attempt to quantify the number of water molecules in the complex. As HDEHTP is ambidentate, it is possible that it may coordinate metal ions with either the oxygen or sulfur site, or both. Although coordination of lanthanides by HDEHTP is unknown, it is plausible that the oxygen coordinates more strongly due to its greater electronegativity. It is likely that the sulfur site is weaker for the coordination of these hard acid cations as demonstrated by the weaker extraction of lanthanides by HDEHDTP than HDEHTP or HDEHP [52]. Co(III) complexes with monothiophosphoric acid been observed with both the sulfur and oxygen coordinating the metal [58]. Although not a monothiophosphoric acid, the monothiophosphinic acid Cyanex 302 (HC302), prefers to coordinate An and Ln ions through the oxygen atoms. EXAFS studies of the Cm, Sm, and Nd complexes of Cyanex 302 indicated each metal was coordinated with 4 oxygen atoms and 1 sulfur atom with a proposed composition of $M(C302)_3(H_2O)$ where the metal was coordinated by all three oxygens from the HC302 and one sulfur out of the three available [18]. The differences between the formulas for HDEHDTP and HDEHTP arise from the tendency for HDEHTP to dimerize much like HDEHP while HDEHDTP is less likely to aggregate due to weaker hydrogen bonding ability brought on by sulfur being less prone to hydrogen bonding than oxygen and more acidic [16,52]. The authors also suggest that some quantity of water is present in the extracted complex, [52] but do not report an attempt to quantify the number of water molecules in the complex. The weakness of the S-H-S hydrogen bond in HDEHDTP is reflected in its aggregation constant, which is reported to be $K_3 = 0.145$ for formation of $(HDEHDTP)_3$ in benzene [57]. This is also consistent with the work of Zucal et al., who found no evidence for dimerization of short chain (ethyl, propyl, and butyl) dithiophosphoric acids in carbon tetrachloride [59].

$$Am^{3+} + 3HDEHDTP_{org} + xH_2O \rightleftharpoons Am(DEHDTP)_3{\bullet}xH_2O_{org} + 3H^+ \qquad (3)$$

$$Eu^{3+} + 3HDEHDTP_{org} + xH_2O \rightleftharpoons Eu(DEHDTP)_3{\bullet}xH_2O_{org} + 3H^+ \quad (4)$$

$$Am^{3+} + 1.5HDEHTP_{2,org} + yH_2O \rightleftharpoons Am(DEHTP)_3{\bullet}yH_2O_{org} + 3H^+ \quad (5)$$

$$Eu^{3+} + 1.5HDEHTP_{2,org} + yH_2O \rightleftharpoons Eu(DEHTP)_3{\bullet}yH_2O_{org} + 3H^+ \quad (6)$$

$$Am^{3+} + 3HDEHP_{2,org} \rightleftharpoons Am(H(DEHP)_2)_{3,org} + 3H^+ \quad (7)$$

$$Eu^{3+} + 3HDEHP_{2,org} \rightleftharpoons Eu(H(DEHP)_2)_{3,org} + 3H^+ \quad (8)$$

In addition to the research done with thiophosphoric acids as the sole extracting species, work has been done with synergistic mixtures of thiophosphoric acids with a neutral organophosphorus species. When tributyl phosphate (TBP) is added to the organic phase, less water is extracted than by HDEHDTP alone and the Am/Eu separation factor significantly increases to 25 [52]. Pattee et al. proposed this is caused by TBP coordinating to the metal in place of water which causes a decrease in the metal-sulfur bond length and this decrease enhances the covalency of the bond between actinides and sulfur [52].

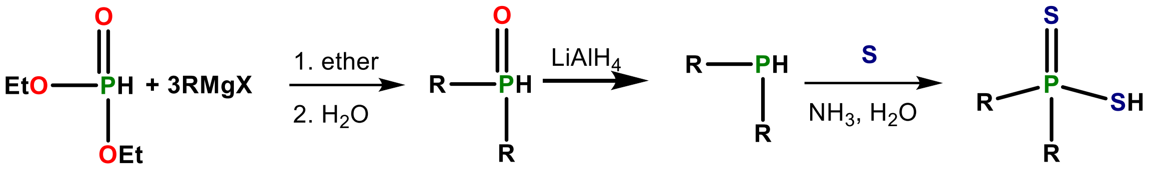
3.3 Dithiophosphinic Acids

Dithiophosphinic acids, Figure 1, have been the most widely studied sulfur bearing class of ligands for the separation of lanthanides and actinides with bis(2,4,4-trimethylpentyl)dithiophosphinic acid (HC301), commercially available as Cyanex 301, being of particular interest. This class of extractants have given some of the highest separation factors observed at this time - up to 100,000 [25–28]. As stronger Lewis Bases, the dithiophosphinic acids also have a greater affinity for metals than their dithiophosphoric acid counterparts if the pH is high enough to enable binding [60]. The selectivity that dithiophosphinic acids display towards actinides due to the ability of actinides to bond more covalently than lanthanides due to energy degeneracy, orbital overlap, or some combination of both. This covalency could cause selectivity by enabling stronger bond with the actinides [18,33] or by forming complexes with different structures and extractabilities [61]. For some cases, the extracted complexes of lanthanides and actinides are the same except for the metal which suggests that stronger interactions between the extractant and actinide drives the observed selectivity [18]. However, in other cases the complexes are different which points to different speciation as the driver of selectivity [61,62]. It may also be possible that both causes can occur simultaneously.

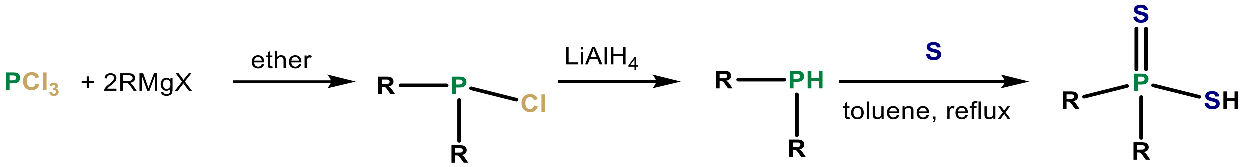
3.3.1 Synthesis

Most dithiophosphinic acids are not commercially available necessitating their synthesis at the laboratory scale. Many synthetic schemes have been developed to produce different types of thiophosphinic acids. Due to the number of different synthesis, only the more widely used procedures that require few unusual or difficult steps will be given here.

