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TUCS: A NEW CLASS OF AQUEOUS COMPLEXING AGENTS FOR USE IN SOLVENT EXTRACTION PROCESSES*

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ABSTRACT

The 1-hydroxyethyl-1,1-diphosphonic (HEDPA) and vinylidene-1,1-diphosphonic (VDPA) acids have been studied as stripping agents for Am, Pu, and U from TRUEX process solvent (0.2 M CMPO-1.2 M TBP-dodecane). Both diphosphonic acids have been shown to be highly effective stripping agents using pristine process solvent as well as radiolytically degraded solvent. The actinide-HEDPA and -VDPA complexes are more soluble than the corresponding oxalate complexes and are readily destroyed by metal-catalyzed H_2O_2 oxidation.

INTRODUCTION

During the course of separations by solvent extraction, it sometimes becomes necessary to use supplementary, aqueous soluble, complexing agents to enhance the selectivity of the extractant or to aid in back-extraction or stripping. Despite the usefulness of aqueous complexants in solvent extraction processes, they sometimes have some major drawbacks. First, the complexants that are available will frequently not function effectively at high acidities, e.g. $[H^+] > 0.1$ M. Second, the complexes formed between metal ions and the complexants are sometimes insoluble, which creates a solids problem in solvent extraction equipment. Third, the complexants are not readily degradable and, therefore, they create serious environmental or waste disposal problems. Of the three drawbacks, the last is becoming the most serious in todays climate of environmental constraints.

We have recently been studying a class of complexants which overcome the problems listed above (Nash and Horwitz, 1990, Gatrone et al., in Press). The new class of complexants must meet three criteria: (1) they form highly stable complexes with metal ions in the III, IV, and VI oxidation states in very acidic media (pH < 1 to 7 M strong acid); (2) their complexes with metal ions are water soluble; and (3) the metal ion-complexes and the uncomplexed reagent readily decompose to innocuous substances either spontaneously or in the presence of moderate oxidizing agents. We call this new class of complexants TUCS, which is an acronym for thermally unstable complexants.

We have focused our studies on substituted methane diphosphonic acids for reasons elaborated in (Nash and Horwitz, 1990). Although complexes containing phosphonate ligands have been extensively studied (Rizkalla, 1983), particularly by Soviet Chemists (Kabachnik

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et al., 1974, Kochethova et al., 1983), diphosphonic acids possessing the three properties of TUCS is an innovation (Horwitz et al., 1988).

Three diphosphonic acids in particular, namely, 1-hydroxyethane-1,1-diphosphonic acid (HEDPA), vinylidene-1,1-diphosphonic acid (VDPA) and 1,2-dihydroxyethane-1,1-diphosphonic acid (DHEDPA), meet the three criteria of a TUC. The DHEDPA is a unique TUC because it is stable as its tetrasodium salt but decomposes spontaneously in acid solution with a half-life of approximately 15 days at room temperature (Gatrone, 1989). The objective of this study was to demonstrate the effectiveness of HEDPA and VDPA as stripping agents for actinides from TRUEX process solvent [0.2 M n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO)-1.2 M tri-n-butyl phosphate (TBP)-dodecane]. DHEDPA was not included in the actinide stripping studies because of its instability in acidic media. Nevertheless, its complexing strength for Eu(III) was compared to the other complexants. Based on the data obtained with TRUEX process solvent the application of these reagents to other solvent extraction processes may be deduced.

2. EXPERIMENTAL

HEDPA was obtained from Albright and Wilson Americas, Inc., Richmond, VA, 26229, USA, as a 65 weight percent solution. The HEDPA was purified by crystallization from acetic acid (Merck Index, 1983). VDPA and DHEDPA were synthesized by a procedure described in (Gatrone et al., in Press). Stock solutions of VDPA, HEDPA and DHEDPA were prepared by dissolving the solid in water and standardizing by titration (Nash and Horwitz, 1990). The properties of DHEDPA, VDPA and HEDPA are described in (Gatrone, 1989), (Nash and Horwitz, 1990) and (Gatrone et al. in Press).

The CMPO used in this study was obtained from Atochem North America, Inc., Parkway, Philadelphia, PA 19102, as a solvent extraction grade (95-98%) product, and was purified by double crystallization from hexane. TBP (> 98%) was obtained from Eastman Chemical Company and was distilled from calcium hydride at reduced pressure. A stock solution of the TRUEX process solvent was prepared by dissolving weighed amounts of CMPO and TBP in n-dodecane (99%, Aldrich).

