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The Extraction of Am(III) and Fe(III) by Selected Dihexyl N,N-Dialkylcarbamoylmethyl-phosphonates, -Phosphinates and -Phosphine Oxides from Nitrate Media

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The Extraction of Am(III) and Fe(III) by Selected Dihexyl N,N-Dialkylcarbamoylmethyl-Phosphonates, -Phosphinates and -Phosphine Oxides from Nitrate Media

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ABSTRACT

A series of neutral bifunctional extractants related to dihexyl N,N,-diethylcarbamoylmethylphosphonate (DHDECMP) have been prepared and studied for the liquid-liquid extraction of Am(III) and Fe(III) from nitrate solutions. Changes in the steric bulk of the substitutent alkyl chains and in the electronegativity of the groups attached to the phosphoryl center in these compounds have brought about large changes in distribution ratios and selectivities for the extraction of these metals. Comparisons of these extractants to related monofunctional phosphorus-based compounds have revealed that these bifunctional species behave as monodentate, rather than chelating, extractants. The presence of the carbamoyl portion of the extractant molecules is important not for coordination to the metal, but for the ability to buffer the extractant against the effects of HNO_3.

INTRODUCTION

The solvent extraction behavior of neutral bifunctional organophosphorus compounds has received a great deal of attention recently (1-8) due, in large part, to the ability of these compounds to extract trivalent actinide ions from nitric acid solutions (7). The feasibility of this extraction is very important in the development of compounds for the selective removal of actinide(III) ions from fission products in nitric acid solutions of high level liquid waste generated in the reprocessing of spent nuclear fuel.

Our previous investigations in this area (1,2) focused on the extraction of Th(IV), U(VI) and selected trivalent lanthanide and actinide ions by dihexyl N,N-diethylcarbamoylmethylphosphonate (DHDECMP). Our results indicated that the superiority of DHDECMP over a typical monofunctional extractant such as dibutyl butylphosphonate for the extraction of these metal ions from acidic media is not due to the ability of DHDECMP to act as a bidentate extractant, as had been previously proposed (7,8), but is a result of the capability of the amide group to act as a sort of internal buffer to protect the metal-phosphoryl bond in the extractable complex from attack by hydrogen ions.

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Our objective in this investigation was to study the effect of changes within the extractant molecule on the selectivity and efficiency of extraction. Substitutions of alkyl substituents for alkoxy groups bound to the phosphoryl moiety were performed to determine the effect of changes in the basicity of the P=O group (as well as to increase the hydrolytic stability of the compounds) while branched substitutents were introduced, both in the amide and phosphoryl portions of the molecule, to study the consequences of increased steric bulk of the extractant. Additionally, comparisons between these new bifunctional extractants and related monofunctional compounds were made to evaluate differences in extraction behavior as a method of determining the mode of coordination of these bifunctional species.

EXPERIMENTAL

The source and purification of the extractants DHDECMP, DB[BP], B[DBP] and TOPO (see Table 1 for explanation of abbre-

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TABLE 1.

Abbreviations for the Extractants Employed in this Work.

