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THERMALLY UNSTABLE COMPLEXANTS: STABILITY OF LANTHANIDE/ACTINIDE COMPLEXES, THERMAL INSTABILITY OF THE LIGANDS, AND APPLICATIONS IN ACTINIDE SEPARATIONS

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ABSTRACT

Water soluble complexing agents are commonly used in separations to enhance the selectivity of both ion exchange and solvent extraction processes. Applications of this type in the treatment of nuclear wastes using conventional complexing agents have found mixed success due to the nature of the complexants. In addition, the residual solutions containing these species have led to potentially serious complications in waste storage. To overcome some of the limitations of carboxylic acid and aminopolycarboxylate ligands, we have initiated a program to investigate the complexing ability, thermal/oxidative instability, and separation potential of a group of water soluble organophosphorus compounds which we call Thermally Unstable Complexants, or simply TUCS. Complexants of this type appear to be superior to conventional analogues in a number of respects. In this report, we will summarize our research to date on the actinide/lanthanide complexes with a series of substituted methanediphosphonic acids, the kinetics of their oxidative decomposition, and a few applications which have been developed for their use.

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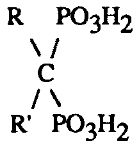
INTRODUCTION

Water soluble complexing agents have found a variety of uses in actinide separation processes. Oxalic acid is often employed both as a stripping agent for the actinides and as a precipitant for the lower oxidation states. The TALSPEAK process for lanthanide/actinide separations is based on the combined complexation effects of lactic acid and diethylenetriamine-N,N,N',N",N"-pentaacetic acid (DTPA) (1)

The most common reagents for the decontamination of radioactive components are based on the aminopolycarboxylate ligands ethylenediamine-N,N,N',N'-tetraacetic acid (EDTA) and DTPA. These reagents are effective at pH above 2 but, though the actinide complexes are soluble, the free complexants suffer from relatively limited solubility in acid solutions. An additional limitation to their use comes from their great resistance to degradation (2). Even under hydrothermal conditions (high pressure, temperatures between 200-300C) complete oxidation of EDTA is not observed.

To overcome some of the limitations of typical complexing agents, we have investigated the complexing ability, thermal/oxidative instability, and separations applications of a new class of relatively simple reagents. To overcome the inherent limitations of carboxylate complexants, this new class of compounds is based principally on phosphonic acids (R-PO_3H_2). Phosphonic acids are stronger acids (for the first ionization) than typical carboxylic acids, which implies higher concentrations of the free ligand species at lower pH. Literature reports on phosphonic acid complexants indicate that the most stable complexes are formed with gem-diphosphonic acid ligands.



$$RR'C(PO_3H_2)_2$$

The simplest of these complexants is methanediphosphonic acid, a structural analogue of malonic acid. Other gem-diphosphonic acid complexants are known, some of which have no stable analogue as carboxylic acids.

The strategy we have adopted for destruction of the ligands and metal complexes after use is that they should be either inherently unstable (but not too unstable), or that they will be readily decomposed in homogeneous, aqueous solution through the action of heat and a mild oxidizing agent. This approach is designed to minimize the threat to the environment posed by complexing agents of this type. The incorporation of a degree of instability in a reagent implies the need for detailed knowledge of the kinetics and mechanisms of decomposition of the free ligands and their pertinent metal complexes.

The purpose of the present manuscript is to summarize the progress we have made in the past few years on understanding the coordination chemistry of the diphosphonic acids, the kinetics of oxidation of a representative TUCS ligand, and to briefly outline a few applications which have been developed for their use.

EXPERIMENTAL

The experimental procedures for the results described below have been presented in detail in previous manuscripts (3-9). We have examined the protonation constants and europium(III) (3), thorium(IV) (4), and uranium(VI) (5) complexation for a total of eight phosphonic acid ligands (though not all ligands with all three metal ions): carboxymethanephosphonic acid (CMPA), $(HO_2C)CH_2(PO_3H_2)$; methanediphosphonic acid (MDPA), $CH_2(PO_3H_2)_2$; ethane-1,1-diphosphonic acid (EDPA), $H_3C\text{-}CH(PO_3H_2)_2$; ethane-1,2-diphosphonic acid (E12DPA), $(H_2O_3P)CH_2\text{-}CH_2(PO_3H_2)$; vinylidene-1,1-diphosphonic acid (VDPA), $H_2C{=}C(PO_3H_2)_2$; 1-hydroxyethane-1,1-diphosphonic acid (HEDPA), $H_3CC(OH)(PO_3H_2)_2$; 1,2-dihydroxyethane-1,1-diphosphonic acid (DHEDPA), $(CH_2OH)C(OH)(PO_3H_2)_2$; carboxyhydroxymethanediphosphonic acid (CHMPDA), $(HO_2C)C(OH)(PO_3H_2)_2$. These structures represent a variety of complexing environments which can be compared with carboxylic acid analogues. They also represent a wide variety of thermal stability limits, as will be described below.