For symmetric dithiophosphoric acids, diethylphosphite can be reacted with the Grignard reagent of the desired alkyl chain [24]. The resulting dialkylphosphine oxide is then reduced to a dialkylphosphine by a strong reducing agent such as lithium aluminum hydride [24]. The dialkylphosphine is reacted with sulfur in aqueous ammonia to yield the crude dialkyldithiophosphinic acid, Scheme 2 [24]. Due to the simplicity of the procedure, this is the most commonly used method. This is the method used by Tian et al. and Xu et al [24,43,44]. A similar procedure for this synthesis uses phosphorus trichloride as an alternative to diethylphosphite as a starting material and forms a chlorodialkylphosphane as an intermediate instead of a dialkylphosphine as shown in Scheme 3 [25,26]. Although normally used for the synthesis of symmetric dialkyldithiophosphinic acids, with careful control of the stoichiometry this method has been used to create asymmetric dithiophosphinic acids [26].

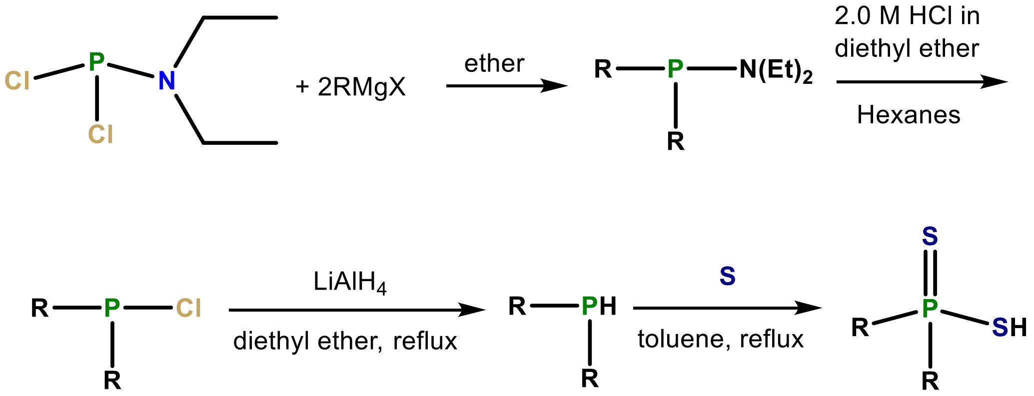


Scheme 2: Synthetic procedure for dithiophosphinic acids as done by Tian et al. [24].



Scheme 3: Synthetic procedure for dithiophosphinic acids as done by Klaehn et al. and Peterman et al. [25,26].

Another procedure for this synthesis uses 1,1-dichloro-N,N-diethylphosphanamine and a Grignard reagent to prepare N,N-diethyldialkylphosphanamine, which is converted into a chlorodialkylphosphane [26]. The chlorodialkylphosphane is reduced to a dialkylphosphine and reacted with elemental sulfur in toluene to prepare the dithiophosphinic acid, Scheme 4 [26].



Scheme 4: Synthesis procedure of dithiophosphinic acids from 1,1-dichloro-N,N-diethylphosphanamine as done by Klaehn et al. [25].

Preparing monothiophosphinic acids is somewhat more difficult than dithiophosphinic acids, but can be done by several means. The dialkylphosphinothioic chloride can be reacted with sodium hydroxide, or the more common treatment of dialkylphosphinic chloride with sodium sulfide, to prepare a monothiophosphinic acid [63].

Throughout the synthesis, storage, and use of these thiophosphinic acids, it is important to be mindful of the formation of impurities. In particular, more oxygenated impurities can have a large impact on the extraction strengths and selectivity of the extractants as these impurities are often stronger extractants and lack selectivity. The effects of these impurities are particularly pronounced when using tracer or small quantities of metals.

3.3.2 Effect of varying alkyl and aryl groups

Many mono- and di-thiophosphinic acids have been tested for their ability to separate f-elements and to determine the impact of the alkyl or aryl group on the separation. Despite the number of different extractants tested, providing a definitive assignment to the role of the alkyl or aryl group on selectivity remains difficult. The thiophosphinic acids evaluated to date and their separation factors for tracer amounts of Am and Eu are shown in Table 1. If the pH at which the separation factor was measured has been published, the pH has been included in Table 1.

Xu et al. have synthesized and evaluated thiophosphinic acids substituted with many different straight chain and branched alkyl groups and several aryl groups. To evaluate the extraction behavior of these thiophosphinic acids, tracer amounts of Am and Eu in 0.1 M $NaClO_4$ were contacted with a solution of the extractant in xylene [43,44]. Alkyl group substituted extractants were found to provide a lower selectivity for Am over Eu than with branched chain substituted extractants [43,44]. Aryl group substituted extractants typically gave better separations than alkyl group substituted extractants [43] and, by being more acidic, they will likely have stronger extraction from more acidic media [24,43,64].

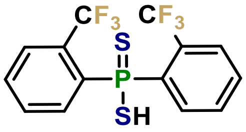
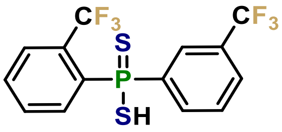
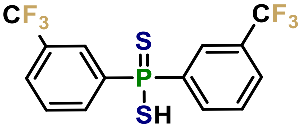
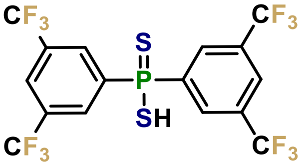
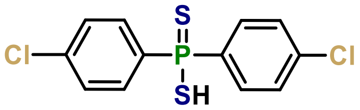
Tian et al. also synthesized several dialkyldithiophosphinic acids and came to a different conclusion regarding the impact of the alkyl chain on selectivity. They found the separation factors for Am and Eu were nearly unaffected by varying the alkyl group between octyl, 1-methylheptyl, 2-ethylhexyl, and 2,4,4-trimethylpenthyl [24]. The separation factors found by Xu et al. and Tian et al. have a difference of several orders of magnitude, with those found by Tian et al. being much closer to other reported separation factors for dithiophosphinic acids [24,28,43,44,65]. This could be due to difference in pH, which were not reported by Quichu et al., or traces of impurities in the organic phase. However, these discrepancies cast some doubt on the findings of Xu et al. as the separation factors they found are substantially different.