Distribution ratios, D, were measured radiometrically using standard gamma counting (241Am) or scintillation counting (233U, 239Pu, and 242Pu) techniques. Prior to each measurement, the organic phase was preconditioned three times (org. to aq. phase ratio = 0.5) with the appropriate nitric acid solution. Phases were mixed for one minute at room temperature. Since D_U and D_{Pu} were measured by scintillation counting, it was necessary to ensure that no interfering activity was present by purifying the stock solutions of these isotopes. Pu(IV) was obtained by adding small portions of hydrogen peroxide to concentrated nitric acid solution of Pu and evaporating to dryness.

Mock stripping experiments were conducted by extracting the appropriate actinide into the organic phase from 1 to 3 M HNO_3 and subjecting it to successive equilibrations with small volumes of fresh aqueous strip solution.

3. RESULTS AND DISCUSSION

A comparison of the complexing ability of HEDPA, VDPA, and DHEDPA with oxalic acid and EDTA for Eu(III) as a function of pH (0.0 to 2.0) is shown in Fig. 1. The formation constants for Eu(III) are from (Nash and Horwitz, 1990); the oxalic acid and EDTA data are from (Martell and Smith, 1977). (Europium was selected as a standin for Am(III) because of its similar chemical properties and the need to apply instrumental methods without danger of contamination or concern for radiolytic effects.) The complexing ability of the ligands is expressed as the stripping factor (D_o/D), which is defined by the equations below. The higher D_o/D, the more effectively the complexant lowers the distribution ratio. The data in Fig. 1 were obtained using bis 2-ethylhexyl phosphonic acid (HDEHP), however, D_o/D is independent of the extractant. HDEHP was used because D_{Eu} is easily adjusted over the pH range of 0 to 2 by changing extractant concentration. The data in Fig. 1 show clearly the superiority of HEDPA, DHEDPA, and VDPA as stripping agents over oxalic acid and EDTA, especially at pH < 1.

The effectiveness of HEDPA and VDPA in reducing the distribution ratios of U(VI), Pu(IV) and Am(III) from a strong neutral organophosphorus extractant is shown in Figs. 2, 3, and 4, respectively. The extractant used was TRUEX process solvent (0.2 M CMPO-1.2 M TBP-dodecane). The lowering of D is most impressive, especially in the case of Pu. D_{Pu} is reduced by > 10^4 even from 6 M HNO_3; in 1 M HNO_3 the reduction is 10^6. Both diphosphonic acids are also very effective in reducing D_U and D_{Am} from the same process solvent. Thus, HEDPA and VDPA are ideal actinide stripping agents in the TRUEX process if all of the actinides are to be routed to vitrification as opposed to recovery.

