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**Impurities That Cause Difficulty in
Stripping Actinides from Commercial
Tetraalkylcarbamoymethylphosphonates**

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OAK RIDGE NATIONAL LABORATORY

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CHEMICAL TECHNOLOGY DIVISION

IMPURITIES THAT CAUSE DIFFICULTY IN STRIPPING ACTINIDES
FROM COMMERCIAL TETRAALKYLCARBAMOYLMETHYLPHOSPHONATES

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C. T. Bahner, R. R. Shoun, and W. J. McDowell

ABSTRACT

Dihexyl[(diethylcarbamoyl)methyl]phosphonate (DHDECMP) in diethylbenzene extracts actinides well from 6 M nitric acid solution, but commercially available DHDECMP contains impurities which interfere with stripping the actinides from the organic extract. DHDECMP purified by molecular distillation does not contain these impurities, but the pot residue contains increased concentrations of them. Heating the purified DHDECMP causes the formation of products which interfere with stripping in the same way, suggesting that high temperatures employed in the manufacture of DHDECMP may produce the offending impurities. These impurities can be separated from the heat-decomposed material or the pot residues by dilution with a large volume of hexanes (causing part of the impurities to separate as a second liquid phase) followed by equilibration of the hexane solution with dilute alkali. After the treatment with hexane and dilute alkali, the DHDECMP is readily recovered and functions well in the actinide extraction process. Dibutyl[(dibutylcarbamoyl)methyl]-phosphonate (DBDBCMP) and di(2-ethylhexyl)[(diethylcarbamoyl)-methyl]phosphonate (DEHDECMP) are purified less effectively by these methods. Similar separation methods using diethylbenzene or CCl₄ as solvent do not remove impurities as completely as the hexane process. Impurities can also be removed from a benzene solution of the DHDECMP pot residue by passing it through a column packed with silica gel or diethylaminoethyl cellulose. These impurities have been separated into fractions for analytical examination by use of various solvents and by column chromatography. Hexyl hydrogen [(diethylcarbamoyl)methyl]-phosphonate has been identified tentatively as a principal objectionable impurity. Dihexyl phosphoric acid and possibly dihexylphosphonate have been identified in other fractions.

INTRODUCTION

In a proposed process for removing actinides from nuclear fuel reprocessing waste solutions, the actinides are extracted from 2 to 6 M nitric acid (or acidic nitrate solutions of similar total nitrate concentration) into a solution of tetraalkylcarbamoylmethylphosphonate in a nonpolar solvent. The actinides are stripped from this extractant

solution with water or very dilute nitric acid. Pilot-plant tests are under way to test extraction of actinides from highly salted wastes by dihexyl[(diethylcarbamoyl)methyl]phosphonate (DHDECMP) in xylene.¹ Anticipated use at ORNL, however, is in extraction from less highly salted solutions and hence will require a less aqueous-soluble compound of higher molecular weight in order to minimize extractant losses to the aqueous phase. We are presently engaged in a search for a carbamoylmethylphosphonate (CMP) with properties appropriate for this application.

All of the CMPs thus far obtained have contained one or more impurities that retain actinides in the organic phase during the stripping process. DHDECMP has been purified by acid hydrolysis of the diluted material followed by caustic scrubbing. Acceptable material may also be obtained by washing DHDECMP diluted in CCl_4 several times with ethylene glycol at 60°C followed by water and nitric acid washes and a final treatment with a strong-base macroreticular resin (Rohm and Haas, A-26).² We have found molecular distillation to be effective in producing a pure, strippable reagent, with most of the undesirable impurities remaining in the pot residue. Such results suggest that the impurities are less volatile than the reagent itself. This report describes work directed toward identifying these impurities (in most cases using the molecular distillation pot residue as enriched sources of the impurities), determining their origin, and attempting to indicate ways to avoid their appearance in future preparations.

EXPERIMENTAL

Materials

Di-2-ethylhexyl[(diethylcarbamoyl)methyl]phosphonate (DEHDECMP), dibutyl[(dibutylcarbamoyl)methyl]phosphonate (DBDBCMP), and DHDECMP were purchased from the Wateree Chemical Company, Lugoff, South Carolina. The crude DHDECMP was subjected to molecular distillation in a Consolidated Vacuum Corporation type CMS-5 centrifugal molecular still. After the

lower-boiling materials had been removed, ~700 g of purified product was obtained at ≤ 5 microns and 85°C. The pot residue, examined in these tests, amounted to ~200 g. A material containing similar impurities was produced by heating the molecular-still-purified DHDECMP to approximately 270°C.