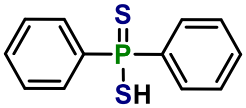
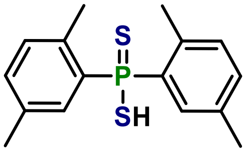
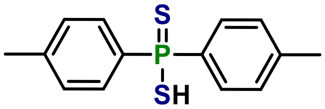
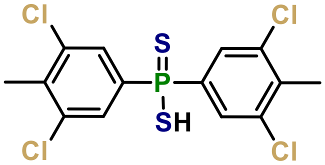
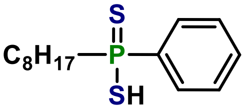
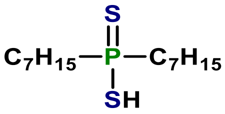
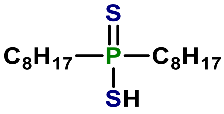
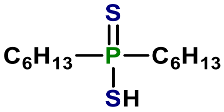
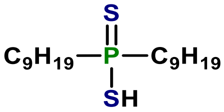
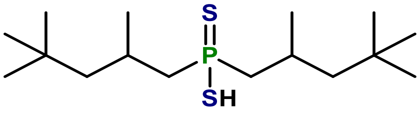
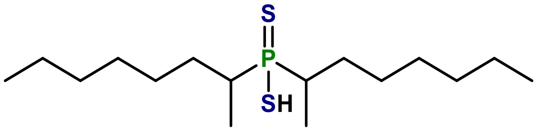
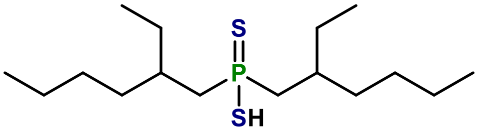
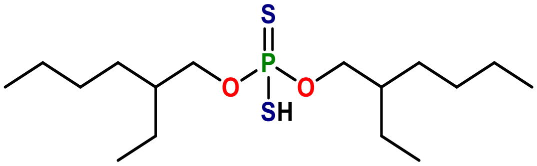
The effect of electron donating and withdrawing groups on aryl dithiophosphinic acids was also tested. With electron withdrawing groups, separation factors were increased and with electron donating groups, the separation factors decrease, but extractant strength is increased [43]. Klaehn et al. and Peterman et al., in addition to developing novel synthetic pathways for dithiophosphinic acids, have tested several aromatic dithiophosphinic acids with trifluoromethyl group on different sites on the benzene rings using phenyltrifluoromethylsulfone (FS-13) as a solvent and a 1 M sodium nitrate aqueous phase. They found that location of the trifluoromethyl group has a profound impact on the selectivity [25,26]. With bis(*o*-trifluoromethylphenyl)dithiophosphinic acid, the remarkably high separation factor of 100,000 [25] was observed. For the isomeric bis(*m*-trifluoromethylphenyl)dithiophosphinic acid, the separation factor was two orders of magnitude less [26].

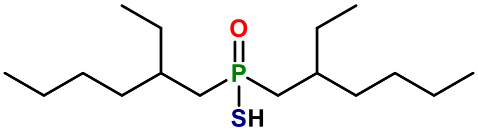
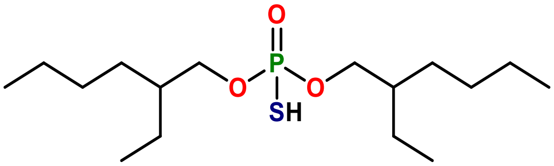
Daly et al. examined this system with sulfur K-edge x-ray absorption spectroscopy and time-dependent DFT. They found that when substituents were present in the *ortho* position, the symmetry of the ligands was reduced to C_2 from C_{2v} due to steric effects and the electron delocalization increased on the aromatic rings [33]. These changes cause the energy of the highest occupied molecular orbital (HOMO) to increase, thus decreasing the HOMO-LUMO gap and creating a softer ligand which promotes greater selectivity for actinides [33]. Pu et al. also found that the steric effects of the trifluoromethyl group greatly impact the extractant's properties [66]. The decreased symmetry may also be responsible for the greater selectivity possessed by branched alkyldithiophosphinic acids as observed by Xu et al. Another possible explanation for the high selectivity of bis(*o*-trifluoro-methylphenyl)dithiophosphinic acid is that that the trifluoromethyl groups are effective at displacing water molecules from the metal center thus raising the entropic contribution to complex formation and increasing selectivity [67].

Overall, the effect of the alkyl or aryl group on selectivity remains unclear. In many cases, little more than the separation factor is known. If more information were available, a more comprehensive explanation for the effect may be determined. Of particular interest would be the structure and coordination of the extracted complexes for extractants other than HC301. This will likely require extended x-ray absorption fine structure (XAFS) as the long alkyl groups of many extractants likely prevent the formation of crystals necessary for single crystal XRD.

Table 1: Various mono- and di-thiophosphinic acids and their separation factors for tracer amounts of Am and Eu from nitric acid media. None of the extractants have been saponified prior to extraction.

Phosphinic Acid	$SF_{Am/Eu}$	Solvent	Aqueous pH	Reference
	100,000	FS-13	2.5	[25]
	10,000	FS-13	~2.3	[26]
	40,000	FS-13	~2.3	[26]
	1,000	FS-13	~2.1	[26]
	20	FS-13	2.5	[25]
	21	Xylene	Not Reported	[43]

	4.4	Xylene	Not Reported	[43]
	1.8	Xylene	Not Reported	[43]
	1.3	Xylene	Not Reported	[43]
	1.0	Xylene	Not Reported	[43]
	3.0[43]	Xylene	Not Reported	[43]
	2.1	Xylene	2.82	[43,44]
	1.4	Xylene	3.51	[43,44]
	9,700	Toluene	Not Reported	[24]
	0.71	Xylene	4.90	[43,44]
	0.3	Xylene	1.94	[43,44]
	5,900	Kerosene	~2.8-4.4	[28]
	6,000	Dodecane	3.4	[65]
	9,800	Toluene	Not Reported	[24]
	8.3	Xylene	4.12	[44]
	10,000	Toluene	Not Reported	[24]
	4.2	Xylene	2.36	[43,44]
	10,000	Toluene	Not Reported	[24]
	1.3	Xylene	Not Reported	[43]

	2.43	Xylene	3.13	[44]
	0.8	Xylene	Not Reported	[43]
	0.96	Xylene	0.86	[44]
	0.3	Xylene	Not Reported	[43]
	0.68	Xylene	2.87	[44]

In addition to the above thiophosphinic acids being considered as the sole extractant, dithiophosphinic acids have been studied in combination with neutral, organophosphorus extractants in a synergistic extraction system. Modolo and Odoj have characterized bis(phenyl)-, bis(fluorophenyl)-, and bis(chlorophenyl)-dithiophosphinic acids with many synergic, solvating extractants. They found the extractant strength increases in the order of phenyl < fluorophenyl < chlorophenyl, but as the extractant strength increases, the separation factor decreases [68,69]. Xu et al. also observed that an increase in extractant strength corresponds to a decrease in selectivity, even though no synergists were used in Xu's work [43].

