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COMPARATIVE EVALUATION OF DHDECMP AND CMPO AS EXTRACTANTS FOR RECOVERING ACTINIDES FROM NITRIC ACID WASTE STREAMS

by

S. Fredric Marsh and Stephen L. Yarbro

ABSTRACT

Certain neutral, bifunctional organophosphorus compounds are of special value to the nuclear industry. Dihexyl-N,N-diethylcarbamoylmethylphosphonate (DHDECMP) and octylphenyl-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) are highly selective extractants for removing actinide and lanthanide elements from nitric acid. We obtained these two extractants from newly available commercial sources and evaluated them for recovering Am(III), Pu(IV), and U(VI) from nitric acid waste streams of plutonium processing operations. Variables included the extractant (DHDECMP or CMPO), extractant/tributylphosphate ratio, diluent, nitrate concentration, nitrate salt/nitric acid ratio, fluoride concentration, and contact time. Based on these experimental data, we selected DHDECMP as the preferred extractant for this application.

INTRODUCTION

Numerous investigators have studied carbamoylmethylphosphoryl derivative extractants during the past decade.[1-6] Of these compounds, carbamoylmethylphosphonates and carbamoylmethylphosphine oxides appear to be the most selective structures for extracting actinide and lanthanide elements from nitric acid. Of particular significance is the high extractability of actinides in their (III), (IV), and (VI) oxidation states, a fact that often eliminates the usual need for prior oxidation state adjustment.

Previous published studies have demonstrated the potential value of dihexyl-N,N-diethylcarbamoylmethylphosphonate (DHDECMP) for full-scale nuclear materials processes. Because no commercial suppliers of pure DHDECMP existed until very recently, these studies used impure or purified DHDECMP in conventional solvent extraction[7-11] and process-scale extraction chromatography[12] systems.

Other investigators[13] developed a reliable but tedious laboratory-scale procedure suitable for preparing small quantities of pure DHDECMP for analytical applications.[14] However, repurification of the large quantities of extractant required for plant-scale applications is impractical. The implementation of a full-scale nuclear materials process based on DHDECMP has therefore had to await a reliable source of pure extractant.

High-purity DHDECMP recently became available from a new commercial supplier who uses a patented phase-transfer catalysis process[15] to synthesize this compound. The advent of this new commercial source prompted us to reevaluate DHDECMP for removing actinides from nitric acid waste streams at Los Alamos. We also elected to evaluate the performance of octylphenyl-N,N- diisobutylcarbamoylmethylphosphine oxide (CMPO), an extractant selected for the proposed TRUEX process.[16] Comparative performance data for both extractants, whose structures are shown in Fig. 1, were determined over a wide range of variables that encompass the composition of typical process feed streams.

REAGENTS AND APPARATUS

DHDECMP, obtained from Occidental Chemical Corporation, Specialty Products Division, Niagara Falls, New York, was used without additional purification.

CMPO, obtained from M&T Chemicals, Inc., Rahway, New Jersey, was purified by contact with cation exchange resin, anion exchange resin, and carbonate washing, the MIX procedure of Horwitz and Gatrone.[17]

Tetrachloroethylene (TCE), obtained from J. T. Baker Chemical Co., Phillipsburg, New Jersey, was used as received.

Isopar H, a highly purified mixture of C_9 to C_{12} isoalkanes, was used as received from the manufacturer, Exxon Chemical Company, Houston, Texas.

Reagent-grade nitric acid, sodium nitrate, and hydrofluoric acid were used as received.

Extraction bottles, 1-ounce, high-density polyethylene with 18-millimeter caps (catalog number 16054-010, were obtained from VWR Scientific, San Francisco, California.

Dispensing spouts (catalog number F12638-0018) to fit the 1-ounce bottles with 18-millimeter caps were obtained from Bel-Art Products, Pequannock, New Jersey.

A Burrell model 75 wrist-action shaker (catalog number 57040-049) was obtained from VWR Scientific, San Francisco, California.

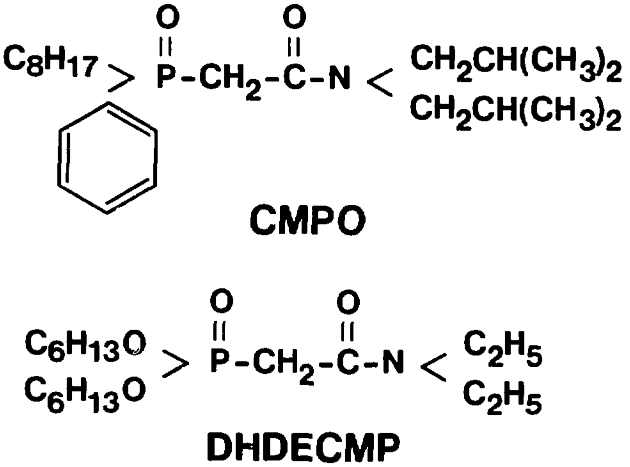


Fig. 1. Chemical structures of octylphenyl-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) and dihexyl-N,N-diethylcarbamoylmethylphosphonate (DHDECMP).

EXPERIMENTAL

General

We measured all distribution coefficients for the **initial contact** of an aqueous solution and organic solution of the specified compositions. Neither the aqueous nor organic solution was pre-equilibrated. Thus, the measured distribution coefficients represent the initial solvent extraction stage rather than a later stage at which each phase has become equilibrated with the other. This distinction is emphasized because some published distribution coefficients are based on measurements using pre-equilibrated solutions.

Extractions

We combined 5-milliliter portions of each combination of extractant solution and aqueous mixture in individual 1-ounce polyethylene bottles. A 0.100-milliliter portion of a Pu(IV) stock solution in 7 *M* nitric acid was added to each bottle immediately before extraction. (All aqueous solution compositions were calculated and prepared to provide the desired acid concentrations after addition of the 0.7 millimole of nitric acid in the plutonium stock solution.)

The addition of 0.100 milliliter of stock solution to each aqueous solution provided a known, constant amount of plutonium plus its ^{237}U and ^{241}Am daughters. The plutonium content of the extracted solutions was always about 4 grams per liter; americium content was about 15 micrograms per liter, and uranium was present only at trace concentrations. The oxidation states of these three actinides immediately before extraction were Am(III), Pu(IV), and U(VI). Any significant change in oxidation state during the brief extraction period was unlikely.

We sealed the polyethylene extraction bottles that contained each aqueous/organic combination with solid Polyseal caps, and the contents were dynamically contacted for a specified time using a wrist-action shaker. Each bottle and its contents then were allowed to stand for at least 5 minutes to allow the phases to separate. Following phase separation, we removed the solid cap and replaced it with a dispensing spout cap, shown in Fig. 2.

Fig. 2. Polyethylene bottle, with a solid cap for extraction and with dispensing spout cap as a separatory funnel, used to separate the two phases.

The lower, aqueous phase was transferred from the extraction bottle to an appropriate assay container as described in the following steps:

1. The dispensing tip of the upright extraction bottle was inserted into an inverted liquid scintillation vial (the assay container).
2. While still being held upright, the extraction bottle was squeezed slightly to expel a few milliliters of air.
3. With the spout tip of the extraction bottle still in the vial, both bottles were inverted to restore the vial to an upright position while pressure was simultaneously released on the extraction bottle. (The incoming air removed any of the upper phase that otherwise could remain in the spout tip as the extraction bottle is inverted.)
4. While the extraction bottle was in the inverted position, the lower phase was expelled from the extraction bottle into the assay vial (if it was aqueous) or into a waste container (if it was organic) by applying gentle pressure until the phase boundary approached the end of the dispensing tip.
5. The few drops that contained the phase boundary were discarded into a waste container along with the upper phase (if it was organic).
6. If the upper phase was aqueous, it was dispensed into a vial for assay.