Recovery of Impurities from Pot Residues

The initial separations on the pot residues were done by stirring 10 to 20 ml of the residue into 900 to 1000 ml of hexane. About 8 to 10% of this material settled out of the solution as a dark brown viscous liquid. The hexane layer was then decanted and washed with three 0.8% volume portions and one 3% volume portion of 1.00 N NaOH. The caustic washes were then combined, acidified, and reextracted with benzene. Pot residues from molecular distillation of DBDBCMP and DEHDECMP were separated in a similar, although not identical, manner. The impurities were retained for further fractionation.

Purity Evaluation Tests

AM test

This was an empirical extraction test used to indicate the presence of the undesirable impurity responsible for the extraction of americium at low aqueous acidity. A tracer amount of ^{241}Am in 6 N HNO_3 was equilibrated with an equal volume of a 30 vol % solution of the extractant in diethylbenzene (DEB). An aliquot of each layer was taken for gamma or alpha counting. The ratio of net counts per minute in the organic layer to that in the aqueous layer was recorded as the AM^1 value, the ratio after the first wash of the organic layer with an equal volume of stripping solution (water or dilute 0.1 M nitric acid) as the AM^2 value, and the ratio after the second wash with an equal volume of water as the AM^3 value.

EUAM test

This test evaluated the quantity of trivalent actinides held by the extractant at loading based on the assumption that the Am^{3+} and Eu^{3+} are

complexed equally, rapidly, and strongly. A 10-mg sample of extractant in 1.00 ml of DEB was equilibrated with 1.00 ml of $1 \times 10^{-3} \text{ M HNO}_3$ containing $1 \text{ or } 2 \times 10^{-3} \text{ M Eu(NO}_3)_3$ spiked with a small amount of ^{241}Am . Aliquots of one or both layers were analyzed, and the number of milliequivalents held in the organic layer per gram of chelating agent was calculated and recorded as the EUAM value. Some fractions tested tended to form precipitates with Eu^{3+} or to form a gel or third phase; therefore, the result was only approximate in some cases. Nevertheless, the test is helpful in seeking the most active fractions as regards the extraction of trivalent elements.

Thin-layer chromatography

This technique was used for further fractionation of the actinide-extracting fraction and for identification of these and other fractions. A small sample was spotted about 2 cm from the bottom end of a 1-cm-wide strip of Eastman Chromogram 13181 silica gel with fluorescent indicator, Eastman Chromogram 13253 alumina with fluorescent indicator, or Whatman No. 1 chromatographic paper. The solvent was evaporated and the chromatogram developed by placing the strip in a 1-liter bottle containing a small amount of solvent. The solvents most often used were hexane, benzene, acetone, and methanol. The solvent front was allowed to advance about 10 cm past the upper edge of the original spot; then the strip was dried and examined by ordinary light, by ultraviolet light of two different wavelengths, and finally by exposure to iodine vapor. This latter procedure often reveals spots not otherwise detected. The distance from the top of the original spot to the top of the final spot divided by the distance from the top of the original spot to the highest level reached by the advancing solvent front was recorded as the R_f value. The usefulness of these chromatograms is limited by the fact that with nonpolar solvents the materials of greatest interest in this study usually remain at or near the point of origin, while polar solvents such as alcohols tend to move everything simultaneously instead of producing sharply defined spots at characteristic distances from the origin. They do reveal some indication of the number of substances

present in a sample and also give some clue as to the nature of the fractions being investigated. For example, it was noted that some of the impurity fractions showed behavior similar to di(2-ethylhexyl) phosphoric acid (when separated on silica gel with a benzene eluent), thus suggesting chemical similarity of these fractions to long-chain dialkyl phosphoric acids.

Spots of complexed ^{241}Am were located by cutting the strip into short sections and counting the gamma radiation from each section.