3.3.3 Mechanisms

3.3.3.1 Cyanex 301

The precise mechanism by which dithiophosphinic acids extract lanthanide and actinide ions is not universally agreed upon, but it is generally accepted that dithiophosphinic acids are cation exchange extractants that exchange protons for metal ions in the extraction process. A more complete understanding of the mechanism by which these acids extract could lead an improvement of the separation of lanthanides and actinides. However, uncertainty remains about the effect of extractant aggregation, stoichiometry of the extracted complexes, impact of saponification, and effect of solvents.

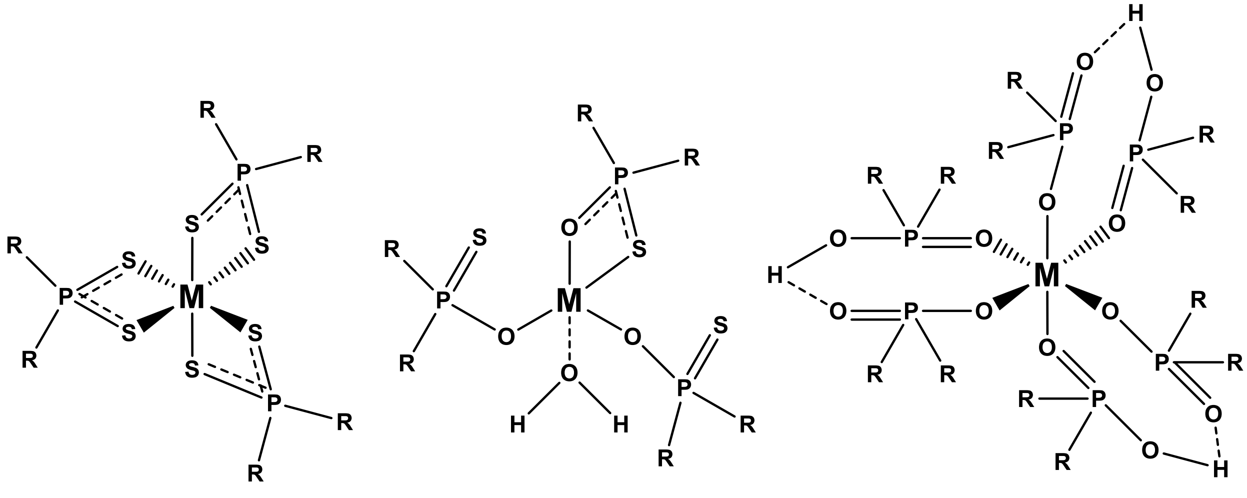
In solution, purified HC301 has been found to weakly dimerize in deuterated *n*-heptane (K_2=0.67) [45] and toluene (K_2=0.78) [70]. Therefore, under typical extraction conditions, both HC301 monomers and dimers are present and able to impact the extraction of metal. In contrast, the monothiophosphinic acid analog, bis(2,4,4-trimethylpentyl)monothiophosphinic acid (HC302), (K_2=20) [71] and its phosphinic acid analog, bis(2,4,4-trimethylpentyl)phosphinic acid (HC272), (K_2=1.0 x 10^3) [72] are substantially dimerized.

When Jensen and Bond conducted distribution experiments in dodecane and accounted for changes in the concentration of extractant dimers, slope analysis showed three molecules of purified HC301 or HC302 are necessary for the extraction of one trivalent lanthanide or actinide as per Equations 9-10, but the more strongly dimerized HC272 extracts trivalent metals using three dimers of $H(C272)_2^-$, Equation 11 [18,45]. The complexes that are proposed to be formed from these reactions are shown in Figure 4. This behavior was further confirmed by SANS studies of the Cyanex 301 solutions [73,74]. Later XAFS studies of the coordination environments of Cm, Sm, and Nd extracted by HC301 were best fit with 6 sulfur atoms which corresponds to three molecules of HC301 [18]. XAFS also showed similar bond lengths for lanthanides and actinides with HC301, and metal-sulfur distances consistent with hexacoordination [18]. Since XAFS shows the same number of sulfur atoms coordinating to both the lanthanides and actinides with HC301, yet selectivity is observed, they proposed that the selectivity must be due to greater covalency with actinides under their extraction conditions [18].

$$M^{3+} + 3HC301_{org} \rightleftharpoons M(C301)_{3,org} + 3H^{+} \tag{9}$$

$$M^{3+} + 3HC302_{org} + H_2O \rightleftharpoons M(C302)_3(H_2O)_{org} + 3H^{+} \tag{10}$$

$$M^{3+} + 3HC272_{2,org} \rightleftharpoons M(H(C272)_2)_{3,org} + 3H^{+} \tag{11}$$



$M(C301)_3$
(1)

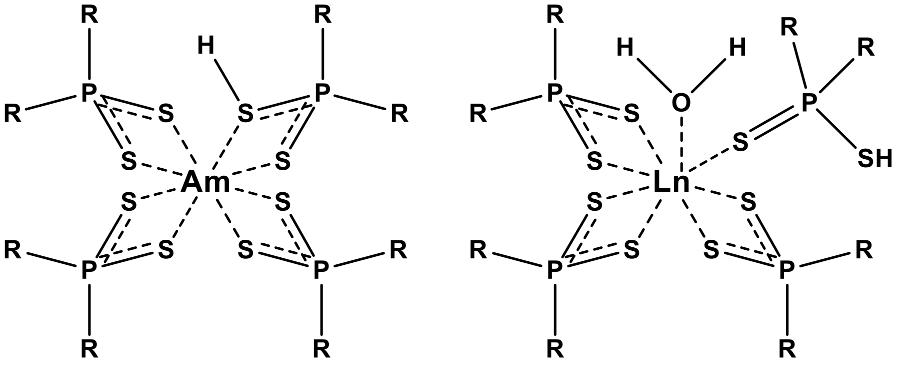
$M(C302)_3(H_2O)$
(2)

$M(H(C272)_2)_3$
(3)

Figure 4: Proposed structures of the complexes extracted in Equations 9 to 11 [18,45]. R=2,4,4-trimethylpentyl.