Gamma Assay Technique

We assayed the extracted aqueous portions in all cases using gamma spectrometry and compared them with an identical unextracted aqueous portion. The difference between these two measurements, for each actinide, represented the quantity extracted. Gamma spectrometric assays were based on the 59.5- keV, 129-keV, and 208-keV gamma-ray peaks of ^{241}Am, ^{239}Pu, and ^{237}U, respectively.

Computation of Distribution Coefficient (Kd) Values

We computed Kds for each extraction using the relationship

$$Kd = \frac{concentration\ of\ actinide\ in\ organic\ phase}{concentration\ of\ actinide\ in\ aqueous\ phase}.$$

Using gamma spectrometry, we indirectly determined the concentration of each actinide extracted into the organic phase by measuring the difference in its concentration before and after extraction in otherwise identical aqueous portions.

Extractants Tested

The value of DHDECMP for extracting actinides has been recognized for many years. More recently, researchers have developed and proposed CMPO as the extractant for the TRUEX process.[16] CMPO is unquestionably a stronger extractant than DHDECMP; however, the higher extractability of actinides makes back-extraction from CMPO more difficult. CMPO is expected to offer superior chemical and radiolytic stability and also lower solubility in aqueous nitrate solutions. DHDECMP, on the other hand, is more selective in rejecting common impurity elements, as shown in Fig. 3.

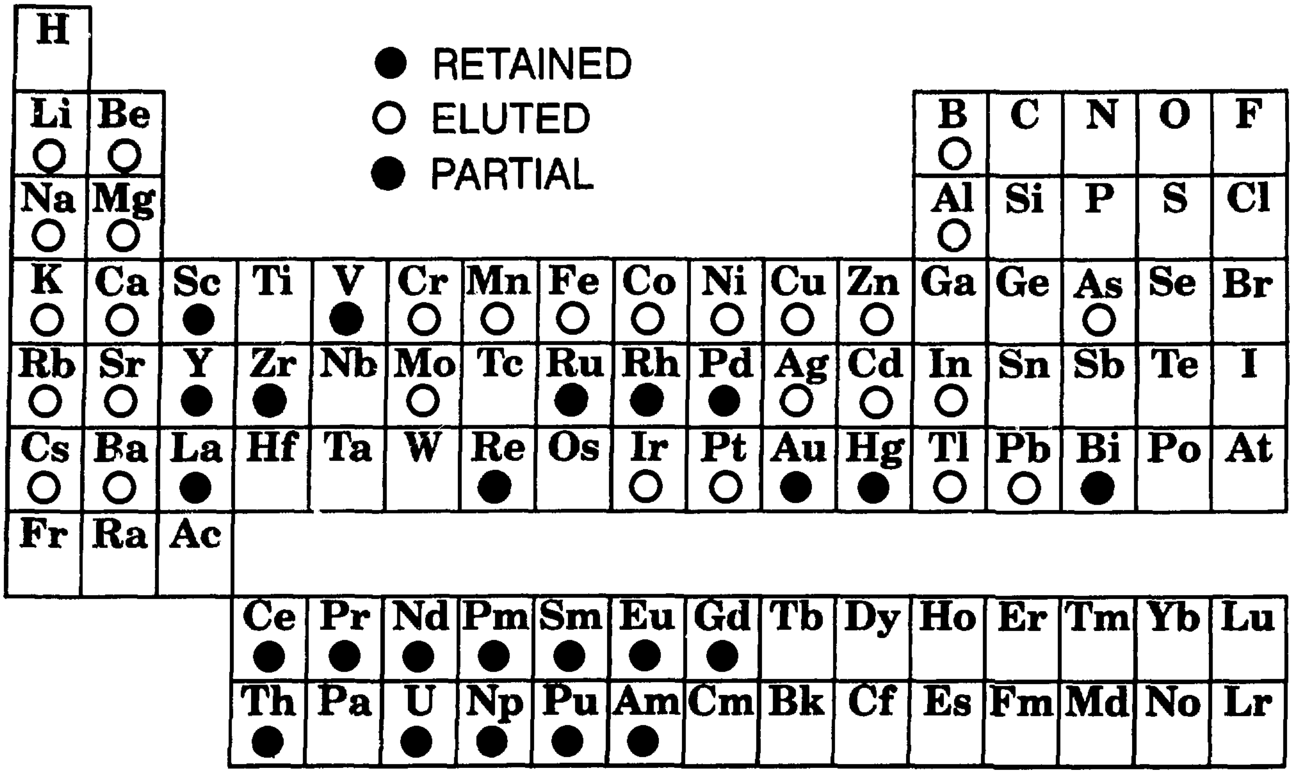


Fig. 3. Distribution of many elements on DHDECMP extraction chromatography column from 5.5 *M* nitric acid.[14]

Because each extractant appears to offer unique advantages and disadvantages, we elected to evaluate both under identical conditions. The only significant difference was that CMPO solutions were 0.25 *M*, whereas DHDECMP solutions were 0.75 *M*. Despite the threefold-higher concentration of DHDECMP, the current threefold-lower price of DHDECMP made the overall costs of the two extractants essentially equal. The present prices of both extractants reflect the small current market; however, the cost of either extractant would be expected to drop substantially as a larger market develops.

Diluents Tested

We evaluated tetrachloroethylene (TCE) as a diluent because researchers have proposed it as the diluent for the TRUEX process, primarily because TCE is nonflammable. The disadvantages of TCE include its propensity for forming persistent organic dispersions in the aqueous phase, its high volatility, its classification as a carcinogen, and its ability to form radiolysis products that are corrosive to stainless steel process environments.

Isopar H, although flammable, has a sufficiently high flash point to make ignition unlikely. The long record of safe operation with such kerosene-type diluents within the nuclear industry attests to the adequacy of this safety margin. Moreover, Isopar H is an order of magnitude less volatile than TCE under identical conditions. It provides rapid and complete phase separation after extraction and is nontoxic. This combination of favorable properties prompted us to also evaluate Isopar H as a diluent.

Other Variables Tested

We evaluated total nitrate concentrations of 0.45 *M*, 1.5 *M*, 4.5 *M*, and 7.5 *M*. Each nitrate level was evaluated as 100% nitric acid, as 2/3 nitric acid and 1/3 sodium nitrate, and as 1/3 nitric acid and 2/3 sodium nitrate. Each of the 12 combinations of total nitrate and nitric acid/nitrate salt ratio was evaluated at fluoride concentrations of zero, 0.02 *M*, and 0.05 *M*.

Evaluation of the 36 different aqueous compositions with each of the 4 extractant/diluent combinations produced Kd values of Am(III), Pu(IV), and U(VI) for each of the 144 unique aqueous/organic combinations.

RESULTS AND DISCUSSION

General

Experimental distribution data usually are presented in a format that illustrates the effect of a single variable. Because this study evaluated multiple variables, we sought a format that would allow presentation of the individual and interactive effects of many variables in a single figure. A "tree" format suggested by Richard J. Beckman of the Los Alamos National Laboratory Statistics Group simultaneously illustrates the effects of total nitrate, nitrate salt/nitric acid ratio, and fluoride concentration.

Effects of Specific Variables

Contact Time. Preliminary experiments demonstrated that Kds for a dynamic contact period of 10 minutes were equivalent to those obtained for a 1-minute contact period. Based on this equivalency, the remainder of this study employed 1-minute dynamic contact periods.