Ligand protonation constants have been determined for all of these ligands except CHMDPA (which is too unstable) by potentiometric titration. The metal ion complexation studies were performed by distribution methods utilizing solvent extraction by bis(2-ethylhexyl) phosphoric acid (3-5). The experiments were confined to pH 1 to 2 for europium and uranyl, and 0.5-2.0 M acidity for Th(IV). This restriction was applied to conform to typical requirements of nuclear waste processing, and to avoid complications from cation hydrolysis.

The oxidative instability of one of the TUCS ligands, vinylidene-1,1-diphosphonic acid (VDPA) in hot nitric acid, has been studied using multinuclear NMR for identification and quantitation of soluble reaction products, and mass spectrometry for the analysis of gaseous products (9). The decomposition reaction was run under nominal pseudo-first order conditions, i.e., with VDPA as the limiting reagent (0.1 M in 6.0-8.0 M HNO_3), in an inert (argon or nitrogen) atmosphere. The nitric acid concentration was varied in the range of 6-8 M at temperatures between 60 and 80 °C. A number of experiments were done to elucidate mechanistic details.

RESULTS AND DISCUSSION

Protonation Constants for the Ligands

The protonation constants for CMPA, E12DPA, MDPA, EDPA, HEDPA, DHEDPA, and VDPA are given in Table 1. For VDPA, HEDPA, CMPA, and MDPA the protonation constants have been determined at both 0.1 and 2.0 M ionic strength. For applications in acidic solutions, only the first two ionization reactions are important. The third and fourth protons are not ionized in complex formation in acidic solutions. The most important feature of these data is that the diphosphonic acids are significantly stronger acids than isostructural carboxylic acids.

Lanthanide and Actinide Complexes

It is generally accepted that the principal features of actinide complexation can be represented by the use of analogues, that is, the trivalent lanthanides are representative of the trivalent actinides, thorium representative of tetravalent actinides, and uranium(VI) is representative of hexavalent actinide cations. We have examined the complexes of europium(III), thorium(IV), and uranium(VI) for a first stage evaluation of the diphosphonic acid complexants.

TABLE 1. PROTONATION CONSTANTS FOR DIPHOSPHONIC ACID LIGANDS AT 25°C (VALUES IN PARENTHESES REPRESENT ±2σ UNCERTAINTY LIMIT).

Ligand	pK_1	pK_2	pK_3[a]	pK_4[b]	I
CMPA	1.40(0.2)	4.74(0.01)	7.85(0.01)	—	0.1 M
	0.92(0.10)	4.57(0.01)	7.23(0.01)		2.0 M
E12DPA	1.25(0.14)	2.46(0.02)	6.39(0.02)	8.53(0.05)	0.1 M
MDPA	1.51(0.20)	2.60(0.02)	6.85(0.02)	10.05(0.02)	0.1 M
	1.30(0.01)	2.35(0.01)	34(0.01)	8.90(0.01)	2.0 M
EDPA	1.43(0.01)	2.48(0.01)	6.56(0.01)	9.93(0.01)	2.0 M
VDPA	1.47(0.20)	2.41(0.03)	6.67(0.01)	10.05(0.02)	0.1 M
	1.41(0.01)	2.06(0.01)	6.01(0.02)	8.60(0.01)	2.0 M
HEDPA	1.49(0.20)	2.50(0.02)	6.80(0.01)	10.52(0.01)	0.1 M
	1.56(0.01)	2.20(0.01)	6.20(0.01)	9.12(0.01)	2.0 M
DHEDPA	1.00(0.01)	1.65(0.01)	5.76(0.02)	7.80(0.01)	2.0 M
Mal^{2-}	2.68(0.2)	5.14(0.03)			2.0 M
$Memal^{2-}$	2.80(0.1)	5.40(0.01)			0.1 M
$Succ^{2-}$	3.94(0.02)	5.10(0.05)			2.0 M

[a] These protonation constants for the gem-diphosphonic acids are not corrected for Na^+-L^{4-} or Na^+-HL^{3-} ion pairing (10) - Mal^{2-} is malonic acid, $Memal^{2-}$ is methyl malonic acid, $Succ^{2-}$ is succinic acid. The carboxylate data obtained from (11).