Abbreviation	Extractant	Nomenclature
DHDECMP	$(C_6H_{13}O)_2\overset{O}{\overset{\|}{P}}CH_2\overset{O}{\overset{\|}{C}}N(C_2H_5)_2$	Dihexyl N,N-diethylcarbamoylmethylphosphonate
HHDECMP	$\begin{matrix}C_6H_{13}\diagdown\\ C_6H_{13}O\diagup\end{matrix}\overset{O}{\overset{\|}{P}}CH_2\overset{O}{\overset{\|}{C}}N(C_2H_5)_2$	Hexyl hexyl-N,N-diethylcarbamoylmethylphosphinate
DHDECMPO	$(C_6H_{13})_2\overset{O}{\overset{\|}{P}}CH_2\overset{O}{\overset{\|}{C}}N(C_2H_5)_2$	Dihexyl N,N-diethylcarbamoylmethylphosphine oxide
DHDBCMPO	$(C_6H_{13})_2\overset{O}{\overset{\|}{P}}CH_2\overset{O}{\overset{\|}{C}}N(C_4H_9)_2$	Dihexyl N,N-dibutylcarbamoylmethylphosphine oxide
DHD(IB)CMPO	$(C_6H_{13})_2\overset{O}{\overset{\|}{P}}CH_2\overset{O}{\overset{\|}{C}}N[CH_2CH(CH_3)_2]_2$	Dihexyl N,N-diisobutylcarbamoylmethylphosphine oxide
DHD(SB)CMPO	$(C_6H_{13})_2\overset{O}{\overset{\|}{P}}CH_2\overset{O}{\overset{\|}{C}}N[CH(CH_3)C_2H_5]_2$	Dihexyl N,N-di(sec-butyl)carbamoylmethylphosphine oxide
D(EB)DECMPO	$[(C_2H_5)_2CHCH_2]_2\overset{O}{\overset{\|}{P}}CH_2\overset{O}{\overset{\|}{C}}N(C_2H_5)_2$	Di(2-ethylbutyl) N,N-diethylcarbamoylmethylphosphine oxide
DB[BP]	$(C_4H_9O)_2(C_4H_9)\overset{O}{\overset{\|}{P}}$	Dibutyl butylphosphonate
B[DBP]	$(C_4H_9O)(C_4H_9)_2\overset{O}{\overset{\|}{P}}$	Butyl dibutylphosphinate
TOPO	$(C_8H_{17})_3\overset{O}{\overset{\|}{P}}$	Trioctylphosphine oxide

viations) have been described previously (1,9). Crude DHDECMPO was synthesized in 58% yield by reaction of dibutyl phosphonate with three equivalents of hexylmagnesium bromide in ether followed by treatment of the resulting dihexylphosphonylmagnesium bromide with one equivalent of N,N-diethyl-2-chloroacetamide (10). A product of 99% purity (by GC) was obtained in 36% overall yield using the procedure of mercury salt purification reported for DHDECMP (11). The related compounds DHDBCMPO, DHD(IB)CMPO, DHD(SB)CMPO and D(EB)DECMPO were prepared similarly from the appropriate Grignard reagents and N,N-dialkyl-2-chloroacetamides (10). Conversion to crude product was greater than 50% in each case while final products of purity in the range of 94-99% were obtained in overall yields of 20-55%. The spectral properties of these phosphine oxide compounds were fully consistent with the assigned structure. MS: small parent peak of appropriate mass and base peak corresponding to the amino moiety R_2N^+. UV: λ_{max} 205-208 nm; ε_{max} $\sim$7800. NMR: CCl_4 solutions exhibited two distinct NCH_2 resonances between 3.1 and 3.5 ppm (rel to TMS) (DHD(SB)CMPO; NCH at 2.93 and 3.96); $OPCH_2CO$ at 2.9 ppm (2.69 and 2.93 for DHD(SB)CMPO); remaining resonances from 0.8 to 2.0 ppm. IR: strong bands at 2850-2960 cm^{-1} (C-H str), 1632-1638 (C=O str), 1422-1465 (C-H bend) and 1167-1172 (P=O str).

HHDECMP was synthesized by the Arbuzov reaction between N,N-diethyl-2-chloroacetamide and dihexyl hexylphosphonite (prepared by treatment of trihexylphosphite with one equivalent of hexylmagnesium bromide). Mercury salt purification (11) resulted in a 28% yield of product (based on trihexylphosphite) contaminated with *ca.* 5% DHDECMP, which was formed as a result of the Arbuzov reaction with residual trihexylphosphite. Spectral properties were quite similar to those reported above for the phosphine oxide compounds with the exception of a resonance at 3.90 ppm in the NMR spectrum (OCH_2) and the appear-

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ance of the P=O str at 1222 cm^{-1} and a new band due to P-O-C str at 1015 cm^{-1}.

Extractant solutions were prepared using p-diisopropylbenzene diluent (Aldrich, 99%) while aqueous solutions were prepared using materials described previously (1). Extraction studies were performed using ^{241}Am (from ANL stocks) and ^{55}Fe (New England Nuclear).