Column chromatography

Columns of BioSil A, a silicic acid material, were used to remove impurities from small samples of the CMPs and to fractionate impurities. BioSil A, of 200-325 mesh, suspended in benzene was used to form a column in a 1-cm-diam tube. The sample to be separated was placed on the column in solution in 10 to 50 times its volume of benzene. Attempts to introduce undiluted sample onto the column produced unsuccessful results. Elution was achieved with pure benzene followed by increasing concentrations of methanol in benzene. Final stripping was effected with pure methanol. The effluent was collected in small weighed beakers or bottles. The volume of each fraction was recorded, and the solvent was removed by evaporation at atmospheric pressure followed by vacuum drying at <1 mm. For the first separation, the sample size was about 0.5 g and fractions collected were usually 15 ml each; however, for further sharper separation, the load was reduced to about 0.2 g in 7 ml, and a uniform 1 or 1.5% methanol concentration in benzene was used to prepare the column and to carry out the elution. Final stripping was done with methanol as before.

For removal of impurities from DHDECMP pot residues, a 0.2-g sample in 10 ml of benzene was applied to a 15-cm-high column and eluted with 0 to 4% methanol in benzene. Less than one-tenth of the material was eluted by pure benzene, while nearly all the rest was eluted using 4% methanol. In some experiments, Cellex-D diethylaminoethyl cellulose (capacity, 0.70 meq/g) was used instead of silicic acid with pure benzene as the eluent. An initial contact time of 20 min was allowed to fix the sample on the column. The DHDECMP was eluted rapidly from this column with pure benzene.

Elemental analyses

Unless otherwise indicated, the carbon, hydrogen, and nitrogen analyses were run by the ORNL Analytical Chemistry Division. Usually a single analysis was done on each sample, but an indication of the precision of the analyses can be obtained from the agreement between repeat determinations shown in Table 1. The nitrogen content of each of these samples was so small that the usual level of uncertainty in such analyses resulted in a relatively large percent error.

Acid value

The acid values (AV) expressed as milliequivalents of acid per gram of sample were determined by the ORNL Analytical Chemistry Division using a Sargent Recording Titrimeter. A 5- to 20-mg sample dissolved in 85% acetone was titrated with 0.030 N NaOH in propanol. Results were calculated by measuring the distance from the starting point to the middle of the break in the curve on a plot of electrode potential vs volume of titrant added (in ml) and are usually considered to be accurate to within only two significant figures.

RESULTS AND DISCUSSION

Decomposition Products Expected

Because of the evidence that the objectionable impurities in DHDECMP are caused by decomposition of the DHDECMP itself, a list of plausible degradation products of the carbamoylmethylphosphonates was prepared. Table 2 presents structures of several compounds which could be formed by splitting off olefin and/or by hydrolysis; the theoretical carbon, hydrogen, and nitrogen contents are listed along with the theoretical EUAM and AV values calculated on the bases indicated in the table. Also included are data for the dialkyl phosphates and dialkyl phosphonates that would be formed if the $-\text{CH}_2\text{CONR}_2$ group were replaced by $-\text{OH}$ or $-\text{H}$. These figures are to be compared with the observed data on various fractions listed in Table 1.