Xu et al. and Pu et al. studied the reaction of lanthanides with the ammonium salts of HC301 [75] and aromatic dithiophosphinic acids [67] in ethanol. UV-vis and calorimetric titrations showed the step-wise addition of dithiophosphinates to the metal center ultimately leading to complexes of one metal coordinated by three dithiophosphinates [67,75]. Formation constants and thermodynamic parameters were determined this data and enable the calculation of speciation for most of the lanthanides with HC301 in ethanol [75]. Although this system is not directly comparable to the solvent extraction system used by Jensen and Bond [18], it is worth noting that the same complex was observed at the endpoint of the titrations and from solvent extraction.

The extraction mechanisms shown in Equations 9-11 are not the only proposed mechanisms. Tian et al. used XAFS to characterize the complexes formed when purified HC301 extracts Am in hydrogenated kerosene [62] and La, Nd, and Eu in toluene [61]. They found seven sulfur atoms and the oxygen from a water molecule are coordinated to the lanthanides and eight sulfur atoms and no oxygens are coordinated to Am, suggesting that 4 molecules of HC301 participate in the extraction as shown in Figure 5 [61,62]. These results were also obtained by a mass spectrometry experiment [61]. Due to the difference in the coordination environments of lanthanides and actinides in these results, they propose that differences in the hydration of the metal are responsible for the selectivity observed with HC301.

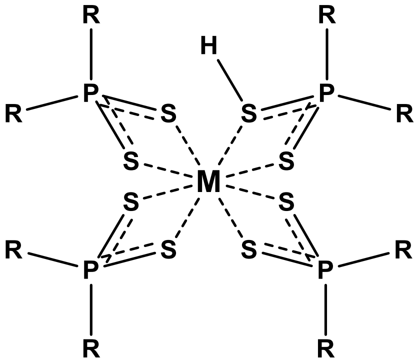


$Am(H(C301)_4)$
(1)

$M(H(C301)_4)(H_2O)$
(2)

Figure 5: Speculative structures of the complexes postulated by Tian et al. [61,62]. R=2,4,4-trimethylpentyl.

Zhu et al. have also studied the extraction of lanthanides and actinides with purified HC301 in kerosene using slope analysis distribution studies. They found four HC301 molecules are required for the extraction of one trivalent actinide or lanthanide when they assumed that all HC301 is dimerized in the slope analysis[28]. This group has also reported the widely cited Am and Eu separation factor of 5900 for purified HC301 with no additional synergistic reagents [28]. This group's studies that show four HC301 moieties used in the extraction of lanthanides also show consistent coordination environments with single crystal XRD studies of dithiophosphinic acids with smaller alkyl groups [31,76,77]. Single crystals of metal complexes with dithiophosphinic acids with more sterically demanding alkyl groups, such as cyclohexyl groups, show three dithiophosphinic acids [74].



$M(H(C301)_4)$
(1)

Figure 6: Speculative structures of the complexes postulated by Zhu et al. [28]. R=2,4,4-trimethylpentyl

A third mechanism for lanthanide extraction by HC301 has also been identified for the heavy lanthanides. While light lanthanides form inner sphere complexes with the Cyanex 301 anion in organic phases, lanthanides heavier than Eu are extracted as fully hydrated cations with the extractant in the outer coordination sphere when extracted from a 0.1 M solution of the lanthanide nitrate adjusted to pH 3.5 with NaOH or HNO_3 [78]. XAFS, UV-vis, and fluorescence measurements of the extracted complexes of heavy lanthanides with 30% saponified HC301 in toluene show only water in the coordination sphere and are similar to the aqua ions whereas the light lanthanides show sulfur and phosphorus from HC301 in the coordination sphere and are quite different than for the aqua ions [78]. Computational studies have also suggested that heavy actinides more prone to be extracted as outer sphere complexes [79]. At higher degrees of saponification, further extraction of water with both light and heavy lanthanides due to the formation of water-in-oil micelles is observed [80,81].

Under the narrow pH ranges tested without saponification of the extractant, slope analysis suggests a consistent metal-to-ligand ratio [28,45]. However, at a higher pH or with a saponified extractant, it is possible that different extracted complexes or micelles may form. Therefore, it is possible that the different mechanisms observed by Tian et al. and Zhu et al., as compared to the mechanism found by Jensen and Bond, arise from saponification of the extractant. Jensen and Bond did not saponify their organic phases for their studies [18,45] whereas Tian et al. and Zhu et al. added a base to partially neutralize the HC301 and promote greater metal uptake [28,61,62]. Therefore, the differences in the observed mechanisms may both be correct for the different conditions used, but further research is needed to verify this.

In addition to the previous studies, where purified HC301 is considered, the commercially supplied form of HC301 has been studied. HC301 as supplied has been found to contain HC301 is 75-83% of the desired dithiophosphinic acid, 5-8% is neutral phosphine sulfides, 3-6% is the monothiophosphinic acid, and the remainder is unknown [82]. Zhu et al. have tested HC301 as supplied by the manufacturer and found that the separation depends on the concentration of lanthanide in the aqueous phase. With higher lanthanide concentrations and tracer amounts of Am, the separation factor increased [56]. They propose that at low concentrations of lanthanides, the impurities which are not selective extract metals, particularly lanthanides, more strongly than bis(2,4,4-trimethylpentyl)dithiophosphinic acid. The lack of selectivity provided by the impurities are responsible for the low separation factors [56]. As the concentration of lanthanides increases, the impurities become saturated with metal leaving bis(2,4,4-trimethylpentyl)dithiophosphinic acid as the only ligand still capable of extraction, which it does selectively [56].