All distribution ratio measurements were performed at 25° using the procedure described previously (1). Radiometric assays of ^{55}Fe were performed by liquid scintillation counting.

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RESULTS AND DISCUSSION

In an attempt to further elucidate the extraction mechanism and behavior of neutral bifunctional organophosphorus compounds studies were undertaken on a series of extractants in which the basicity of the phosphoryl group and the steric bulk of the substituent groups were systematically varied. The effect of these changes on the extraction of Am(III) and Fe(III) were studied to evaluate modifications which would be desirable in the synthesis of extractants for the selective removal of the actinides from corrosion products in liquid waste solutions.

Extractant Dependency

For the extractants DHDECMPO and HHDECMP it was found, as in the case of DHDECMP(2), that the distribution ratio for the extraction of Am^{3+} varied as the third power of the extractant concentration. Thus, the expression for the extraction of Am^{3+} by these compounds can be written as

$$Am^{3+}_{aq} + n\ E_{org} + 3NO^{-}_{3aq} \rightleftharpoons Am(NO_3)_3 \cdot nE_{org} \qquad (1)$$

where n=3 and E is DHDECMP, HHDECMP or DHDECMPO.

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It was quite surprising to find that when the extractant DHDBCMPO was substituted for DHDECMPO the extractant dependency for Am(III) decreased from third to second power. This dependency was also found for the other two extractants containing isomeric butyl groups attached to the amide nitrogen. Therefore the stoichiometry for extraction by these compounds can be written as in Eq. 1 with n=2 for E=DHDBCMPO, DHD(IB)CMPO or DHD(SB)CMPO.

In the case of the extractant with branched alkyl groups attached directly to the phosphoryl group, D(EB)DECMPO, an extractant dependency of 2.4 was found. Such a dependency may be due in this case to the greatly increased steric demands of the extractant resulting from the branching. Apparently americium is unable to accommodate three coordinated nitrate ions as well as the three bulky extractant molecules (cf. extractant dependency of Th(IV) with DHDECMP (1)).

This argument of steric crowding for the low extractant dependency of D(EB)DECMPO cannot be invoked to explain the second order dependency of DHDBCMPO and its isomers, however. Other results (see below) indicate changes in the amide substituents have little effect on extraction behavior. It is also quite difficult to explain the difference in extractant dependency between DHDECMPO and DHDBCMPO, where the length of the alkyl chains attached to the nitrogen atom is the only modification.

The differences in extractant dependency for these compounds is even more extreme in the extraction of Fe^{3+}. Whereas a fourth power dependency is found for the extraction of iron by DHDECMPO, the other bifunctional phosphine oxide extractants, D(EB)DECMPO, DHDBCMPO, DHD(IB)CMPO and DHD(SB)CMPO, were found to have a second power of dependency. As with Am(III), it may be possible to reconcile some of these large differences on the basis of the steric requirements of the extractants,

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while differences in the kinetics of extraction indicate that there may be gross differences in the extraction mechanism as well.

Kinetics of Fe(III) Extraction

Preliminary studies of the extraction of Fe(III) by these bifunctional compounds produced inconsistent results for duplicate experiments with several of the extractants. Upon further investigation it was found that the source of this inconsistency was the slow kinetics of extraction by DHDBCMPO and its isomers. It was therefore necessary to determine distribution ratios for these extractants by back-extraction of Fe(III) from the organic phase. Distribution ratios so determined were found to be reproducible and one to two orders of magnitude greater than those determined by forward extraction performed with the usual 1-2 minute mixing period. Extraction of Fe(III) by DHDECMPO, D(EB)DECMPO and HHDECMPO, as well as the extraction of Am(III) by all of the extractants, proceeded rapidly, showing no evidence of slow kinetics.

This variation in extraction rates indicates the possibility of fundamental differences in the extraction mechanism of these compounds. Further, more detailed investigations into these kinetic differences may prove valuable in elucidating mechanistic variations in the extraction of iron.