No Aqueous Complexes

$$D = \frac{[M(EHE)_n]}{[M^{n+}]} = D_0$$

Aqueous Complexes Formed

$$D = \frac{[M(EHE)_n]}{[M^{n+}] + \sum\sum\sum [M_m H_h L_l]}$$

$$D = \frac{D_0}{1 + \sum\sum\sum \beta_{mhl} [M]^{m-1} [H]^h [L]^l}$$

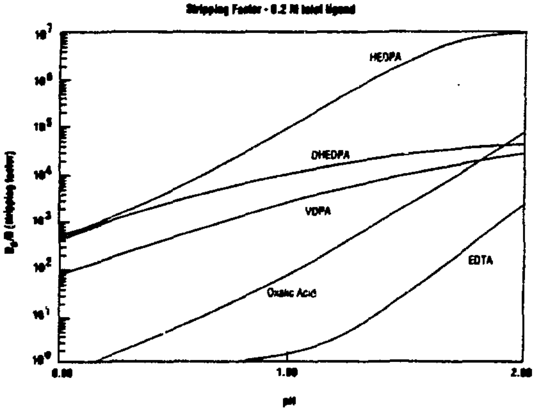
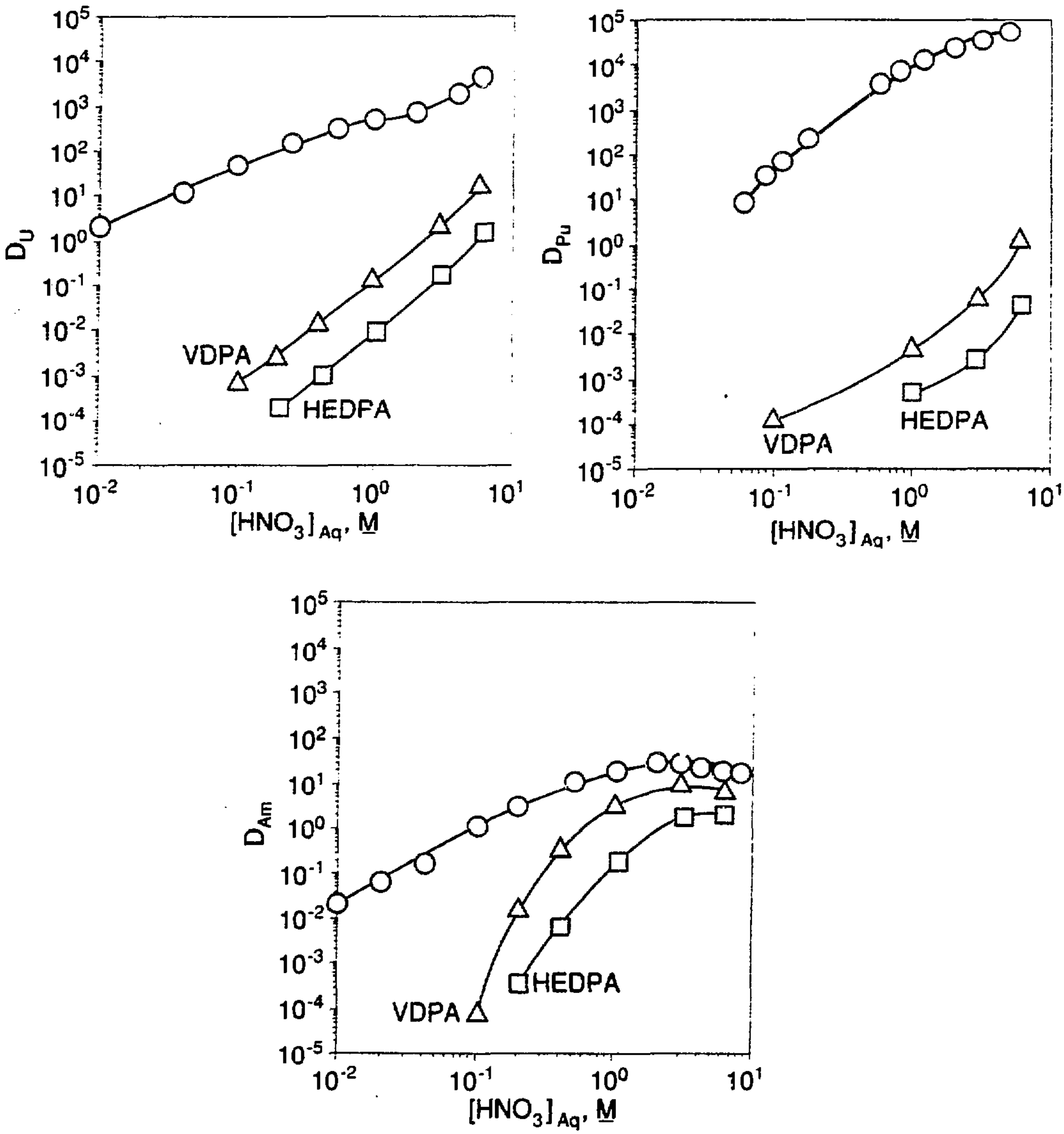


Fig. 1. The effect of aqueous complexes on the metal ion distribution ratios of Eu(III) as predicted from stability constants.



Figs. 2, 3 and 4. Comparison of the acid dependencies of D_U, D_{Pu}, and D_{Am} in the presence and absence of VDPA and HEDPA. Organic phase 0.20 M CMPO-1.2 M TBP-dodecane. HEDPA and VDPA = 0.25 M.

The D_{Am}, on successive stripping of TRUEX process solvent with different concentrations of VDPA is shown in Table 1. The data again show the extreme effectiveness of the TUCS reagent. The higher D_{Am} values obtained on the first contact are due to the extraction of excess nitric acid from the solvent which lowers the pH.*

TABLE 1

Stripping TRUEX-NPH Process Solvent * with VDPA.