Extractant. CMPO consistently extracts americium, plutonium, and uranium more strongly than does DHDECMP. This fact is reflected in Figs. 4-6, which show the distribution coefficients of individual actinides as a function of the extractant/diluent combinations from nitric acid solutions (without salt or fluoride).

The higher extraction of actinides by CMPO from medium concentrations of nitric acid can be beneficial; by contrast, high Kds from dilute nitric acid are a distinct disadvantage because they make back-extraction much more difficult. DHDECMP, however, provides adequately high Kds from medium concentrations of nitric acid but offers Kds from dilute acid that are sufficiently low to allow americium and plutonium to readily be back-extracted.

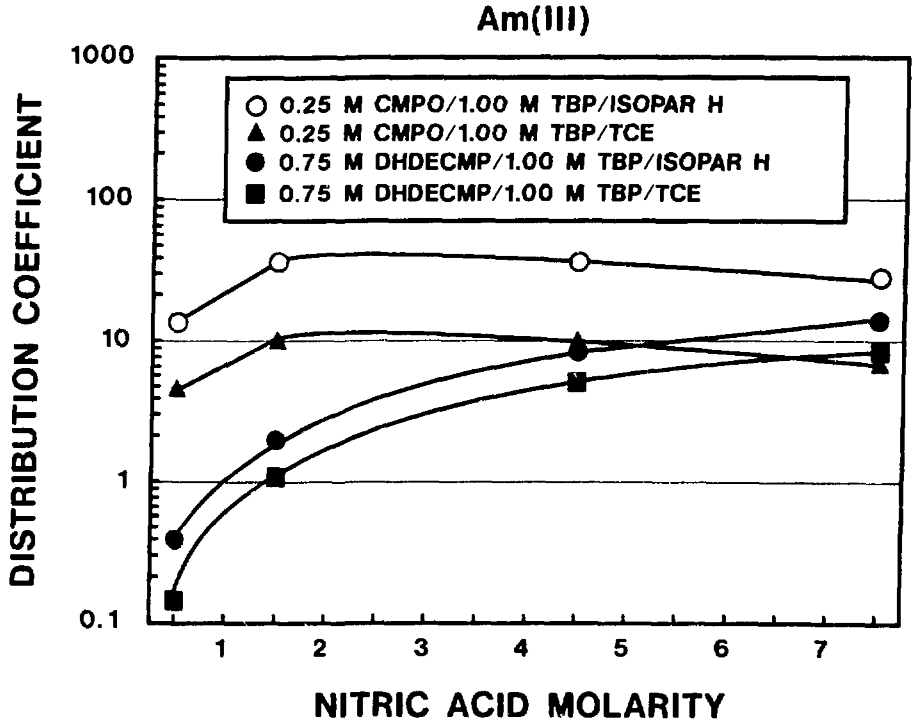


Fig. 4. Extraction of Am(III) into various extractant/diluent combinations as a function of nitric acid concentration.

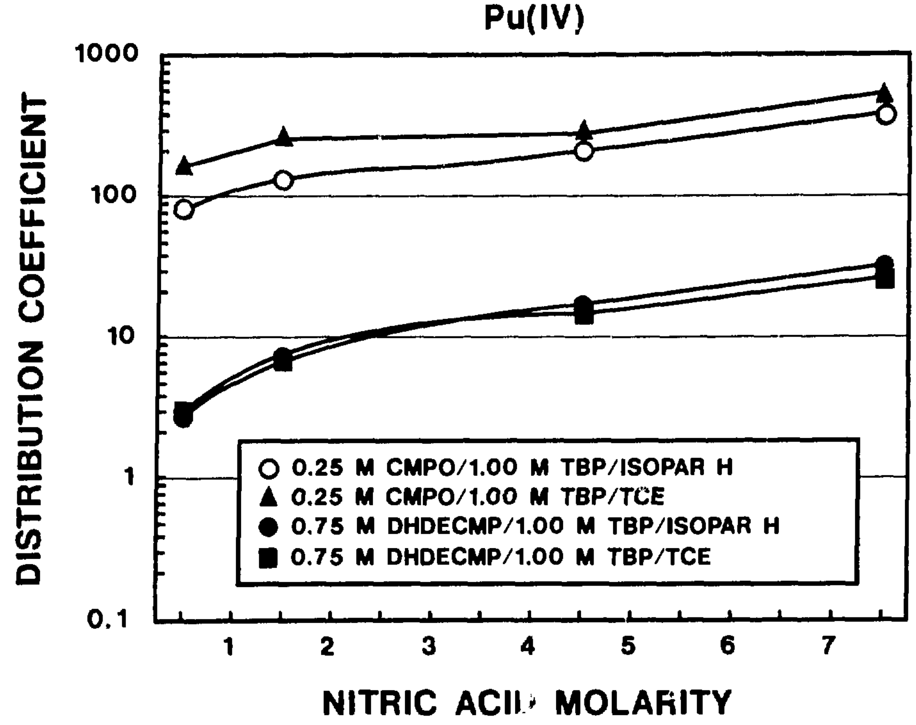


Fig. 5. Extraction of Pu(IV) into various extractant/diluent combinations as a function of nitric acid concentration.

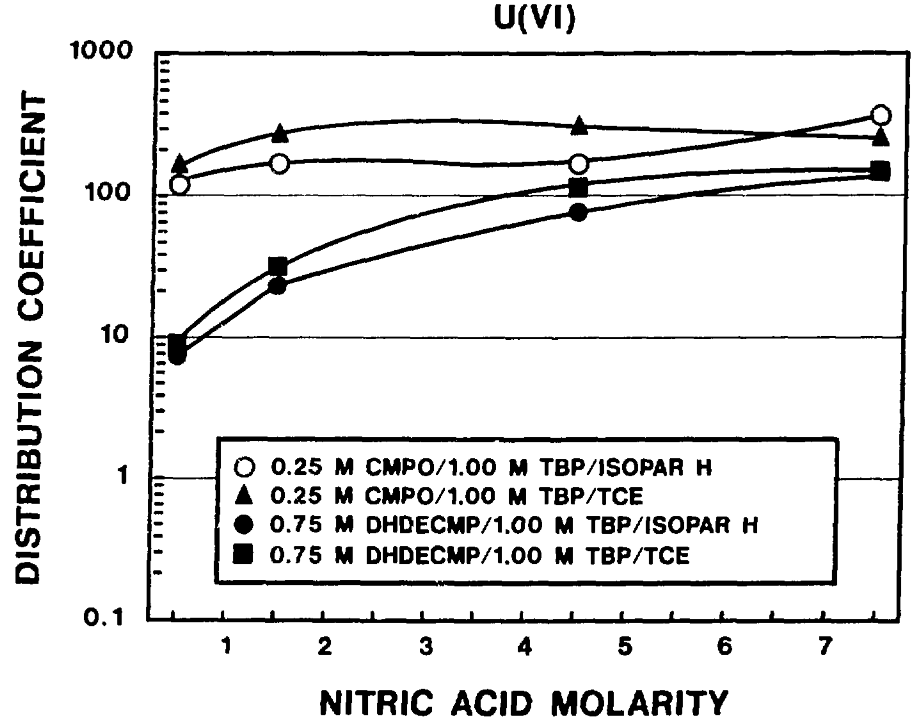


Fig. 6. Extraction of U(VI) into various extractant/diluent combinations as a function of nitric acid concentration.