Effect of Steric Bulk of Extractant

A series of extractants in which the extent of branching in the alkyl substituents was varied was studied to evaluate the effect of such changes on the distribution ratios of Am(III) and Fe(III). When branching was introduced into the alkyl substituents bonded directly to the phosphorus atom it was found to have a marked effect on the extraction of both Am^{3+} and Fe^{3+} (Fig. 1 and 2, Table 2). Such a reduction of K_d with

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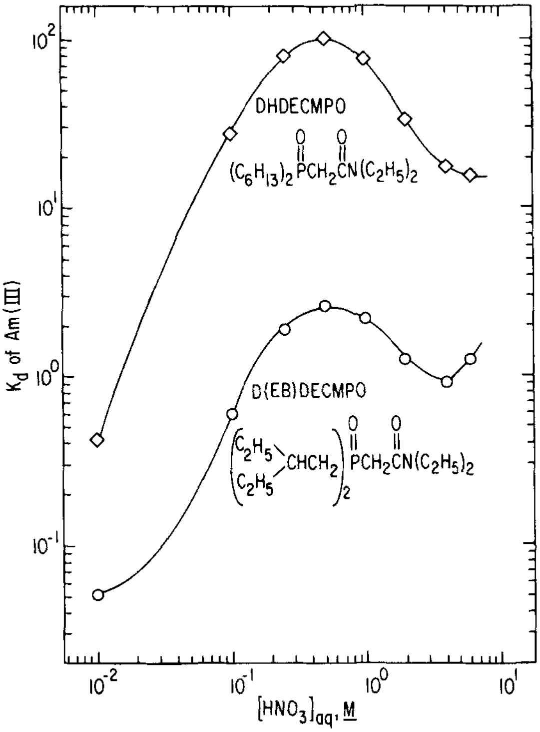

FIGURE 1. Distribution ratios for the extraction of Am(III) by 0.50 M DHDECMPO and D(EB)DECMPO as a function of aqueous acid concentration.

increased branching near the phosphoryl group, which has been observed previously in the extraction of Am(III) (12) (as well as Eu(III) (12) and Th(IV) (9)) by neutral, monofunctional phosphorus-based extractants, apparently is an entropic effect resulting from increased congestion about the metal center in the extracted complex. From these data it seems that this effect is also responsible for the reduction in the distribution ratio for the extraction of Fe(III) by D(EB)DECMPO.

When the alkyl groups attached to the amide portion of the extractant molecule were modified in the series DHDBCMPO,

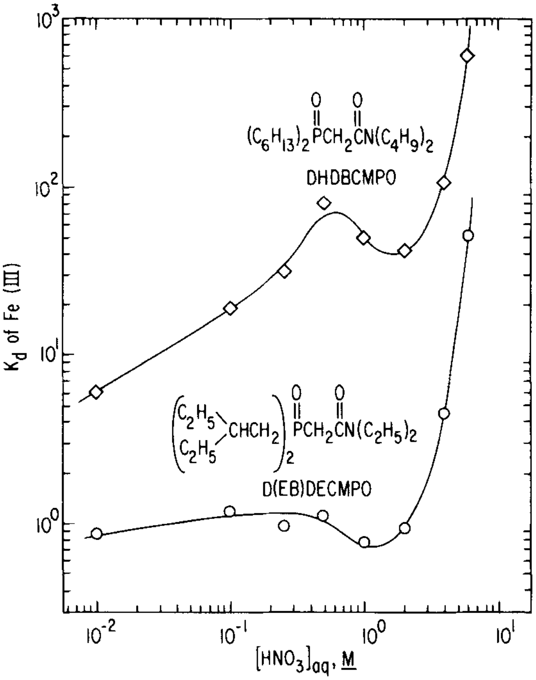

FIGURE 2. Distribution ratios for the extraction of Fe(III) by 0.50 M DHDBCMPO and D(EB)DECMPO from HNO_3.