Table 1. Elemental analysis of representative fractions of separated impurities

Fraction	Elemental analysis			Acid titration (AV value)		Extraction test	Reference to theoretical analysis, Table 3
	Carbon	Hydrogen	Nitrogen	First break	Second break	EUAM value	
----- From DHDECMP Pot Residue -----							
32-B-Bz	45.7	8.7	6.2	2.8	4.6	2.0	
Repeat	45.5	8.3	6.2				
71-2	60.3	9.2	5.5				
71-5	49.7	8.2	4.1				
71-15	70.0	14.6	7.9				
71-27	47.6	8.4	10.5				
71-33	42.7	8.3	9.3				
32-1-Bz				0.1	0.2		
32-1-ww				1.2	1.5	2.3	
72-C	76.9	14.6	7.3 ^a				
72-D	50.1	9.2	4.8				II A
72-E	50.1	9.0	4.6				II A
72-FF	45.6	8.4	5.3				
72-GG	43.6	8.0	7.3				
32-1-0				3.1	3.6	2.3	
36-5 ^{b,c}	52.6	9.6	1.0	3.6	none	1.9	
36-8 ^{b,c}	51.3	9.4	4.4	3.1		2.4	
69-8 ^d	57.2	11.0	0.2				VIII A
69-10 ^d	55.3	10.5	0.1				
69-12 ^d	53.8	9.9	0.3				VII-A
68-XVII ^d	50.3	9.4	4.8				II-A
68-XVIII ^d	50.0	9.5	4.9				II-A
Repeat ^d	50.8	9.6	4.9				
68-XIX	50.2	9.3	5.1				II-A
Repeat	50.2	10.0	5.0				
----- From Heat-Decomposed DHDECMP -----							
47-(1,2)-0				3.4	4.7		
50-1	53.9	10.2	0.1	3.4	3.6	Ge1	VII-A
50-6	47.6	9.8	0.1	4.7	5.1	0.41	VII-A
50-7	46.3	9.1	1.8	4.1	5.5	1.8	
50-8	48.5	9.5	3.8	3.7	5.3	2.4	
50-9	48.9	9.4	4.0				
Repeat	49.0	9.5	4.0	2.1	3.9	2.2	II-A
50-17	53.2	10.5	9.3	2.3	None		
50-20	50.8	9.8	4.8	2.7	None	1.4	
----- From DEHDECMP Pot Residue by Process Similar to That Used for DHDECMP Residues -----							
37-1-0	55.2 ^c	9.8 ^c	3.2 ^c	2.9	None	2.2	
65-B	59.8	10.8	0.3				VII-C
65-F	54.0	10.0	4.4				II-C
Repeat	54.0	10.3	4.4				II-C
----- From DBDECMP Pot Residue -----							
41-2,3-ww-2	44.8	8.7	4.1				
45-G	50.7	9.1	3.8	2.5	None	2.6	
45-I	52.9	9.7	4.9				
Repeat	53.2	9.8	5.8				
Repeat	55.9	10.2	5.2	1.7	2.1	2.5	II-B
45-K	51.8	8.8	4.8	2.0	2.6	2.3	
45-M				2.5	4.5		
45-O	52.8	9.7	7.3	0.6			

^aCalculated for C₁₂H₂₇N: C, 72.8%; H, 14.6%; N, 7.65%.

^bObtained from single-pass column chromatography of 32-1-0.

^cAnalyses by Galbraith Laboratories.

^dObtained from repeated chromatography of 32-1-0.

Table 2a. Possible degradation and/or hydrolysis products of tetraalkyl CMPs

Table 2b. Composition of possible degradation and/or hydrolysis products of tetraalkyl CMPs

	C (%)	H (%)	N (%)	Eu ³⁺ binding (meq/g)	Acid (meq/g)
$R = C_6H_{13}$ and $R' = C_2H_5$					
II-A	51.60	9.38	5.02	3.58 (1.79) ^a	3.58
III-A	36.95	7.18	7.18	5.13 (2.56)	10.26 (5.13) ^b
IV-A	54.52	9.48	0	3.25 (1.62)	3.25
V-A	42.85	7.67	0	4.46 (2.23)	8.92 (4.46)
VI-A	17.14	3.57	0	4.08 (2.04)	12.24 (4.08)
VII-A	54.14	9.77	0	3.76 (1.88)	3.76
VIII-A	57.58	10.87	0	4.00 ?	4.00?
$R = C_4H_9$ and $R' = C_4H_9$					
II-B	54.70	9.84	4.56	3.25 (1.62)	3.25
III-B	47.80	8.76	5.58	3.98 (1.99)	7.96 (3.98)
IV-B	47.61	8.33	0	3.97 (1.98)	3.97
V-B	36.93	6.63	0	5.10 (2.05)	10.20 (5.10)
VI-B	17.14	3.57	0	4.08 (2.04)	12.24 (4.08)
VII-B	45.71	9.05	0	4.76 (2.38)	4.76
VIII-B	49.47	9.86	0	5.15 ?	5.15 ?
$R = C_3H_{17}$ and $R' = C_2H_5$					
II-C	54.70	9.84	4.56	3.25 (1.62)	3.25
III-C	36.95	7.18	7.18	5.13 (2.56)	10.26 (5.13)
IV-C	59.32	10.23	0	2.74 (1.37)	2.74
V-C	47.43	8.33	0	3.95 (1.98)	7.90 (3.95)
VI-C	17.14	3.57	0	4.08 (2.04)	12.24 (4.08)
VII-C	59.60	10.94	0	3.10 (1.55)	3.10
VIII-C	62.71	11.51	0	3.26 ?	3.26 ?

^aValues in parentheses are based on three molecules of dimer per europium atom.^bValues in parentheses are based on one equivalent of hydrogen ion per mole.