Diluent. Investigators have proposed TCE for use in the TRUEX process not only because it is nonflammable but also because it is a reasonably good solvent for CMPO and CMPO/metal complexes. In our studies, however, TCE formed persistent organic dispersions in the aqueous phase, a drawback that made assay of the aqueous phase difficult and unreliable. These dispersions required that the extracted aqueous phase be scrubbed with a fresh portion of TCE to remove residual extractant before we could obtain the TCE-diluent data reported herein. Diluents that have been used safely for many decades in the nuclear industry include certain flammable liquids such as kerosene, whose high flash points provide an adequate margin of safety. Although DHDECMP and CMPO are only slightly soluble in kerosene, the addition of tributylphosphate (TBP) makes the three components miscible.

Initial experiments with Isopar H, a kerosene-type diluent approved for use in the Los Alamos Plutonium Facility, showed much-improved phase separation, which eliminated the need to scrub the aqueous phase as done with TCE. An additional benefit of Isopar H was its ability to provide higher Kds for Am(III) using either extractant than provided by TCE (Fig. 4). The Kd enhancement with Isopar H is especially pronounced for Am(III) extraction by CMPO. Comparative data for Pu(IV) and U(VI) extraction into DHDECMP and CMPO, using TCE or Isopar H as the diluents, are shown in Figs. 5 and 6.

Nitrate Salt/Nitric Acid Ratio. High concentrations of nitrate salts are common components of nuclear process solutions. Evaluation of the effect of nitrate in the form of nitrate salts was therefore essential. The general effect of replacing nitric acid with nitrate salt is a small increase in the distribution coefficient in all of the systems studied. This increase is attributed to the higher activity of nitrate ion that results from the more complete dissociation of nitrate salt as compared with nitric acid.

TBP/Extractant Ratio. The PUREX process has used TBP for many years to extract uranium and plutonium from various nitrate solutions. TBP, proposed as a phase modifier with CMPO in the TRUEX process, decreases the extraction of actinides from dilute acid, although it increases the extraction of actinides from medium concentrations of nitric acid when compared with extraction by only CMPO.[18] Moreover, TBP increases the solubility of CMPO and CMPO/metal complexes in the organic phase.

Our preliminary study that compared 1.00 *M* DHDECMP/TCE and 1.00 *M* DHDECMP/0.35 *M* TBP/TCE showed that the Kds of uranium, plutonium, and americium were not significantly affected by the presence or absence of TBP. We elected to include TBP as a component of both organic extractants studied, however, (1) to be consistent with the recommended TRUEX composition when CMPO was the extractant, (2) to increase the solubility of the DHDECMP and its metal complexes when DHDECMP was the extractant, and (3) to maintain similar compositions where possible during the comparative evaluation of DHDECMP and CMPO.

A serious disadvantage of TBP is that it also extracts large quantities of nitric acid. The extracted acid subsequently back-extracts into dilute acid used to back-extract the extracted actinides. The net result is a requirement for additional strip stages that serve no purpose other than to remove the excess acid previously extracted by TBP. Substitution of a different organic phase- modifier that does not extract nitric acid would allow the number of strip stages to be minimized. (This possibility is being investigated.)

Behavior of Individual Actinide Elements

Figures 7–30 show the results of actinide element extraction under various conditions.

Americium

DHDECMP/TBP/TCE. (Figs. 7 and 8) Americium extraction increases slightly with nitrate salt levels. A small but consistent increase results from increasing fluoride when nitrate salt is absent; however, a consistent decrease results from increasing fluoride at the highest nitrate salt levels.

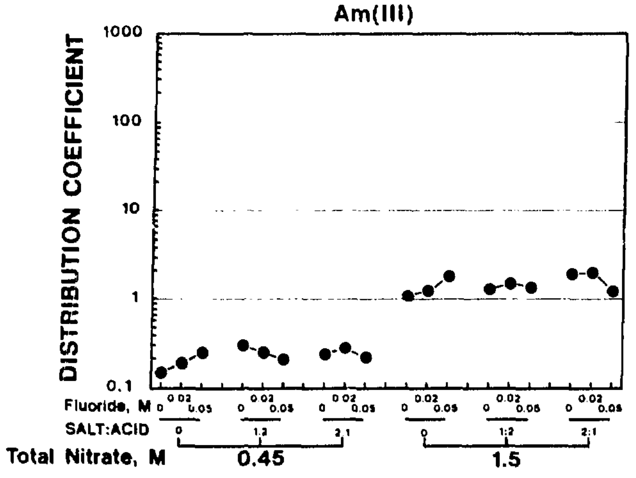


Fig. 7. Extraction of Am(III) into 0.75 M DHDECMP/1.00 M TBP/TCE as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

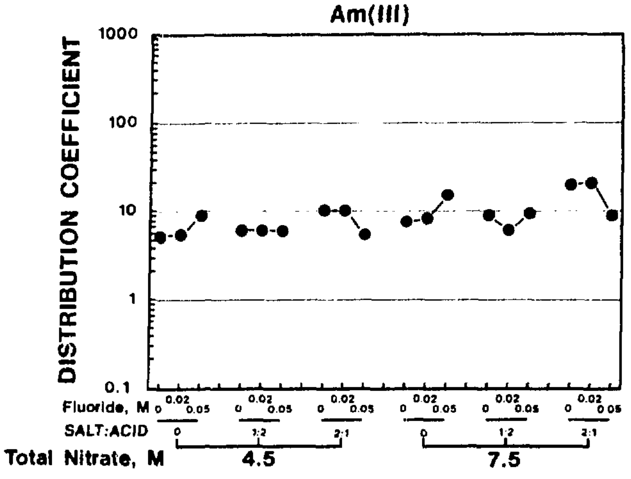


Fig. 8. Extraction of Am(III) into 0.75 M DHDECMP/1.00 M TBP/TCE as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

DHDECMP/TBP/Isopar. (Figs. 9 and 10) Americium extraction increases significantly with nitrate salt levels but is essentially unaffected by fluoride. Kd values with Isopar diluent are generally double to triple those obtained with TCE diluent.

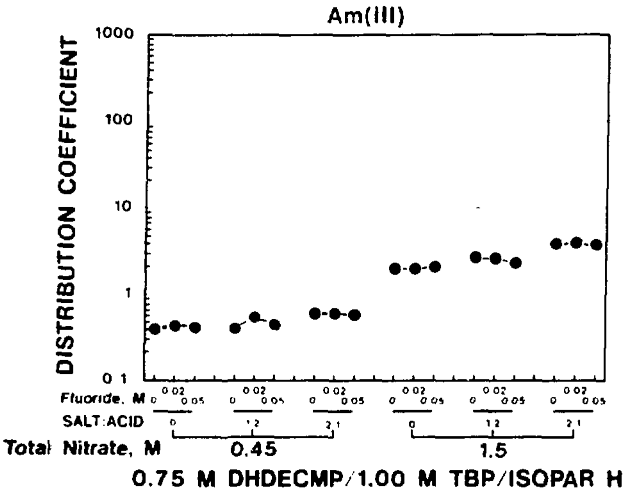


Fig. 9. Extraction of Am(III) into 0.75 M DHDECMP/1.00 M TBP/Isopar H as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

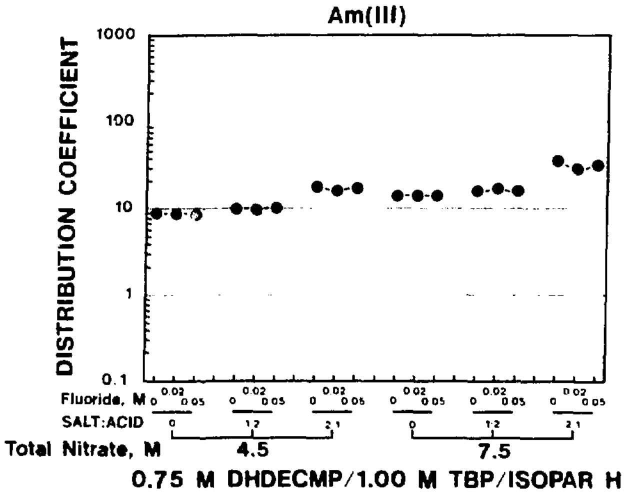


Fig. 10. Extraction of Am(III) into 0.75 M DHDECMP/1.00 M TBP/Isopar H as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

CMPO/TBP/TCE. (Figs. 11 and 12) Americium extraction increases significantly with nitrate salt levels. Fluoride has no effect on americium extraction. Kd values are similar from 7.5 *M* nitrate but are approximately 30 times higher from 0.45 *M* nitrate when compared with the DHDECMP/ TBP/TCE system. Thus, CMPO offers little improvement in extraction from medium concentrations of nitric acid, but back-extraction into dilute acid is far more difficult.