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DHD(IB)CMPO and DHD(SB)CMPO, there was little noticeable effect on the extraction of Am^{3+} (Fig. 3). All three extractants produced very similar extraction behavior although it is interesting to note that the K_d's in the 1 to 6 M HNO_3 range progessively decrease slightly as the steric hindrance about the amide group increases. With Fe^{3+}, however, (Fig. 4) the branching of the amide substituents resulted in quite substantial reductions in the extraction of the metal, although to a lesser degree than that observed when branching occurred in the phosphoryl substituents. This behavior indicates that the amide moiety plays a more important role in the extraction of Fe^{3+} than of Am^{3+}. Based on the differences in the ionic radii of

TABLE 2.

Distribution Ratios and Separation Factors for the Extraction of Am(III) and Fe(III) by 0.50 M Extractant as a Function of Aqueous Phase Acid Concentration[a]

Extractant		$[HNO_3]_{aq}$, M							
		0.01	0.10	0.25	0.50	1.00	2.00	4.00	6.00
DHDECMP	K_d^{Am}	3.39×10^{-3}	7.70×10^{-3}	3.43×10^{-2}	1.21×10^{-1}	4.00×10^{-1}	1.11	2.41	2.51
	K_d^{Fe}	--	--	2.15×10^{-5}	2.37×10^{-5}	8.11×10^{-5}	2.74×10^{-4}	7.99×10^{-4}	4.32×10^{-3}
	α	--	--	1.6×10^{3}	5.1×10^{3}	4.9×10^{3}	4.1×10^{3}	3.0×10^{3}	5.8×10^{2}
HHDECMP	K_d^{Am}	4.79×10^{-2}	1.32	2.70	4.71	7.35	1.00×10^{1}	1.10×10^{1}	9.60
	K_d^{Fe}	3.38×10^{-2}	2.52×10^{-2}	1.76×10^{-2}	1.78×10^{-2}	2.42×10^{-2}	4.24×10^{-2}	2.60×10^{-1}	2.55
	α	1.4	5.2×10^{1}	1.5×10^{2}	2.6×10^{2}	3.0×10^{2}	2.4×10^{2}	4.2×10^{1}	3.8
DHDECMPO	K_d^{Am}	4.19×10^{-1}	2.77×10^{1}	8.07×10^{1}	1.05×10^{2}	7.64×10^{1}	3.32×10^{1}	1.75×10^{1}	1.55×10^{1}
	K_d^{Fe}	2.16	5.54	1.39×10^{1}	1.73×10^{1}	1.47×10^{1}	1.80×10^{1}	1.75×10^{2}	1.57×10^{3}
	α	1.9×10^{-1}	5.0	5.8	6.1	5.2	1.8	1.0×10^{-1}	9.9×10^{-3}
D(EB)DECMPO	K_d^{Am}	5.21×10^{-2}	5.98×10^{-1}	1.91	2.63	2.20	1.24	9.20×10^{-1}	1.25
	K_d^{Fe}	8.65×10^{-1}	1.18	9.79×10^{-1}	1.12	7.8×10^{-1}	9.52×10^{-1}	4.57	5.18×10^{1}
	α	6.0×10^{-2}	5.3×10^{-1}	2.0	2.3	2.8	1.3	2.0×10^{-1}	2.4×10^{-2}
DHDBCMPO	K_d^{Am}	3.41	3.84×10^{1}	1.52×10^{2}	1.04×10^{2}	8.84×10^{1}	2.53×10^{1}	1.02×10^{1}	6.67
	K_d^{Fe}	5.90	1.91×10^{1}	3.13×10^{1}	8.04×10^{1}	4.94×10^{1}	4.18×10^{1}	1.07×10^{2}	6.11×10^{2}
	α	5.8×10^{-1}	2.0	4.9	1.3	1.8	6.1×10^{-1}	9.5×10^{-2}	1.1×10^{-2}
DHD(IB)CMPO	K_d^{Am}	3.65	1.44×10^{2}	2.10×10^{2}	1.72×10^{2}	7.14×10^{1}	1.97×10^{1}	6.05	4.34
	K_d^{Fe}	8.05	6.36	8.72	7.44	5.21	5.25	1.47×10^{1}	9.34×10^{1}
	α	4.5×10^{-1}	2.3×10^{1}	2.4×10^{1}	2.3×10^{1}	1.4×10^{1}	3.8	4.1×10^{-1}	4.6×10^{-2}
DHD(SB)CMPO	K_d^{Am}	6.44×10^{-1}	5.36×10^{1}	1.29×10^{2}	1.10×10^{2}	4.97×10^{1}	1.31×10^{1}	3.38	2.06
	K_d^{Fe}	3.19	4.25	8.59	8.70	7.10	6.32	2.08×10^{1}	1.03×10^{2}
	α	2.0×10^{-1}	1.3×10^{1}	1.5×10^{1}	1.3×10^{1}	7.0	2.1	1.6×10^{-1}	2.0×10^{-2}