The results to date indicate that, for a given complexant geometry, phosphonic acid ligands are markedly superior to carboxylic acid ligands in acidic solutions. Correlations of the derived thermodynamic data for Eu/Th/U complexes yield a number of factors which collectively account for the enhanced strength of the diphosphonate complexes in acidic media:

1. Protonated species are dominant (MH_hL_l) implying that the metal ion does not have to completely displace all protons from the ligand to form a complex, as is typically observed for carboxylate ligands;
2. Diphosphonates are stronger acids as explained above;
3. Correlation of free energies for complex formation with the appropriate free energies for protonation reactions indicate that the intrinsic binding strength of phosphonic acid groups is 1.5 times that of carboxylic acid groups, exactly proportional to the ratio of the number of oxygen donor atoms in each (4).

Some other features of metal-diphosphonate complexation are:

1. Thermodynamic studies (6) indicate complex stability is derived from a favorable entropy contribution;
2. Substitution of a hydroxy group in the a position of the gem-diphosphonic acid structure increases both the stability and the M:L stoichiometry of the complexes (3-4);
3. Solubility of several of the diphophosphonate complexes exceed that of corresponding oxalates;
4. The order of complex stability is An(IV) > An(VI) > An(III) but unlike typical carboxylate ligands, An(VI) is nearly comparable to An(IV) in acidic solutions.

The relative effectiveness (calculated based on the best available thermodynamic data) of selected diphosphonate ligands as aqueous complexants in separations is shown in Figures 1-3 for europium, thorium and uranium respectively. In Figure 1, the effectiveness of HEDPA and VDPA is compared with that of oxalic acid, DTPA, and H_3PO_4 for stripping of europium from a bis-(2-ethylhexyl) phosphoric acid (HDEHP) solution. It is evident that the diphosphonates are superior to both oxalate and DTPA at pH < 2, but less so above this pH. The phosphoric acid generated in the decomposition of the TUCS does not interfere in the extraction (ignoring its potential effect on metal ion solubility).

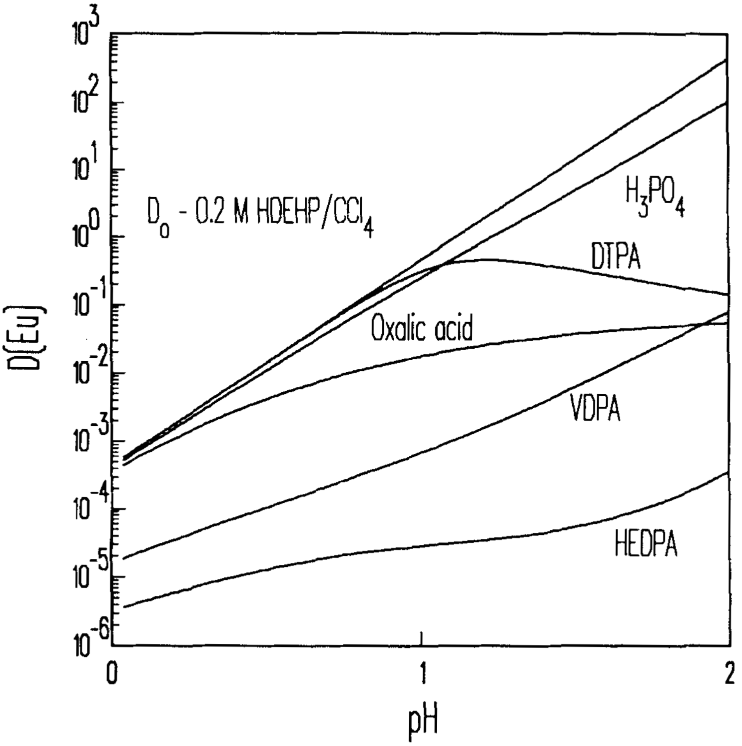


FIGURE 1. Europium distribution ratios (calculated based on thermodynamic data in references 3, 11) for extraction by 0.2 M HDEHP/CCl_4 in contact with 0.1 M solutions of various complexing agents as a function of pH.