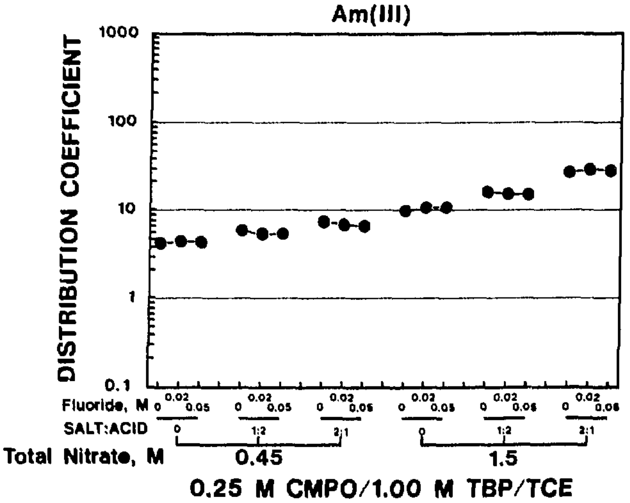


Fig. 11. Extraction of Am(III) into 0.25 *M* CMPO/1.00 *M* TBP/TCE as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

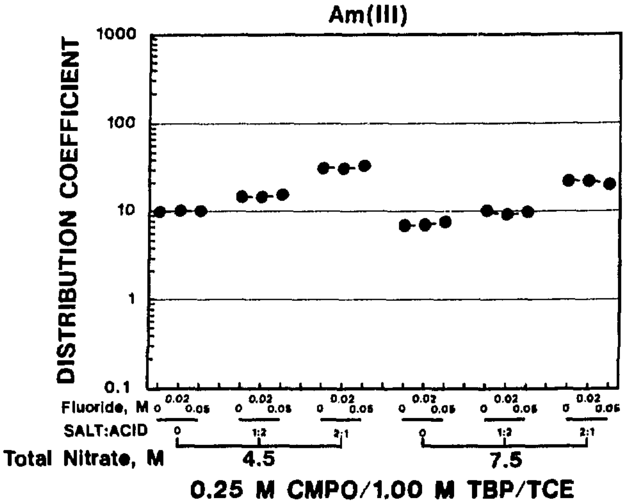


Fig. 12. Extraction of Am(III) into 0.25 *M* CMPO/1.00 *M* TBP/TCE as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

CMPO/TBP/Isopar. (Figs. 13 and 14) A slight decrease in americium extraction is associated with increasing fluoride levels. Kd values with Isopar diluent are approximately four times those obtained with TCE diluent. (This difference represents the largest diluent effect of the entire study.) Kd values of this CMPO/TBP/Isopar system, when compared with the DHDECMP/TBP/ Isopar system, are only double to triple from 7.5 *M* nitrate but are approximately 40 times higher from 0.45 *M* nitrate. Again, the demonstrated increased difficulty in back-extracting americium from CMPO is a major disadvantage.

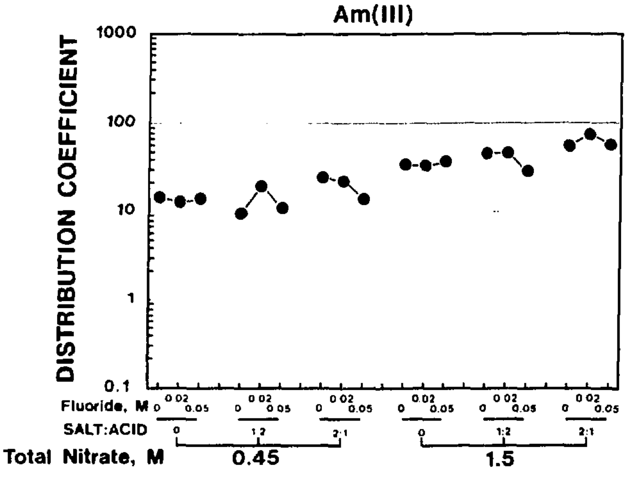


Fig. 13. Extraction of Am(III) into 0.25 *M* CMPO/1.00 *M* TBP/Isopar H as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

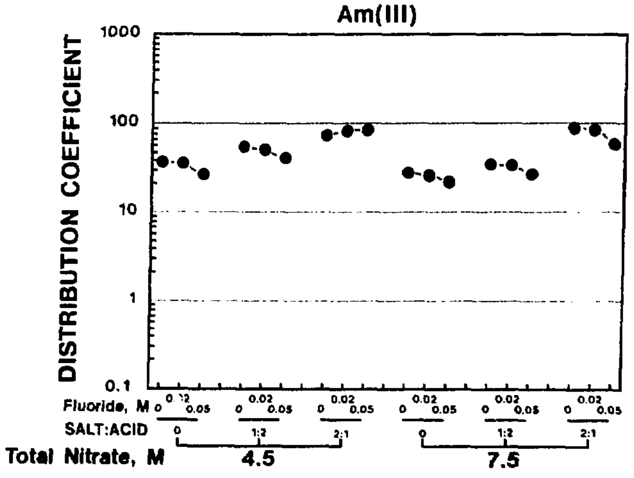


Fig. 14. Extraction of Am(III) into 0.25 *M* CMPO/1.00 *M* TBP/Isopar H as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

Plutonium

DHDECMP/TBP/TCE. (Figs. 15 and 16) Plutonium extraction increases slightly with increasing nitrate salt levels. Fluoride, however, causes a significant decrease in extraction for all conditions studied, with the greatest effect observed at low nitrate concentrations. This is fortunate because the effect of fluoride is lowest during extraction conditions and greatest during back- extraction conditions, where fluoride could be intentionally added to facilitate removal of plutonium from the organic phase.