[a] Measurements performed at 25.0°C. Separation factor (α) = K_d^{Am}/K_d^{Fe}.

these two ions (0.962 Å for Am^{3+} (13) vs 0.645 Å for Fe^{3+} (14)) it is not totally unexpected that changes in the bulk of the amide substituents should have a greater effect on the extraction of Fe(III).

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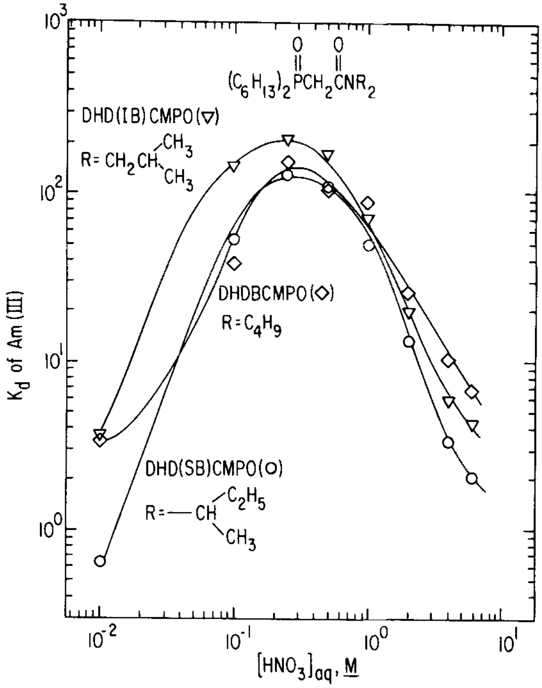

FIGURE 3. Extraction of Am(III) from HNO_3 by 0.50 M DHDBCMPO, DHD(IB)CMPO and DHD(SB)CMPO.

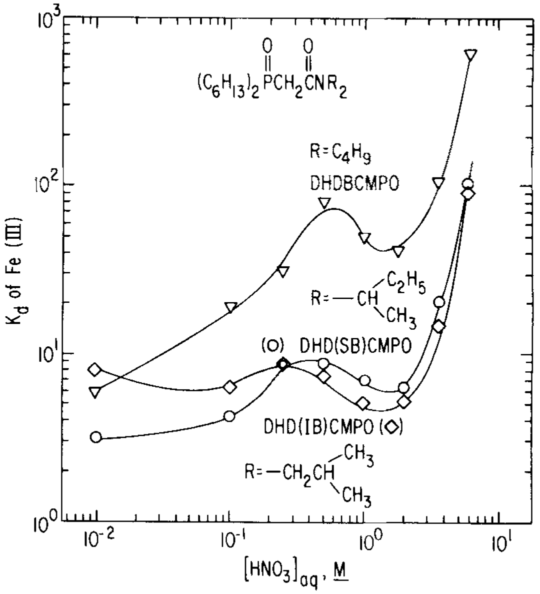

FIGURE 4. Extraction of Fe(III) from HNO_3 by 0.50 M DHDBCMPO, DHD(IB)CMPO and DHD(SB)CMPO.