In Figure 2, the extraction of uranyl by 0.2 M CMPO/1.2 M TBP/dodecane (TRUEX process solvent) at 0.5 M acid is shown in the presence of varying concentrations of several phosphonic acids and oxalate, the latter included for comparative purposes only as uranyl is typically stripped from this solution by aqueous carbonate wash in a solvent clean-up step (12). The gem diphosphonic acid ligands MDPA, VDPA, and HEDPA are all quite effective stripping agents for uranyl under these conditions, vastly superior to oxalate. By comparison with the carbonate scrub for uranium removal, the diphosphonate complexants offer the advantage of minimal acidity adjustment, and therefore might be preferred under

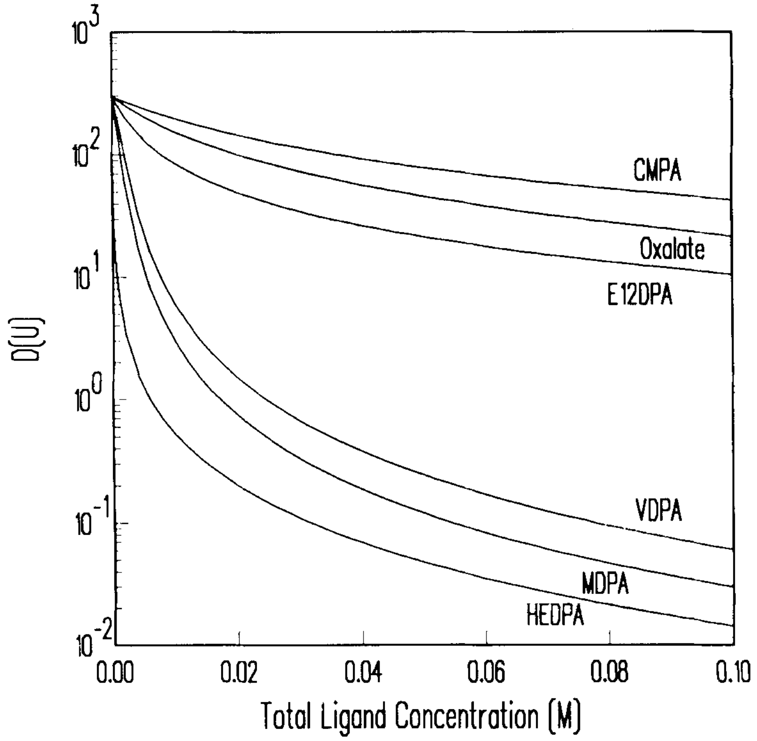


FIGURE 2. Uranium(VI) distribution ratios (calculated based on thermodynamic data in references 5,11) for extraction by 0.2 M octyl-(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide/1.2 M tributyl phosphate/dodecane in contact with 0.5 M HNO_3 containing varying concentrations of selected complexing agents.

certain conditions. The results for the phosphonate complexants E12DPA and CMPA illustrate the effect of increased ring size and carboxylate substitution on the complexing ability of MDPA.

In Figure 3, a generic factor for distribution coefficient lowering of thorium by 0.1 M solutions of HEDPA, VDPA, DTPA, oxalic acid, and H_3PO_4 are shown for acidities between 0 and 2 molar. D_0/D (ratio of the distribution coefficients in the absence (D_0) and presence (D) of the aqueous complexant) is a generic multiplicative factor to demonstrate the predicted effect of the aqueous complexation