The available literature suggests that the splitting off of an alkene, leaving an -OH group, is likely for compounds similar to the phosphonate end of the CMPs. For example, heating triethyl phosphate to 160°C has been reported to produce diethyl phosphate and monoethyl phosphate.³ Tributyl phosphate is reported to split off C_4H_8 groups in the mass spectrograph, and dibutyl phosphate is said to be the chief radiolysis product from tributyl phosphate.⁴ Hydrolysis of the ROP linkage would give the same compounds as olefin elimination (see Table 2); however, since this linkage is not easily hydrolyzed and since these products were obtained in both the original preparations and in our thermal degradation experiment in the absence of any substantial amount of water, we propose that olefin elimination is the principal route to the acid phosphate impurities.

The behavior of the offending impurity in the CMPs indicates that it is an acidic material; that is, it extracts trivalent actinides at low acid concentration as would a moderately strong-acid cation exchanger. Thus compounds of type VIII are eliminated from the possible suspect list because they are not strongly acidic. Further, information in the literature indicates that such compounds would not be good extractants.^{5,6}

Of the remaining proposed degradation products, the properties of the separated impurities (e.g., their acidic nature and extraction of americium from 0.01 M HNO_3) suggest that type II or VII compounds (Table 2) are probably among the chief agents that prevent stripping of americium from the CMPs at pH 2.0. Although compounds containing carboxylic acid groups (type IV) are possible acidic degradation products, the carboxylic acid would probably be a very weak extractant at pH 2.0 since it would be little ionized in the presence of 0.01 M HNO_3 . Compounds of type V have both the carboxyl and the phosphoric acid groups and thus might extract americium effectively at pH 2, but they are not believed present for the following reasons: (1) no analyses corresponded well to that expected for type V; (2) the two acid groups should be detectable by potentiometric titration, and no consistent double end-point titrations were observed; and (3) such compounds would be very water

soluble and (except for possibly V-C) would not be likely to remain in the organic phase.

Compounds of type VI are phosphonacetic acids and have been described by Nylen⁷ as being very soluble in water and acetone but insoluble in ether and benzene. These compounds are thus clearly eliminated as suspect extractants.

General Nature of the Impurities

The impurities removed from the pot residues consist of an acidic mixture of nitrogenous and nonnitrogenous compounds. Similar impurities can be produced by heating pure DHDECMP to about 275°C. Under these conditions the pure, clear material darkens and becomes acidic. The heated material contains very strong americium extractants similar in behavior to those left in the pot residue after molecular distillation of commercial DHDECMP and to those present in crude DHDECMP, suggesting that the undesirable impurities in original preparations may be the result of thermal degradation during synthesis. When the AM test was applied to the heated material, the results were $AM^1 = 28$, $AM^2 = 76$, $AM^3 = 186$, demonstrating that a strong complexing agent was present which retained the americium in the organic layer even after two water washes. Samples of the radioactive organic layer were examined by thin-layer chromatography after the second washing. Two radioactive regions were found, suggesting a mixture of complexes with americium.

Fractionation of Impurities

Examination of pot residues

Although the following results are primarily from DHDECMP pot residues, some work was done on DBDECMP and DEHDECMP pot residues and heat-decomposed DHDECMP as well. The principal substances recognized were of types II and VII, Table 2, although one fraction was obtained having an analysis corresponding to dihexyl phosphonate (compound VIII-A) and another had analyses corresponding to an amine, $C_{12}H_{27}N$.

The DHDECMP pot residue contained 10% hexane--insoluble oil. The benzene-soluble portion of this material (32-B-Bz, Table 1) contained a fraction that appeared from analysis to be primarily compound II-A. None of the other proposed compounds were identified in any other fractions. It is significant, however, that each fraction contained 5.5 to 10.5% nitrogen, suggesting that nitrogen-free substances such as compounds IV-A and VII-A do not predominate.

Measurement of the pH of sodium hydroxide equilibrated with a benzene solution of DHDECMP pot residue indicated that the pot residue contained between 7 and 14 meq of acidic material per 15 ml. Equilibration of the combined caustic extracts with benzene yielded a small amount of oil which had a very low EUAM value and was probably largely DHDECMP that was entrained or dissolved. Acidification of the sodium hydroxide extract produced an oily liquid, which was only slightly water soluble. A water-soluble portion was fractionated by column chromatography, and significant fractions were analyzed; the results are given in Table 1 (Samples 72-C, -D, -E, -FF and -GG). Analyses of the largest fractions, 72-D and -E, matched the composition of compound II-A (Table 2). Later fractions (72-EE, -FF and -HH) appeared to be mixtures whose elemental analyses did not match any of the proposed degradation products.