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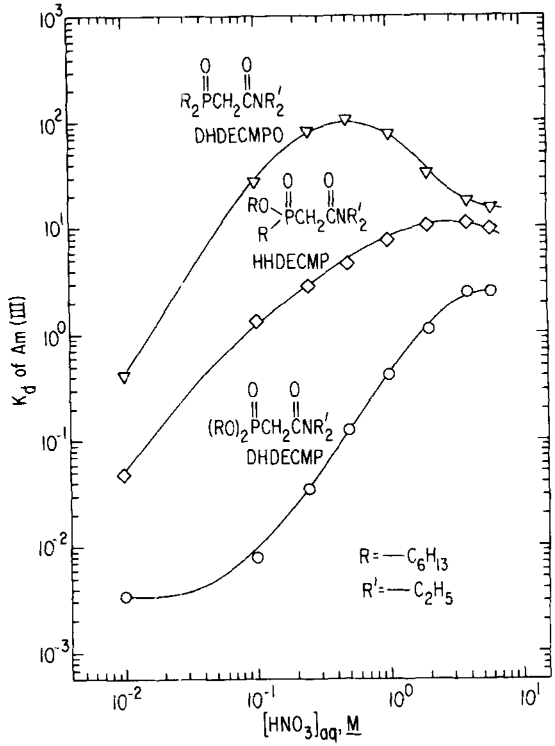

FIGURE 5. Comparison of the extraction of Am(III) from HNO_3 by 0.50 M DHDECMP, HHDECMP and DHDECMPO.

Effect of Phosphoryl Basicity

It was of great interest to see what effect modification of the basicity of the phosphoryl group would have not only on the efficiency of extraction of Am(III), but also on the selectivity of extraction of Am(III) over Fe(III). In figures 5 and 6 the distribution ratios for the extraction of Am(III) and Fe(III) are plotted as a function of aqueous phase acidity for the series of extractants DHDECMP, HHDECMP and DHDECMPO. These extractants, in which the basicity of the P=O group should be the major factor influencing extraction (15), show major

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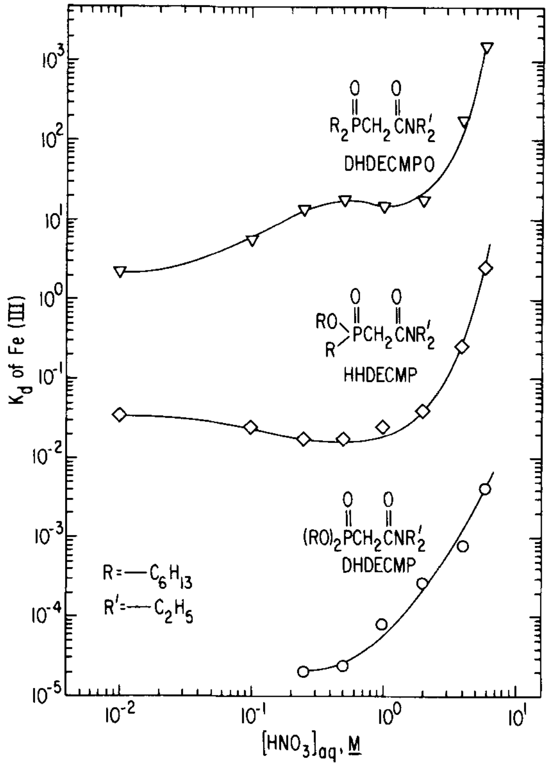

FIGURE 6. Comparison of the extraction of Fe(III) from HNO_3 by 0.50 M DHDECMP, HHDECMP and DHDECMPO.

differences in behavior for the extraction of Am^{3+} and even greater differences for the extraction of Fe^{3+}. As the basicity of the extractant increases, so do the distribution ratios for Am(III) and Fe(III). But as the extent of extraction increases for these two metal ions, the selectivity decreases. For example, with 0.50 M HNO_3 in the aqueous phase, the separation factor $\left(\frac{K_d^{Am}}{K_d^{Fe}}\right)$ for 0.50 M DHDECMP is 5.1×10^3, compared to 2.6×10^2 for HHDECMP and only 6.1 for DHDECMPO. Thus, as has