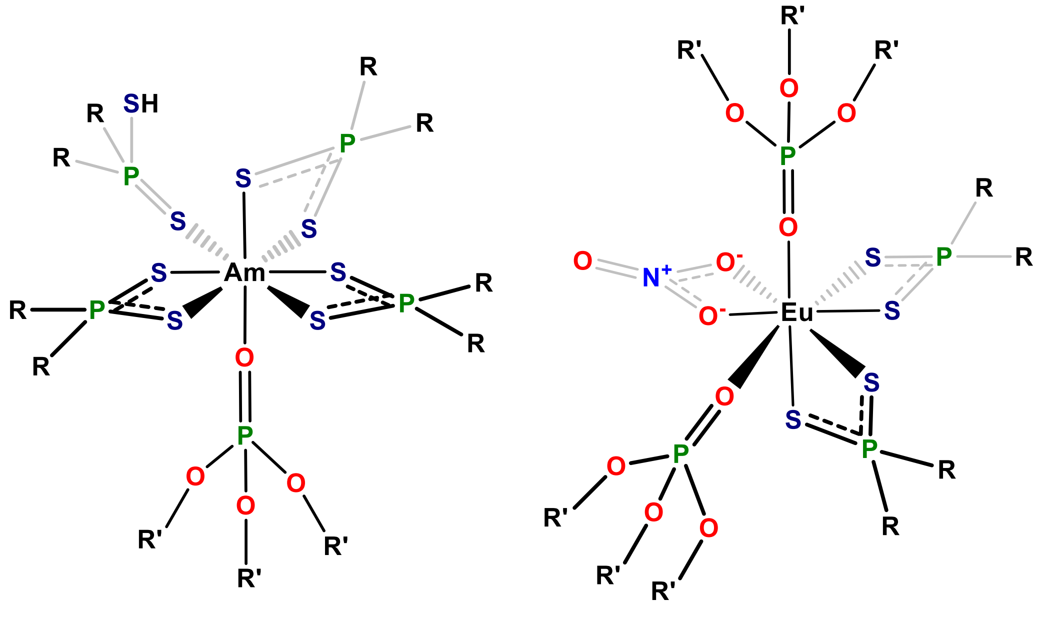
3.3.3.2 Dithiophosphinic Acids in Synergistic Mixtures

Dithiophosphinic acids have been considered in conjunction with other neutral, oxygen donor extractants in synergistic mixtures. Hill et al. have studied lanthanide and actinide separations with synergistic mixtures of purified HC301 and TBP. Using slope analysis of distribution experiment results, they found Am and Eu are extracted through the formation of different complexes as shown in Equations 12 and 13 [65]. Structures of the complexes extracted in

Equations 10 and 11 are shown in Figure 7. A maximum separation factor of this HC301 and TBP synergistic mixture was observed at 10% TBP (SF≈6,000), where the separation factor was greater than that of only HC301 (SF≈3,500) [65]. In addition to testing synergistic mixtures of HC301 and TBP, Hill et al. tested mixtures of HC301 with either triphenylphosphate (TPP) or diphenylsulfoxide (DPSO) and were able to modulate the distribution values and separation factors with the use of other synergic agents [65]. Ionova et al. have continued studying synergistic effects of neutral, oxygen donating extractants. They found that for both HC301 and bis(chlorophenyl)dithiophosphinic acid with TBP, tri-*tert*-butylphosphate (T*t*BP), TPP, trioctylphosphine (TOPO), and CMPO, the distribution ratio of Am and Eu is linearly related to both the effective charge on the oxygen of the neutral extractant and the chemical shift of the molecule with ^{31}P NMR [60,83].

$$Am^{3+} + 2HC301_{2,org} + TBP_{org} \rightleftharpoons AmH(C301)_4TBP_{org} + 3H^+ \qquad (12)$$

$$Eu^{3+} + NO_3^- + HC301_{2,org} + 2TBP_{org} \rightleftharpoons EuNO_3(C301)_2TBP_{2,org} + 2H^+ \qquad (13)$$



$AmH(C301)_4TBP$ $EuNO_3(C301)_2TBP_2$

Figure 7: Speculative structures of the Am and Eu complexes extracted in Equations 12 and 13. R=2,4,4-trimethylpentyl and R'=*n*-butyl.

The synergistic effect of TBP or other synergic agents likely arises from the increased coordination of the metal ion by lipophilic moieties [41,42]. In the mechanisms for the extraction of metal solely by HC301 as proposed by Jensen and Bond, three HC301 molecules are coordinated to a metal ion [45]. With all of the sulfur from the HC301 and no water molecules coordinating the metal, as supported by XAFS, [18] the metal would be under coordinated with a coordination number of six. Being incompletely coordinated allows the coordination of a TBP molecule or similar moiety causing the entire complex to become more lipophilic and thus more readily extracted. This effect would increase the distribution ratio, but it does not fully explain the increase of the separation factor from 3,500 to 6,000 or the different complexes extracted in Equations 12 and 13 observed by Hill et al. [65].

The greater separation factor with TBP or similar synergic agents may be explained by competition between HC301 and the neutral, solvating extractant. Since the lanthanides are bound less strongly than actinides by HC301, the HC301 bound to a lanthanide can be replaced by TBP more easily as evidenced by the Eu complex from Equation 11 having two TBP molecules and only two $C301^-$ species versus the three $C301^-$ from Jensen and Bond's findings. The substitution of an anionic $C301^-$ with a neutral TBP species requires the coordination of another anion to maintain the charge neutrality required for organic phase solubility.

In the work done by Hill et al., this anion was nitrate which is not lipophilic and therefore poorly extracted. The extraction of nitrate roughly balances the increased lipophilicity resulting from the coordination of TBP to the complex. This crude balance causes the distribution ratio of Eu to change only slightly with the addition of TBP [65]. For Am, the lipophilicity would increase by the addition of a TBP and the retention of HC301. In this case, Am extraction increases with the addition of TBP [65]. This increase in the Am distribution ratio, while the Eu distribution ratio remains relatively unchanged, has been argued to generate the separation factor to increase shown by Hill et al. [65].

The solvent effects on the synergistic extraction by a mixture of bis(chlorophenyl)dithiophosphinic acid and TOPO has been briefly studied. Ionova et al. tested the effect of using toluene, xylene, *t*-butylbenzene, or tri-*i*-propylbenzene as the diluent for this extraction and found that the distribution ratio of Am greatly increases as the polarizability of the diluent increases. The degree of increase in the Eu distribution ratio reduces as the bulkiness of a solvent molecule increases.[83] As a result, the separation factor increases from 23.5 for toluene to 45.6 for tri-*i*-propylbenzene [83].