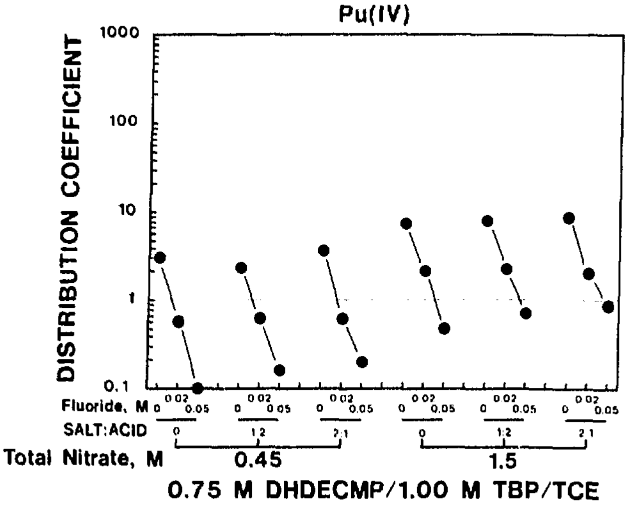


Fig. 15. Extraction of Pu(IV) into 0.75 *M* DHDECMP/ 1.00 *M* TBP/TCE as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

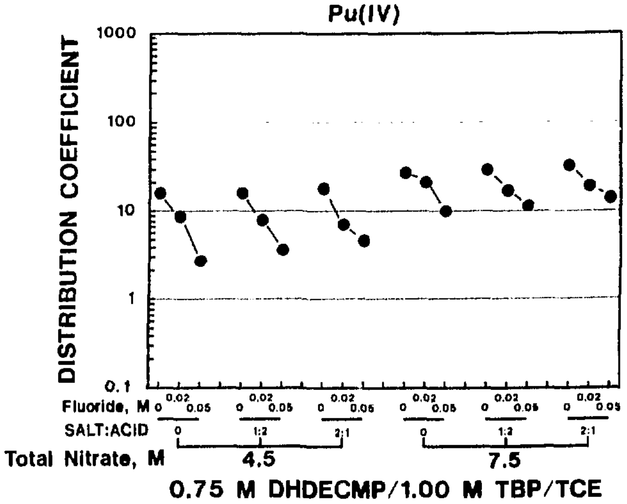


Fig. 16. Extraction of Pu(IV) into 0.75 *M* DHDECMP/ 1.00 *M* TBP/TCE as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

DHDECMP/TBP/Isopar. (Figs. 17 and 18) The slight increase in plutonium extraction with increasing nitrate salt levels is very similar to that observed with TCE diluent. The Kd values for no fluoride also are very similar to those observed with TCE diluent. The effect of added fluoride, however, is somewhat less for the Isopar system, particularly at low nitrate/low salt conditions.

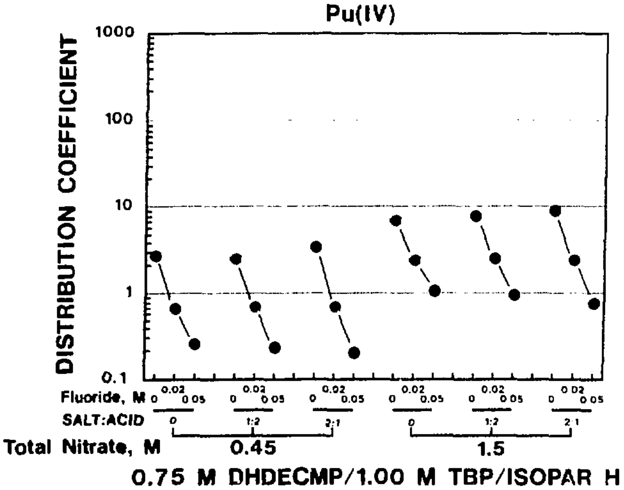


Fig. 17. Extraction of Pu(IV) into 0.75 *M* DHDECMP/ 1.00 *M* TBP/Isopar H as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

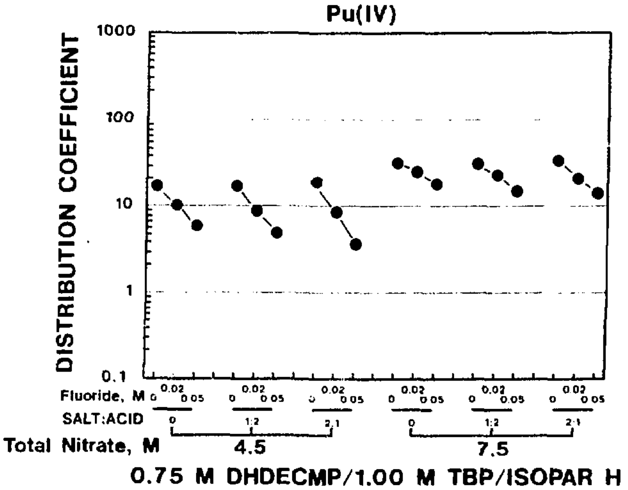
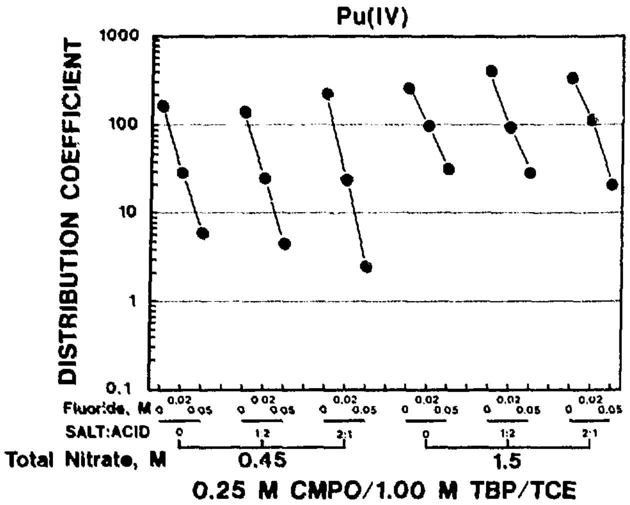


Fig. 18. Extraction of Pu(IV) into 0.75 *M* DHDECMP/ 1.00 *M* TBP/Isopar H as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

CMPO/TBP/TCE. (Figs. 19 and 20) No consistent pattern relates overall Kd value to nitrate salt level. A significant decrease in extraction with increasing fluoride is observed for all conditions studied, with the greatest fluoride effect at low nitrate/high salt conditions.



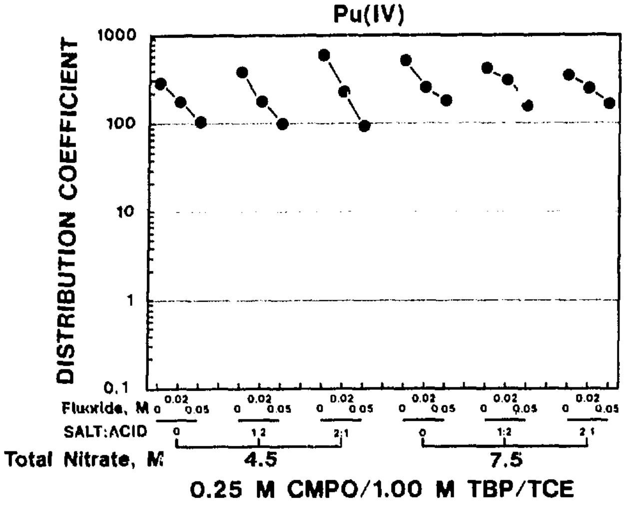
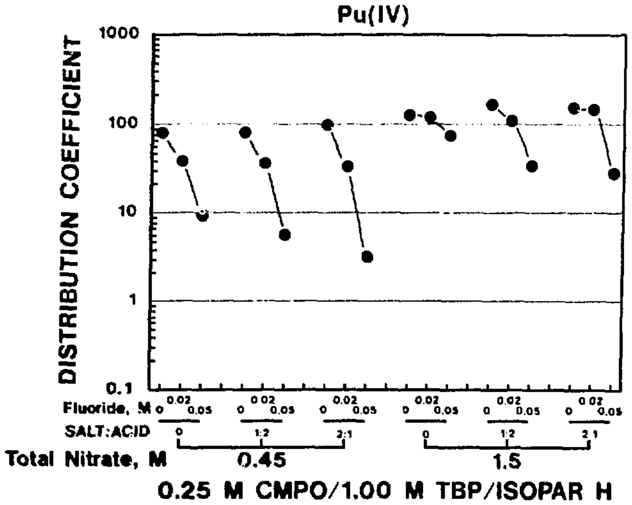


Fig. 19. Extraction of Pu(IV) into 0.25 *M* CMPO/1.00 *M* TBP/TCE as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

Fig. 20. Extraction of Pu(IV) into 0.25 *M* CMPO/1.00 *M* TBP/TCE as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

CMPO/TBP/Isopar. (Figs. 21 and 22) Again, little or no correlation is observed between plutonium extraction and nitrate salt level. The extraction of plutonium is lower than that obtained with TCE diluent, especially at low nitrate concentrations. The presence of fluoride consistently decreases plutonium extraction more when Isopar H is the diluent than in the comparable TCE system. Added fluoride decreases the extraction most at low nitrate concentrations.