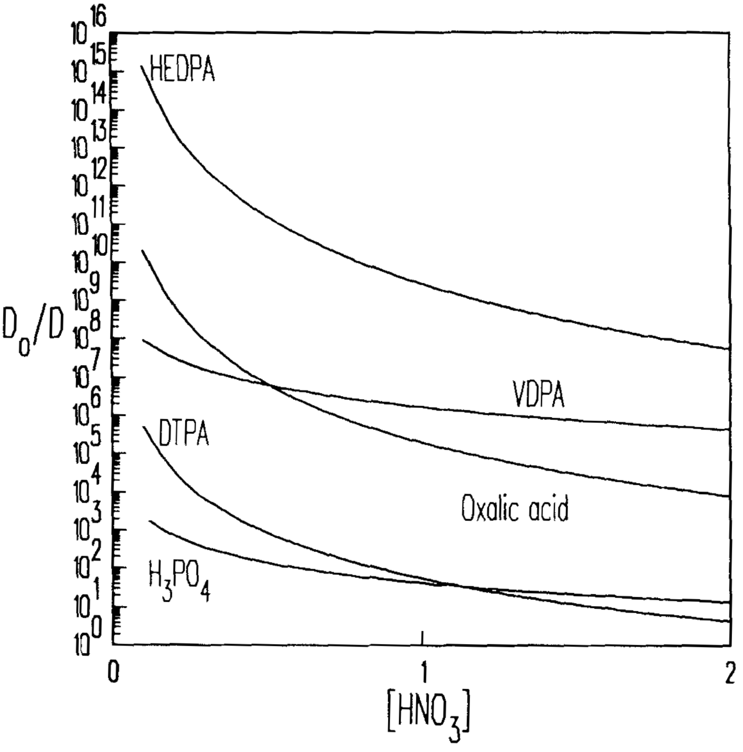


FIGURE 3. Generic factor for the lowering of distribution ratios (calculated based on thermodynamic data in references 3,4, 11) of thorium(IV) as a function of $[HNO_3]$ in the contact with 0.1 M solutions of various complexing agents.

reaction on the metal ion distribution ratio. Within the implicit assumption that the aqueous complex is not extracted or sorbed, the D_0/D term should describe the effectiveness of the complexant independently of the separation system (that is, it should be correct for both ion exchange and solvent extraction processes). The key feature of this plot is the remarkably high value for D_0/D ($\approx 10^8$) observed for HEDPA even at 2 M acidity.

TABLE 2. DECOMPOSITION CONDITIONS FOR SELECTED DIPHOSPHONIC ACID COMPLEXANTS

Complexant	Stability at room temperature		Decomposition
	Acid	Salt	Conditions
MDPA	Stable	Stable	Difficult to Destroy
HEDPA	Stable	Stable	50%, 18 hr, 8 M HNO_3, 100 °C
			100%, H_2O_2, 100 °C, Catalyst
CMPA	Stable	Stable	100%, 4 hr, 8 M HNO_3, 100 °C
VDPA	Slow	Stable	100%, ≥ 5 M HNO_3, ≥ 50 °C
DHEDPA	$t_{1/2} = 15$ d	Stable	100%, with heat in acid
CHMDPA	Unstable Under all Conditions		$t_{1/2} < 5$ min. in HNO_3

Decomposition Rates and Mechanism

The decomposability of selected diphosphonate complexants has been previously reported (7). For the complexants tested, the relative order of thermodynamic stability, as indicated by their resistance to oxidation, is CHMDPA << DHEDPA < VDPA < HEDPA < MDPA (Table 2). The net oxidation half-cell reactions for these ligands are:

CHMDPA; $H_2O + HO_2C\text{-}C(OH)(PO_3H_2)_2 \rightarrow 2\,CO_2 + 2\,H_3PO_3 + 2\,H^+ + 2\,e^-$

DHEDPA; $2\,H_2O + CH_2OH\text{-}C(OH)(PO_3H_2)_2 \rightarrow 2\,CO_2 + 2\,H_3PO_3 + 6\,H^+ + 6\,e^-$

VDPA; $4\,H_2O + H_2C{=}C(PO_3H_2)_2 \rightarrow 2\,CO_2 + 2\,H_3PO_3 + 8\,H^+ + 8\,e^-$

HEDPA; $3\,H_2O + CH_3\text{-}C(OH)(PO_3H_2)_2 \rightarrow 2\,CO_2 + 2\,H_3PO_3 + 8\,H^+ + 8\,e^-$

MDPA; $2\,H_2O + H_2C(PO_3H_2)_2 \rightleftarrows CO_2 + 2\,H_3PO_3 + 4\,H^+ + 4\,e^-$.

The phosphorous acid product is readily oxidized to H_3PO_4. The relative order of ease of oxidation for CHMDPA, DHEDPA and VDPA/HEDPA/MDPA is consistent with the requirement of 1, 3 and 4 electrons lost per equivalent of CO_2 produced. The difference in stability of VDPA, HEDPA, and MDPA (all 4 electrons per CO_2 equivalent) can be ascribed to differences in the reactivity of the carbon backbone of the three ligands (thus to kinetic factors). A recent review of the kinetics of oxidation of organic materials by Ce(IV) would suggest that the kinetic inertness of MDPA is a result of the absence of a readily oxidized "handle" (13).