3.3.4 Degradation Studies

One concern about the use of dithiophosphinic acids for separating the components of used nuclear fuel is their radiolytic stability. Chen et al. have studied the effects of irradiating both commercial and purified HC301 in an open glass tube with a ^{60}Co γ-source in the absence of an aqueous phase [22]. From NMR spectra of the irradiated extractants, they found both decompose to the monothiophosphinic acid and phosphinic acid, sulfuric acid, and an unidentified, neutral phosphorus containing molecule as shown in Figure 8 [22]. Initially, both the purified and commercial HC301 are primarily the dithiophosphinic acid with a ^{31}P NMR peak at 65 ppm [22]. As the radiation dose increases, an ingrowth of peaks occurs corresponding to the monothiophosphinic acid (93.5 ppm), phosphinic acid (59.8 ppm), and other phosphorus compounds. Photodegradation of HC301 also produces the monothiophosphoinic and phosphinic acids plus an unknown compound [84]. Accompanying the decomposition of the HC301, the separation factors also markedly decrease [22]. Although both the commercial and purified HC301 decompose, the purified HC301 is more robust, being able to effectively separate tracer amounts of Am and Eu after 1×10^5 Gy whereas the commercial HC301 only retains that ability up to 1×10^4 Gy [22].

Despite the radiolysis, Chen et al. propose that under typical process conditions, purified HC301 would be capable of the industrial separation of lanthanides and actinides for approximately 10 hours [22]. Modolo and Odoj have also studied the radiolytic stability of purified HC301 and confirmed the findings of Chen et al. Modelo and Odoj have also found that after irradiation, the separation factor between Am and Eu more sensitive to pH [23]. In addition to HC301, Modelo and Odoj found the irradiation characteristics of bisphenyldithiophosphinic acid and bis(chlorophenyl)dithiophosphinic acid to be much more resistant than HC301 [68]. At a dose of 1x10^6 Gy, 82% of the HC301 had decomposed, [23] but under the same conditions, <2% decomposition was observed for the aromatic dithiophosphinic acids [68]. Although not discussed by Modolo and Odoj, these dithiophosphinic acids likely decompose into their monothiophosphinic and phosphinic acid analogues similarly to how HC301 decomposes [22]. Modolo and Seekamp further examined the radiolysis and hydrolysis of bis(chlorophenyl)dithiophosphinic acid. They found that both radiolysis and hydrolysis produce the monothiophosphinic acid and phosphinic acid and that the nitrous acid scavengers amidosulfuric acid, hydrazine, and urea prevent hydrolysis [85]. Although untested, further decreases in radiolysis may be possible by adding a radical scavenger to the organic solution. The greater stability of the aromatic dithiophosphinic acids, in combination with the higher separation factors they provide, is promising for the use of such extractants for the industrial separation of actinides and lanthanides.

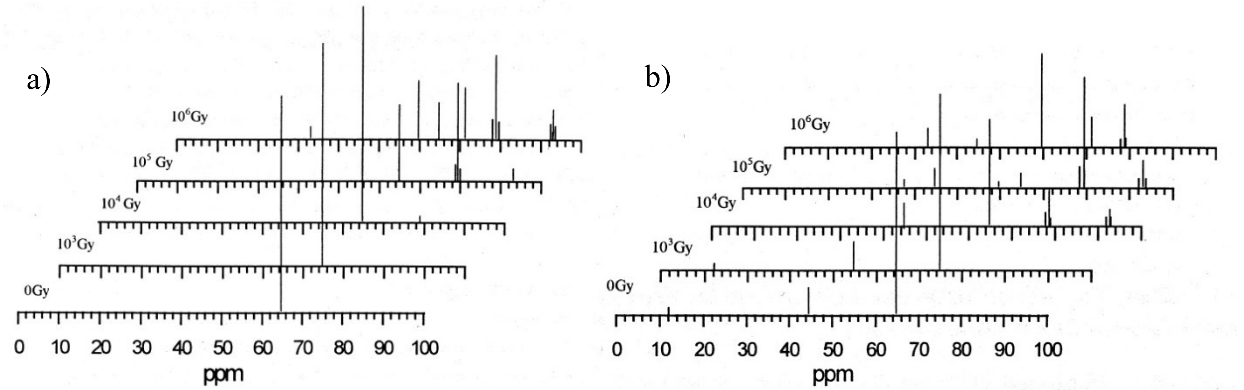


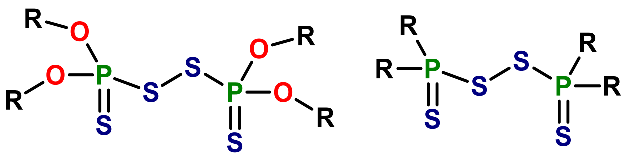
Figure 8: a) ^{31}P NMR spectra of purified HC301 at various doses of radiation and b) ^{31}P NMR spectra of commercial HC301 at various doses of radiation [22].

HC301 was also found to be susceptible to degradation by nitric acid [86–88], but not sulfuric acid [86]. As seen with radiolysis and photolysis of HC301, this degradation results in the formation of the monothiophosphinic and phosphinic acids [86]. An intermediate that consists of two HC301 molecules linked by a disulfide bridge has been observed [87,88]. This disulfide intermediate is produced more quickly at higher nitric acid concentrations [87] and therefore should be less of a problem at the low nitric acid concentrations typically used for separations.

The stability of bis(*o*-trifluoromethylphenyl)dithiophosphinic acid has also been tested when in contact with aqueous nitric acid during irradiation. Klaehn et al. found that after 140 days of being in contact with 0.01 M nitric acid, 68% of the dithiophosphinic acid remained and when no acid was present, 81% remained [25]. When the high radiolytic stability of similar bisphenyldithiophosphinic acids is also considered, bis(*o*-trifluoromethylphenyl)dithiophosphinic acid is likely to be quite stable under typical reprocessing conditions.

3.4 Miscellaneous Sulfur Containing Extractants

In addition to the sulfur containing extractants detailed above, other reagents have been considered. Zalupski et al. have tested the cation exchange extractant P,P'-di(2-ethylhexyl)-methylenebisthiophosphonic acid and its oxygen analog, P,P'-di(2-ethylhexyl)methylenebisphosphonic acid. They found the bisthiophosphonic acid has lower extractant strength for both Am and Eu than for the phosphonic acid, but has higher selectivity for Am [89]. This increase in selectivity does not enable an effective separation, as Am and Eu are extracted with nearly the same strength, whereas the phosphonic acid extracts Eu more strongly [89]. This behavior is similar to that of monothiophosphinic acids such as HC302, where lanthanides and actinides are extracted to approximately the same degree [45]. Bisdithiophosphonic acids have not been tested for the separation of trivalent actinides and lanthanides although they may be expected to display more selectivity due to additional sulfur sites. They have been observed to extract Gd^{3+} poorly though they hydrolyze below pH 2 and above 11 to 12 [90].



bis(thiophosphoryl)disulfane (5)

bis(thiophosphinyl)disulfane (6)

Figure 9: Structure of a bis(thiophosphoryl)disulfane (5) and bis(thiophosphinyl)disulfane (6).