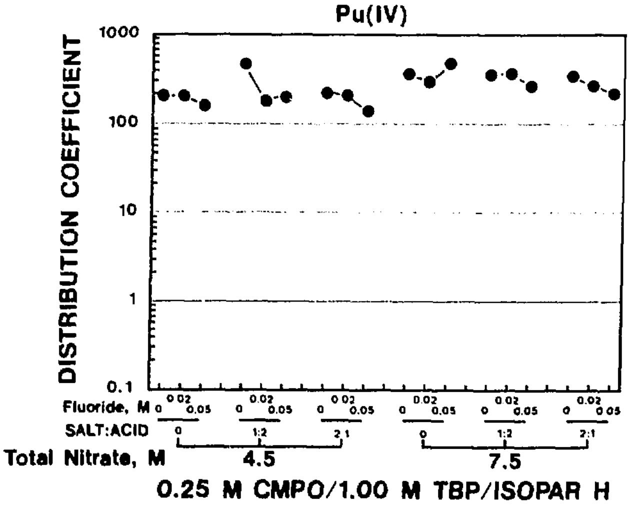


Fig. 21. Extraction of Pu(IV) into 0.25 *M* CMPO/1.00 *M* TBP/Isopar H as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

Fig. 22. Extraction of Pu(IV) into 0.25 *M* CMPO/1.00 *M* TBP/Isopar H as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

Uranium

DHDECMP/TBP/TCE. (Figs. 23 and 24) Uranium extraction shows a slight increase with increasing nitrate salt level. The highest level of fluoride causes a decrease in Kd values at low nitrate levels, but at high nitrate levels fluoride causes decreased Kd values only at higher salt levels.

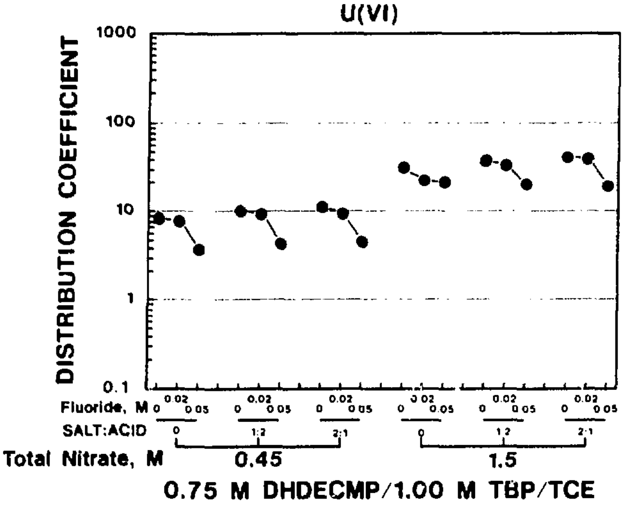


Fig. 23. Extraction of U(VI) into 0.75 *M* DHDECMP/1.00 *M* TBP/TCE as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

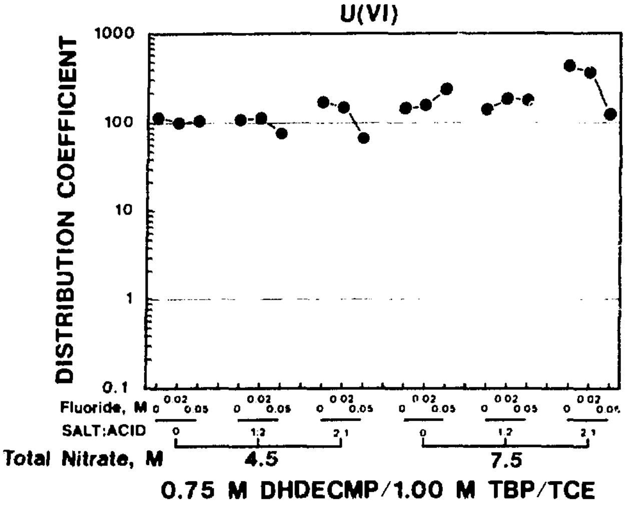


Fig. 24. Extraction of U(VI) into 0.75 *M* DHDECMP/1.00 *M* TBP/TCE as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

DHDECMP/TBP/Isopar. (Figs. 25 and 26) Overall Kd values are similar to those obtained with TCE diluent. The effects of nitrate salt and fluoride also are roughly similar to those observed with TCE diluent except that the data scatter appears to be greater in this system.

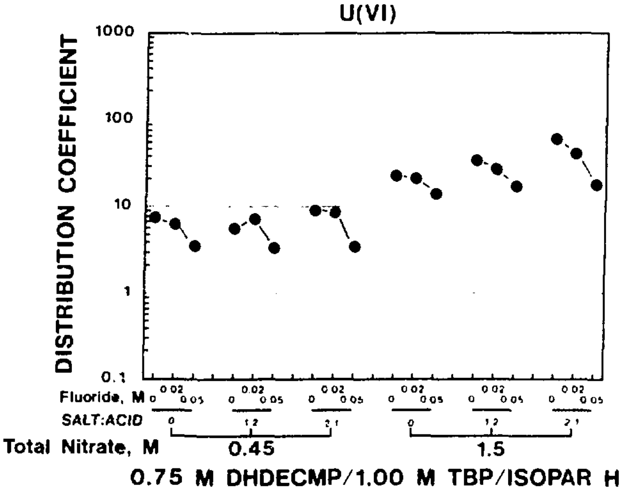


Fig. 25. Extraction of U(VI) into 0.75 *M* DHDECMP/1.00 *M* TBP/Isopar H as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

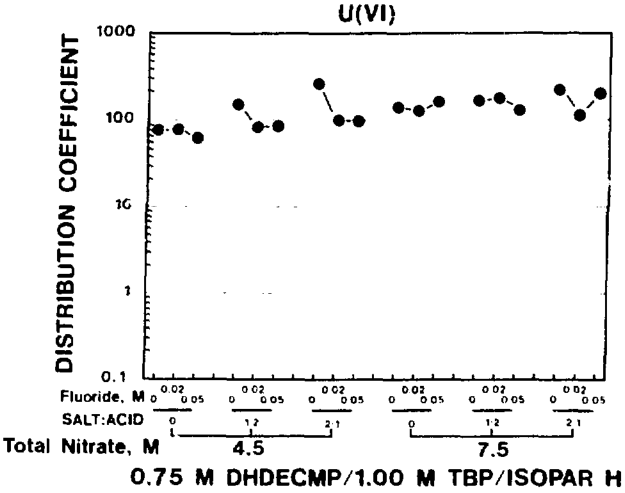


Fig. 26. Extraction of U(VI) into 0.75 *M* DHDECMP/1.00 *M* TBP/Isopar H as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

CMPO/TBP/TCE. (Figs. 27 and 28) Uranium Kd values are more than an order of magnitude higher at low nitrate levels but are only severalfold higher at high nitrate levels when compared with DHDECMP systems. A slight but consistent increase in Kd values is associated with increasing salt levels. Fluoride appears to suppress uranium extraction, but only at the two lowest nitrate levels.