The water-insoluble portion (32-1-0) of the material precipitated by sulfuric acid from the sodium hydroxide extract would be expected to contain a major portion of the offending acidic impurities since they are acidic materials, aqueous soluble as sodium salts but aqueous insoluble in the acid form, and thus would be expected to remain in the extractant (CMP) solution. Chromatographic separation of this fraction gave several fractions (prefix Nos. 36, 68, and 69, Table 1) with analyses matching compound II-A. Fraction 36-8 was such a fraction having a particularly high americium extraction from dilute acid (see Table 3). Some other samples gave analyses matching those of compounds VIII-A and VII-A; however, as was mentioned before, VIII-A is not believed to be a good americium extractant. Further, there is independent evidence that the parent fraction 32-1-0 was primarily acidic material since water

contacted with it had a pH of 1.9. Dihexyl phosphoric acid contacted with water produces an aqueous pH of 2.8. However, the results shown in Table 3 indicate that dihexyl phosphoric acid (VII-A) is not the offending impurity either since it is a much poorer extractant for americium than fraction 36-8, which is believed to be largely compound II-A. The above indicates strongly that the principal offending impurity in crude DHDECMP is hexyl hydrogen [(diethylcarbamoyl)methyl]phosphonate, compound II-A (Table 2).

Table 3. Comparison of extraction behavior of dihexyl phosphoric acid (DHP) with that of fraction 36-8, believed to be impure hexyl hydrogen [(diethylcarbamoyl)methyl]phosphonate, compound II-A

System	D_{Am}	
	36-8	DHP
0.1 M $Eu(NO_3)_3$ --0.001 N HNO_3	3.83	
First scrub 1 N HNO_3	0.49	
Second scrub 1 N HNO_3	0.29	
Third scrub 6 N HNO_3	0.041	
Carrier-free Am, 0.1 N HNO_3	135.	0.041
Carrier-free Am, 1.0 N HNO_3	0.82	$<10^{-3}$

Examination of heat-decomposed DHDECMP

The water-insoluble portion of the sodium hydroxide extract of heat-decomposed DHDECMP (analogous to 32-1-0 from the pot residue) was also fractionated on a BioSil-A column, and analyses of these fractions are labeled with the prefix number 50 in Table 1. The compositions of two of these fractions match compound VII-A but show low americium extraction, partly because of gel formation. Fractions 50-9 and 50-20 match the composition of compound II-A and show high americium extraction. Thus the predominant compounds in the heat-decomposed material that extract americium, as well as those in the pot residue, appear to have compositions very close to that of compound II-A (Table 2).

Pot residues from both DEHDECMP and DBDBCMP were fractionated (as described above for DHDECMP), and analyses of fractions that contained substantial amounts of material are reported in Table 1. Again, both contained fractions matching the compositions of compounds II-B and II-C, respectively, and again in the latter case this was shown to be a good americium extractant. One fraction, 65-B, had a composition matching that of compound VII-C.

Purification of Pot Residues

The extraction data shown in Table 4 show that the use of hexane precipitation combined with sodium hydroxide extraction removes the impurities from the DHDECMP pot residue to an extent that makes practical stripping of the americium possible. There was less complete removal of impurities from DBDBCMP and DEHDECMP pot residues. Possible explanations are: (a) a smaller ratio of hexane to the phosphonate was used with DBDBCMP, and (b) the larger hydrophobic portion of the DEHDECMP impurities led to their less favorable distribution to aqueous sodium hydroxide, or (c) the concentration of impurities in the DBDBCMP and DEHDECMP pot residue may have been greater. The hexane dilution--NaOH scrub method appears to be nearly as effective as molecular distillation for removing undesirable impurities from DHDECMP but not as effective as molecular distillation for DBDBCMP and DEHDECMP.

The relative effectiveness of various modifications of the purification process (by varying the type and ratio of nonpolar solvent and the type of base) is shown in Table 5. Although each of the modifications is effective, the hexane and sodium hydroxide treatment gives the most favorable result. This table also shows that effective purification can be obtained by use of cilicic acid or diethylaminoethyl cellulose column chromatography.