Another class of extractants that may merit more study are the bis(thiophosphoryl)disulfanes and bis(thiophosphinyl)disulfanes. They have been used as extractants for soft, transition metal cations and their complexes with several lanthanides have been characterized [91–94]. Although they have yet to be studied in the context of lanthanide/actinide separations, they may have implications on the use of dithiophosphinic or dithiophoshoric acids as they can form bis(thiophosphinyl)disulfanes or bis(thiophosphoryl)disulfanes by the formation of a disulfide bond in oxidizing conditions [91].

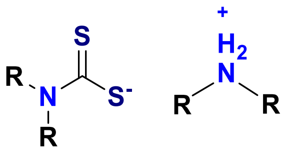


Figure 10: Generic structure of a dialkylammonium dithiocarbamate. R= butyl, octyl, phenyl, or benzyl.

Dithiocarbamates have shown high separation factors of up to 32,000. Miyashita et al. have prepared dialkylammonium dialkyldithiocarbamates *in situ* where the alkyl groups were butyl, octyl, phenyl, or benzyl and tested their ability to separate Am and Eu in different organic solvents [95–97]. They act as cation exchange extractants that extract metal as complexes with one trivalent metal ion and three dithiocarbamates to form a neutral complex [95–97]. To avoid the rapid hydrolysis of these extractants when contacted with an acidic aqueous phase, they were synthesized *in situ* by combining carbon disulfide and the appropriate disubstituted amine [96].

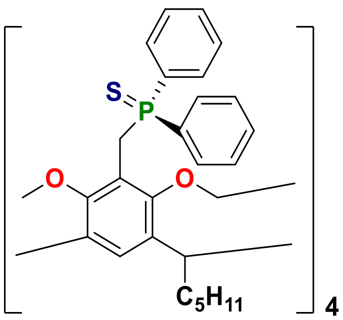


Figure 11: Tetrakis(phosphane sulfide) cavitand.

Tetrakis(phosphane sulfide) cavitands have been synthesized and their efficacy for separations has been tested [98]. They were found to extract both Am^{3+} and Eu^{3+} very weakly if at all and with a SF of 1.7 [98]. These cavitands were also tested in the presence of the synergists TBP and TOPO. Although the distribution ratios of both Am^{3+} and Eu^{3+} were increased, almost no selectivity was observed with SFs ranging from 1.1 to 1.2 [98].

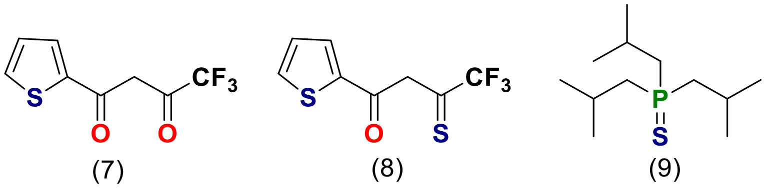


Figure 12: Structure of thenoyltrifluoroacetone (7), thiothenoyltrifluoroacetone (8), and tri-iso-butylphosphine sulfide (9).

Thenoyltrifluoroacetone (HTTA) is often used as an extractant for f-block metals that has been tested in conjunction with the sulfur donating synergist tri-iso-butylphosphine sulfide (TBPS) for the separation of Am^{3+} and Eu^{3+} [99]. In extractions from perchlorate media, metal was weakly extracted as complexes of the form $M(TTA)_2(ClO_4)(TBPS)$ in cyclohexane [99]. The SF for this separation is approximately 0.59 [99]. A sulfur donating version of HTTA was also prepared, thiothenoyltrifluoroacetone (HSTTA) [99]. It was found to extract trivalent metals as complexes of the form $M(STTA)_2(ClO_4)(HSTTA)$ [99]. The addition of TBP caused the formation of $M(STTA)_3(TBP)$ and $M(STTA)_3(TBP)_2$ complexes while increasing the distribution ratio and selectivity for Am^{3+} [99].

4. Conclusions

Soft, sulfur donating ligands have shown remarkable success for the difficult, laboratory scale separation of lanthanides and trivalent actinides. Although many of the sulfur containing ligands have not yielded usable separations, several molecules show promise for an efficient industrial scale separation. Generally, extractants that contain anionic sulfur donors and can form chelate rings, such as the dithiophosphinic acids, dithiophosphoric acids, and dithiocarbamates display the best selectivity for actinides. Of these three extractants, dithiophosphinic acids have shown the most promise as the dithiophosphoric acids give lower separation factor and are weaker extractants while the dithiocarbamates rapidly hydrolyze at low pH. Extractants that have neutral sulfur donor sites are much weaker extractants and require the ability to form chelate rings to extract lanthanides or actinides as the sole extractant as seen with the phosphane sulfide cavitands and STTA. Yet extractants with neutral sulfur sites that cannot form chelates can increase selectivity as a synergist, such as TBPS. Perhaps the best example of a successful sulfur based extractant is bis(*o*-trifluoromethylphenyl)dithiophosphinic acid as this extractant has a high Am/Eu separation factor [25,26] and usable stability [25]. Other sulfur containing extractants, even those that do not show great separations, indicate what drives trivalent actinide/lanthanide selectivity and can help guide the design of better molecules for this challenging separation.

There are several benefits and drawbacks that would be associated with the implementation of one of these extractants on a scale suitable for processing large quantities of used nuclear fuel. There are several extractants with high separation factors [25,26,28] that would enable a more compact and efficient process flowsheet for the separation of actinides and lanthanides. However, these sulfur based extractants will introduce sulfur to the waste stream which adds an additional waste treatment challenge [21] and the synthesis and purification of these extractants is not trivial [24–26]. More research is needed to develop this class of extractants into a useful, scalable separation process.

While many unknown facets of this type of chemistry still exist, the most pressing question relevant to this and other soft donor work is the precise cause of the selectivity that sulfur and other soft donors have for the actinides over the lanthanides. It has been shown that sulfur sometimes forms shorter bonds with the actinides than the lanthanides, [13,30,31] but the cause of this bond shortening remains unknown and may contribute to the observed selectivity of some sulfur donating ligands. Work on structure-function relationships for this class of extractants is needed and would assist in assessing the source of sulfur's selectivity towards the actinides, ultimately leading to improvements in the challenging separation of trivalent actinides and lanthanides.

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