To utilize the TUCS compounds in actinide separations, it is imperative that the kinetics and mechanism(s) of their decomposition be well understood. To better characterize the physical chemistry of the decomposition reactions, we have examined the rate of the reactions of VDPA in nitric acid solutions (9). The objectives of such studies are to determine specific rate parameters for the reactions of interest, and to derive generic information on the most probable pathways for oxidation reactions of organic complexants in homogeneous aqueous solutions.

The combined results of a number of experiments for VDPA reactions in 8 M HNO_3 at 80 °C are shown in Figure 4. Under these conditions, the disappearance of VDPA from the solution (Figure 4a) can be described by a reaction sequence involving three distinct zones. In the first 230 minutes, representing one half life for VDPA, first order conversion of VDPA to a different gem-diphosphonic acid is observed. We believe this intermediate to be a hydroxy substituted derivative of ethane-1,1-diphosphonic acid. In Zone II, both VDPA and the intermediate disappear in an apparent zero order process. Concomitant with this reaction is observed zero order growth of $[H_3PO_4]$, and the first appearance of gaseous decomposition products (Figure 4b). In the third reaction zone, the same trends continue, but without significant gas generation. Though our analysis is not yet complete, it is clear that stage I of this process represents an induction period leading up to the oxidation of the diphosphonate ligands in Zone II.

Mass spectrometric analysis of the gas indicates 60% of the carbon in VDPA is converted to CO_2, 6% to CO. After 24 hours contact, the remaining soluble carbon was identified by NMR spectroscopy as primarily formic and glycolic acids with no evidence of organophosphorus compounds. Gaseous nitrogen species include N_2, N_2O, and NO in a 1:2:6 mole ratio. The total volume