Table 4. Performance of extractants purified by hexane dilution and NaOH scrub

Test	DHDECMP ^a		DBDBCMP ^b		DEHDECMP ^c	
	Americium distribution coefficient	% Am remaining in organic	Americium distribution coefficient	% Am remaining in organic	Americium distribution coefficient	% Am remaining in organic
Initial extn., 30% extractant in DEB vs 6 M HNO ₃ (AM ¹)	5	---	18	---	76	---
Strip No. 1, 0.01 N HNO ₃ (AM ²)	1.2	55	71	100	226	100
Strip No. 2, 0.1 N HNO ₃ (AM ³)	0.37	13.6	327	100	>10 ³	100
Strip No. 3, 0.1 N HNO ₃ (AM ⁴)	0.45	3.9	Discontinued			
Strip No. 4, 0.1 N HNO ₃ (AM ⁵)	1.04	1.9				
Strip with 0.02 M Eu(NO ₃) ₃ -- 0.001 M HNO ₃	0.68	0.7	6.6	87	0.28	20
Second strip with 0.02 M Eu(NO ₃) ₃ -- 0.001 M HNO ₃	0.23	0.1	1.9	54	0.29	4.5

^aRecovered from 15 ml of pot residue dissolved in 900 ml of hexane and washed with three 7-ml and one 25-ml portions of 1.00 M NaOH.

^bRecovered from 30 ml of pot residue dissolved in 900 ml of hexane and washed with four 7-ml and one 25-ml portions of 1 M NaOH.

^cRecovered from 30 ml of pot residue dissolved in 900 ml of hexane and washed with two 7-ml and one 25-ml portions of 1 M NaOH.

Table 5. Comparison of selected scrub methods for removing impurities from DHDECMP

Purification			D _{Am} shown by Am-Eu bearing organic phase after indicated treatment	
Solvent	Ratio	Base	Equilibration with equal volume 0.01 M Eu(NO ₃) ₃ + 0.001 M HNO ₃	Equilibration with equal volume 0.01 M HNO ₃
Unpurified pot residue			7.4	29
Hexane	10:1	0.10 M NaCO ₃	0.0014	0.007
Hexane	10:1	0.10 M NaOH	0.0011	0.0047
Benzene	10:1	0.10 M NaOH	0.0057	0.011
DEB	10:1	0.10 M NaOH	0.0037	0.019
DEB	2:1	0.10 M NaOH	0.032	0.043
CCl ₄	10:1	0.10 M NaOH	0.0039	0.017
CCl ₄	2:1	0.10 M NaOH	0.029	0.047
BioSil-A ^a			0.014	0.063
Cellex-D ^b			0.059	0.20

^aA solution of 201 mg of pot residue in 10 ml of benzene was applied to a 15-cm-long, 1-cm-diam column of BioSil-A, 200-325 mesh, and diluted with benzene containing 0 to 4% methanol, using gradually increasing concentrations of methanol. A cut containing 146 mg of DHDECMP was taken, and a 100-mg sample was dissolved in 0.90 ml of DEB.

^bA solution of 282 mg of pot residue dissolved in 10 ml of benzene was put through a 15-cm-long, 1-cm-diam column containing 2.5 g of Cellex-D, diethylaminoethyl cellulose (0.70 meq/g). A cut containing 237 mg of DHDECMP was taken, and a 100-mg sample was tested as described for BioSil-A.

CONCLUSIONS

The principal impurity responsible for strong americium extraction and retention during water stripping of the neutral bidentate extractant DHDECMP appears to be the acidic material designated as compound II-A in Table 3. Other impurities such as dihexyl phosphonate and an amine $C_{12}H_{27}N$ are probably present but do not appear to be as important in the low-acid extraction of trivalent lanthanides and actinides. The acid material predominates in both the pot residue and heat-decomposed samples, suggesting that it is the result of thermal decomposition during preparation of the original material. Analogous compounds appear to be present in DBDBCMP and DEHDECMP. Dilution of the impure product in hexane followed by washing the resulting solution with caustic appears to be a workable method of purifying DHDECMP. The presence of the undesirable impurities may possibly be minimized in CMP preparation by maintaining as low a temperature as practical.

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