	D_{Am}, O/A = 2	
VDPA, M	1st Strip	2nd Strip
0.50 M	8.1×10^{-4}	-
0.25 M	2.1×10^{-3}	1.6×10^{-4}
0.10 M	7.8×10^{-3}	1.9×10^{-4}

	D_{Am}, O/A = 5		
VDPA, M	1st Strip	2nd Strip	3rd Strip
0.25 M	9.3×10^{-3}	2.3×10^{-3}	1.4×10^{-3}

*Am extracted from 1 M HNO_3 and scrubbed twice with 0.1 M HNO_3, O/A = 2.

In addition to being effective stripping agents, the solubility of the UO_2^{2+}, Eu^{3+}, and Th^{4+} complexes with HEDPA and VDPA are at least an order of magnitude greater than the corresponding oxalate complexes. (Eu^{3+} and Th^{4+} were used as standins for Am^{3+} and Pu^{4+}, respectively.)

The ability to readily decompose TUCS and their metal ion complexes is an important property of these reagents. HEDPA, VDPA, and DHEDPA may be decomposed in < 5 hrs by metal catalyzed oxidation with H_2O_2 at 80 °C. The solution to be decomposed is made 2 to 3 M in H_2O_2 and 10^{-3} M in Na_3VO_4. Identified decomposition products are phosphoric acid and CO_2 with lesser amounts of acetic and formic acids (McEwen and Meisinger, Personal Communication). VDPA and DHEDPA (but not HEDPA) may be completely decomposed in < 3 hrs. in 8 M HNO_3 at 100 °C. Decomposition of VDPA and HEDPA in the presence of macro-concentrations of actinides and lanthanides yields granular precipitates which are believed to be insoluble phosphates. In the case of Nd(III) the precipitate has been identified as hexagonal $NdPO_4 \cdot 0.5H_2O$ (Morss, Personal Communication).

The effectiveness of HEDPA and VDPA in complexing actinides at low pH's may also be exploited in stripping hydrolytically and radiolytically degraded solvent. Radiolytic and hydrolytic degradation of a neutral extractant such as CMPO or TBP is manifested by an increase in the distribution ratio of e.g., Am(III), at low acidity because of the the generation of acidic extractants. (Acidic extractants are very effective at low acid concentration, whereas neutral extractants have very low D's under the same condition.) For example, the footnote in Table 2 compares D_{Am} at 0.04 M HNO_3 for pristine and degraded TRUEX process solvent. The presence of acidic extractants is responsible for the 8-fold increase in D_{Am}. Table 2 shows the reduction in D for Am(III), Pu(IV), and U(VI) by using 0.25 M HEDPA and an organic-to-aqueous phase ratio (O/A) equal to five on degraded TRUEX process solvent. For each transuranic element the reduction is over 10^4 in three successive contacts.

Very large reductions in alpha activity from process solvents are very important in nuclear waste processing. To reduce the level of toxicity of TRU or high-level waste, very large decontamination factors for all transuranic elements are required. These large decontamination factors require the recycling of the process solvent with negligible levels of alpha activity. The HEDPA and VDPA are far superior to any chemical reagent for stripping actinides and Zr and rare earth fission products. By preceding the alkaline (Na_2CO_3) solvent wash step (which is used to remove organic degradation products) with a TUCS strip, one can avoid generating an alkaline TRU waste stream. The TUCS strip reagent may be recycled a number of times before decomposing the diphosphonic acid by oxidation. Since only very low concentrations of actinides are involved in solvent cleanup and, thus, no precipitate will be formed, the decomposed TUCS solution may be recycled to the feed. This procedure avoids generating additional TRU waste streams in solvent cleanup operations.

TABLE 2

Stripping of Degraded* TRUEX Process Solvent (0.2 M CMPO - 1.2 M TBP in Dodecane)
Aqueous Strip: 0.25 M HEDPA, O/A = 5.

Strip No.	D_{Am}	D_{Pu}	D_U
1	$4.3\text{x}10^{-3}$	$1.6\text{x}10^{-4}$	$1.6\text{x}10^{-3}$
2	$1.8\text{x}10^{-3}$	$\sim 9\text{x}10^{-3}$	$\sim 9\text{x}10^{-3}$
3	$\sim 4\text{x}10^{-3}$	---	$\sim 2\text{x}10^{-3}$
Overall reduction in nuclide conc.	$2.8\text{x}10^{5}$	$3.9\text{x}10^{4}$	$3.6\text{x}10^{4}$

*Hydrolytic and Radiolytic Degradation

$D_{Am} = 1.6$ at 0.4 M HNO_3

$D_{Am}^{ref} = 0.2$ at 0.4 M HNO_3

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