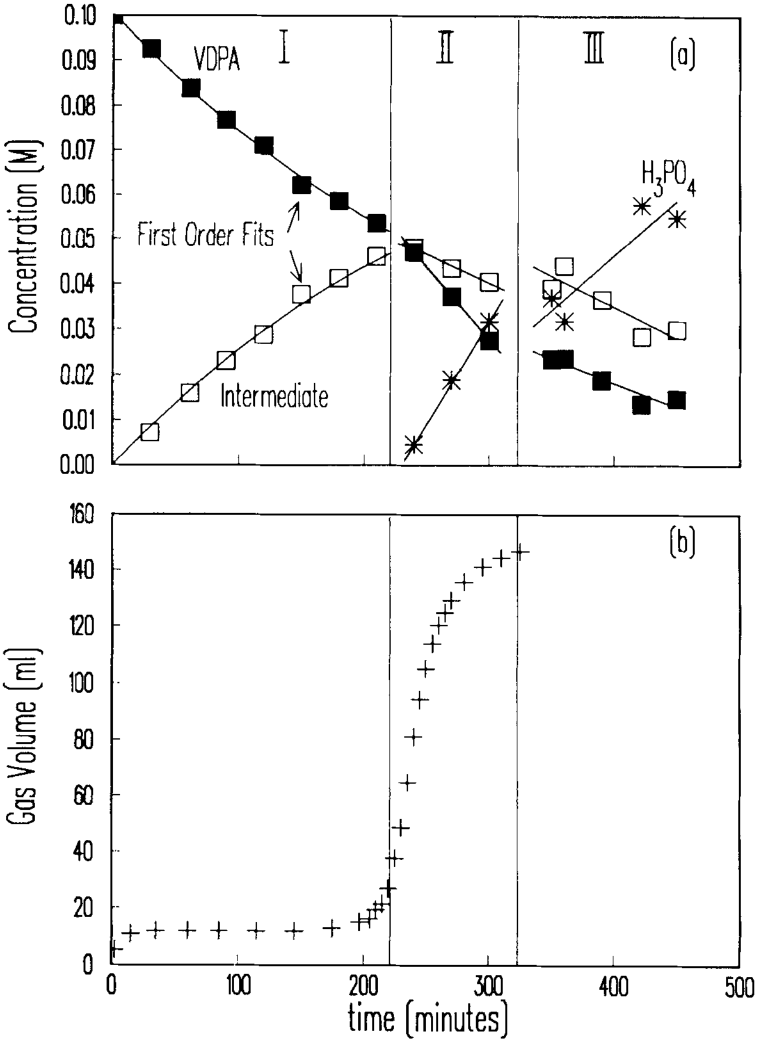


FIGURE 4. a) Observed rate of decomposition of 0.1 M vinylidene-1,1-diphosphonic acid in 8.0 M HNO_3 at 80 °C showing growth of first intermediate in zone I, growth of phosphoric acid and decomposition of VDPA and the intermediate in zones II and III.
b) Gas generation rate under the same conditions.

of nitrogenous gases was approximately equivalent to that of CO and CO_2, though electronic balance is complex. NO_2 was not detected among the gaseous products.

The second (oxidative) stage of the reaction could be induced by the addition of either ethanol or $NaNO_2$ to the VDPA/HNO_3 mixture. It appears that a central role may be played in the oxidation stages of the reaction by nitrous acid. Two routes for nitrous acid participation can be envisioned. A recent review of the mechanisms of nitration reactions indicate that nitrous acid may act as a catalyst in addition of nitroso (NO^+) in electrophilic aromatic substitution reactions (14). The nitroso addition product rapidly reacts with HNO_3 to produce the corresponding nitro derivative and regenerate HNO_2. It is assumed that this nitro addition product is unstable and rapidly decomposes. Alternatively, nitrous acid may react with itself according to the following reactions:

$$3\ HNO_2 + 5\ H^+ + 5\ e^- \rightarrow N_2O + NO + 4\ H_2O$$

$$3\ HNO_2 + 5\ H^+ + 5\ e^- \rightarrow H_2N_2O_2 + NO + 3\ H_2O.$$

Both hyponitrous acid ($H_2N_2O_2$) and nitric oxide (NO) are powerful oxidants in aqueous, acidic solutions. The presence of either could account for the increased importance of the oxidation reaction in the second stage of the reaction. This system is still under investigation.

Applications of TUCS

Complexing agents having the unusual combination of properties described herein could have a number of important applications, particularly in the processing of radioactive wastes. At least two examples have already been reported for their use in solving existing problems (15-17). A supported liquid membrane method for the removal and concentration of uranium from contaminated groundwaters has been suggested (15, 16). The membrane material using Cyanex 272 (a phosphinic acid extractant) has great affinity for uranium(VI) and exhibits good selectivity over ubiquitous Ca^{2+} at pH 2. However, the extractant has such good affinity for uranyl that it is difficult to strip from the membrane without the use of a powerful complexing agent. Both VDPA and HEDPA are suitable for this application. The process has been demonstrated to achieve at least 1000 fold concentration of