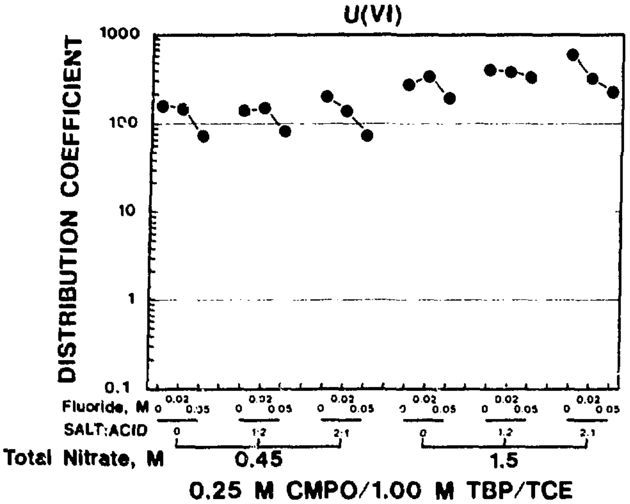


Fig. 27. Extraction of U(VI) into 0.25 *M* CMPO/1.00 *M* TBP/TCE as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

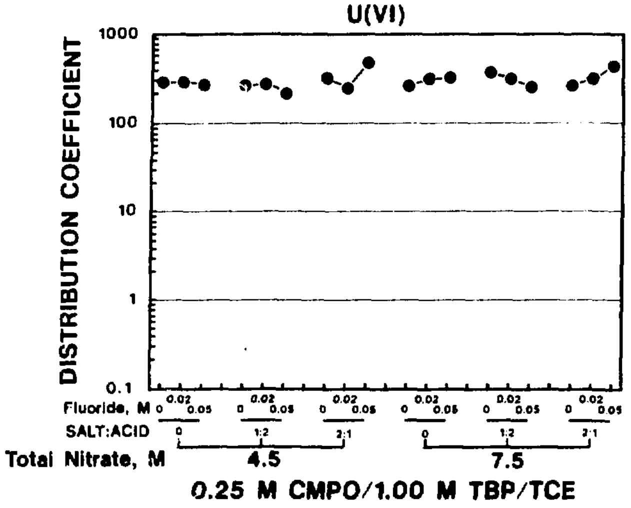


Fig. 28. Extraction of U(VI) into 0.25 *M* CMPO/1.00 *M* TBP/TCE as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

CMPO/TBP/Isopar. (Figs. 29 and 30) Uranium behavior from this system is very similar to that of the CMPO/TCE system.

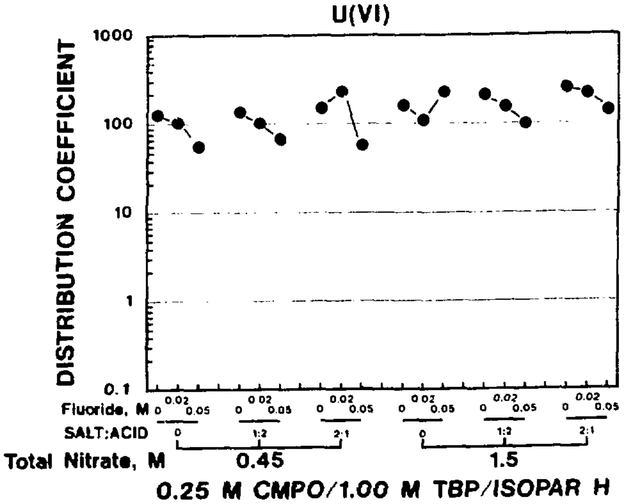


Fig. 29. Extraction of U(VI) into 0.25 *M* CMPO/1.00 *M* TBP/Isopar H as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

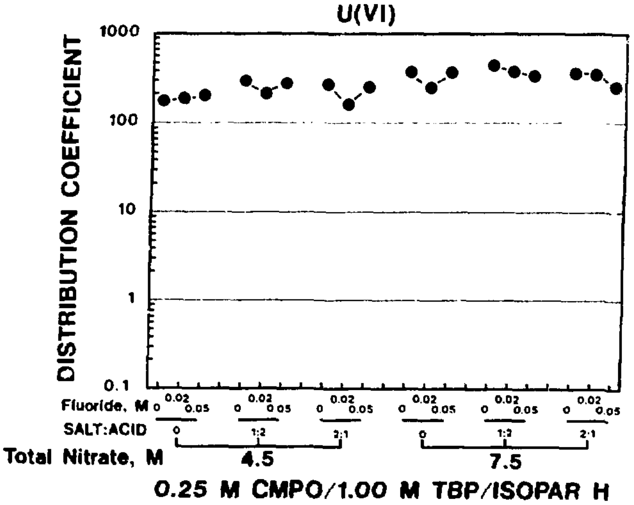


Fig. 30. Extraction of U(VI) into 0.25 *M* CMPO/1.00 *M* TBP/Isopar H as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

CONCLUSIONS

1. CMPO extracts Am(III), Pu(IV) and U(VI) more strongly from all of the aqueous compositions studied than does DHDECMP. This difference, however, is much greater from low nitrate concentrations than from high nitrate concentrations. Consequently, back-extraction of these actinides by dilute acid is difficult from CMPO but relatively easy from DHDECMP.

2. Higher nitrate salt levels yield higher extraction of all three actinides; however, this enhancement is greatest for Am(III).

3. The extraction of Am(III) is essentially unaffected by the maximum fluoride levels of 0.05 *M* studied. U(VI) extraction is slightly suppressed by similar fluoride concentrations, whereas Pu(IV) extraction is strongly suppressed.

4. Fluoride suppresses Pu(IV) extraction most at low nitrate concentrations. The intentional addition of fluoride therefore could be used to facilitate the back-extraction of Pu(IV) into dilute acid.

5. Persistent organic dispersions remained in the aqueous phase after extraction with TCE-diluted extractants. An additional scrub step using pure TCE was required to minimize the extracted actinides in this dispersion before the aqueous phase could be reliably assayed.

6. Phase separation was more rapid and complete when Isopar H was the diluent. Extractants diluted with Isopar H provided low-dispersion aqueous phases that required no subsequent scrub step.

7. Americium(III) Kd values were significantly higher for extractants diluted with Isopar under all conditions tested. Kd values for Pu(IV) were generally lower for CMPO diluted with Isopar H. DHDECMP extractions of Pu(IV) were essentially unaffected by the diluent. Kd values of U(VI) for both extractants were slightly lower with Isopar H diluent.

8. DHDECMP/TBP/Isopar H offers Kd values of at least 10 for Pu(IV) and Am(III) from nitrate concentrations of 4.5 *M* to 7.5 *M*.Thus, >90% extraction of these actinides is attainable from each extraction stage.

9. DHDECMP/TBP/Isopar H offers Kd values <0.5 for Am(III) and Pu(IV) from 0.45 *M* nitrate/0.05 *M* fluoride. This result (and even lower Kd values from lower nitrate concentrations not included in this study) should allow efficient back-extraction of these two actinides.

10. TBP modifies the extraction properties of CMPO in useful ways, but serves only to increase the extractant solubility when DHDECMP is used. TBP, unfortunately, also extracts large quantities of nitric acid, which requires many additional stripping stages to remove this acid before significant back- extraction of actinides occurs. Substitution of a diluent that dissolves DHDECMP and its metal complexes, but not nitric acid, will be explored as a means of minimizing the number of strip stages in the process eventually used.

11. The unique combination of adequate extraction from high nitrate solutions and efficient back-extraction from low nitrate solutions justifies the selection of DHDECMP as the extractant of choice for decontaminating actinides from aqueous nitrate waste streams from plutonium process operations.

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