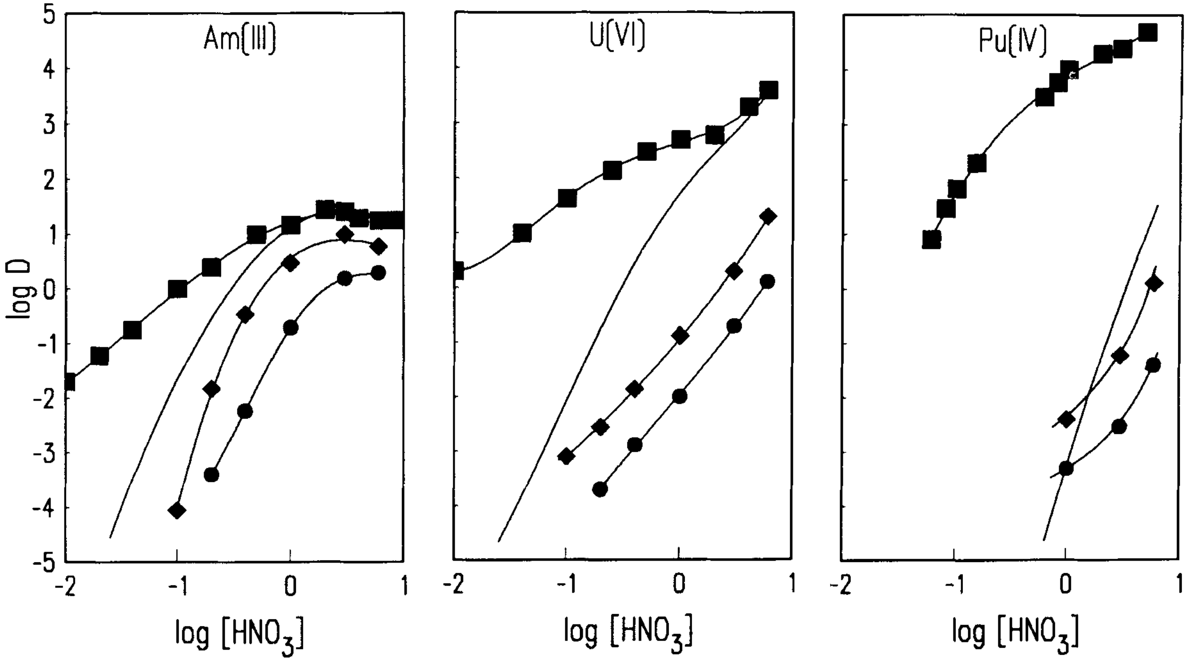


FIGURE 5. Experimental demonstration of the stripping ability of TUCS compounds VDPA (◆), HEDPA (●), and calculated performance of oxalic acid (all complexants at 0.25 M, (■) are the distribution ratios in the absence of complexes).

TABLE 3. HYPOTHETICAL SCHEME FOR ACTINIDE PARTITIONING IN TRUEX PROCESSING USING THERMALLY UNSTABLE COMPLEXANTS

	Calculated Distribution Ratios		
Aqueous Solution	Am(III)	U(VI)	Pu(IV)
2 M HNO_3	28	600	20000
2 M HNO_3, 0.005 M HEDPA	13	9	0.06
0.04 M HNO_3	0.18	10	—
0.04 M HNO_3, 0.01 M HEDPA	—	7×10^{-5}	—

uranium using the TUCS complexants. Greater concentration factors are possible if the thermal instability of the ligands and complexes is exploited.

A second application for the TUCS reagents is as a degradable reagent for the decontamination of equipment. In this study it is assumed that the contamination is present in the form of material sorbed on iron oxide rust (the most stable form of iron oxide in air is FeOOH - Goethite). Combining the complexing ability of the diphosphonic acids with the reducing power of sodium-formaldehydesulfoxylate (SFS - tradename Rongalite from Kodak), the kinetics of dissolution of goethite can be made remarkably rapid at room temperature (17). Complete dissolution of a sample of goethite was achieved in less than 50 minutes using a mixture of 1 M HEDPA in 0.1 M SFS. Only 60% of a similar sample was dissolved by 1 M oxalic acid/0.1 M SFS and less than 10 % by 2 M HCl/0.1 M SFS under the same conditions.

Finally, we have demonstrated by calculation and experimentally the efficacy of HEDPA and VDPA as stripping reagents for the actinides in the TRUEX process (18). The observed reduction in the distribution ratios of americium(III), plutonium(IV) and uranium(VI) from TRUEX process solvent in the presence of 0.25 M VDPA or HEDPA are shown in Figure 5a-c. The performance of oxalic acid under these conditions is shown for comparison.

One can envision a scheme for the selective stripping of the actinides from TRUEX process solvent using HEDPA as a complexant. As shown in Table 3, all three elements are strongly extracted by the TRUEX process solvent from 2.0 M HNO_3. Addition of only 0.005 M HEDPA to the aqueous solution results in the retention of Pu(IV) in the aqueous phase while both Am and U are extracted. The Pu could be recovered from the aqueous solution either as the phosphate after thermal decomposition, or perhaps precipitated as an oxalate to eliminate the phosphorus. Contact of the loaded organic solvent with the normal americium strip solution of 0.04 M HNO_3 permits selective removal of Am from U. The residual uranium in the organic solution could be removed from the organic phase by introducing a trace of HEDPA into the 0.04 M HNO_3.

CONCLUSIONS

This report has been a summary of the current status of an ongoing program. We have gained sufficient insight into the lanthanide/actinide complexation chemistry with phosphonic acid complexants to believe that we can produce ligands with the potential for greater selectivity for metal ions in specific oxidation states. Our understanding of the rates and mechanisms of oxidation of these ligands also has improved. The applications described here illustrate the potential for reagents having the unusual properties of TUCS. A number of other uses in radioactive waste processing and outside of this arena can readily be imagined.

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