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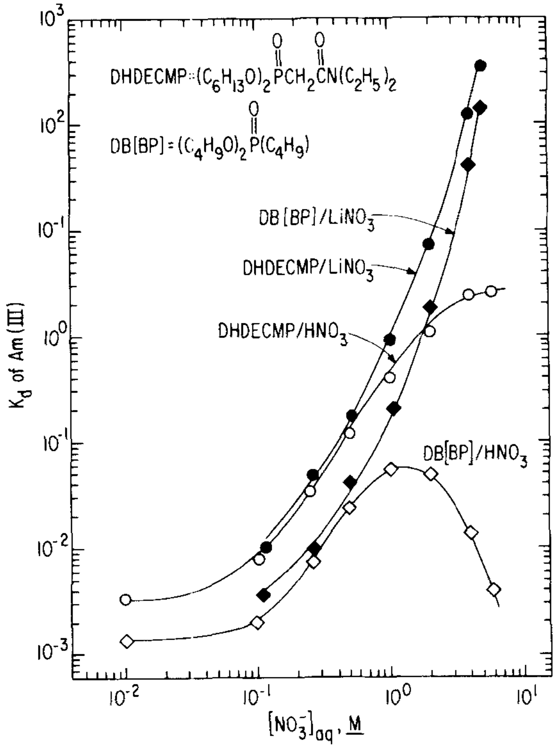

FIGURE 7. Comparison of the extraction of Am(III) from HNO_3 and $LiNO_3$ by 0.50 M DHDECMP and DB[BP].

been observed before for monofunctional extractants (16), increases in the basicity of the phosphoryl group result in increases in the distribution ratio at the expense of selectivity.

Extraction of Am(III) from $LiNO_3$ and HNO_3 Using Mono- and Bifunctional Extractants

A series of experiments was undertaken to compare the extraction behavior of Am(III) from HNO_3 and $LiNO_3$ solutions using the series of extractants DHDECMP, HHDECMP and DHDECMPO and their monofunctional analogues DB[BP], B[DBP] and TOPO. The results of this study, shown in Figs. 7, 8 and 9, reveal

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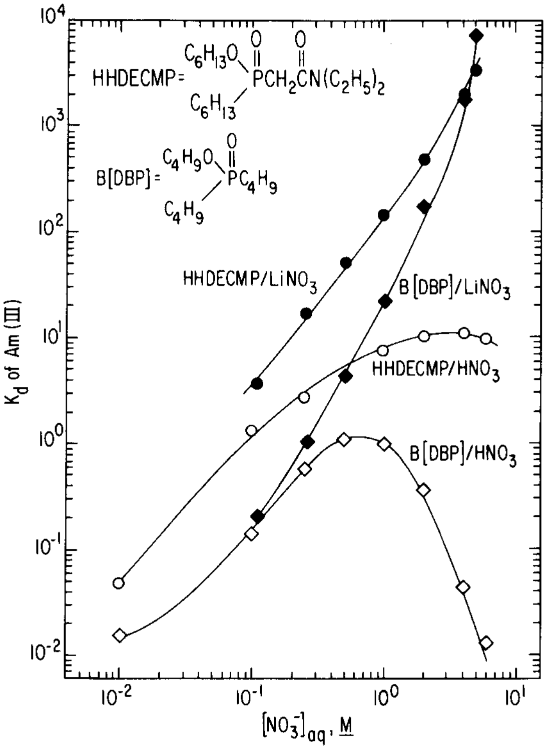

FIGURE 8. Comparison of the extraction of Am(III) from HNO_3 and $LiNO_3$ by 0.50 M HHDECMP and B[DBP].

the striking differences between the monofunctional and bifunctional extractants at moderate to high levels of aqueous acid concentration, whereas when the extractions were carried out using an aqueous phase of $LiNO_3$ (containing 0.01 M HNO_3) the differences between the pairs of extractants are considerably less. While the extraction of Am^{3+} from $LiNO_3$ by the pairs of related compounds follow the same general trend with distribution ratios of similar magnitude, the extraction from HNO_3 results in increasingly divergent K_d values as the acidity is increased.

This behavior has been discussed previously for the extraction of Th(IV) and Am(III) by DHDECMP and DB[BP] (1,2)

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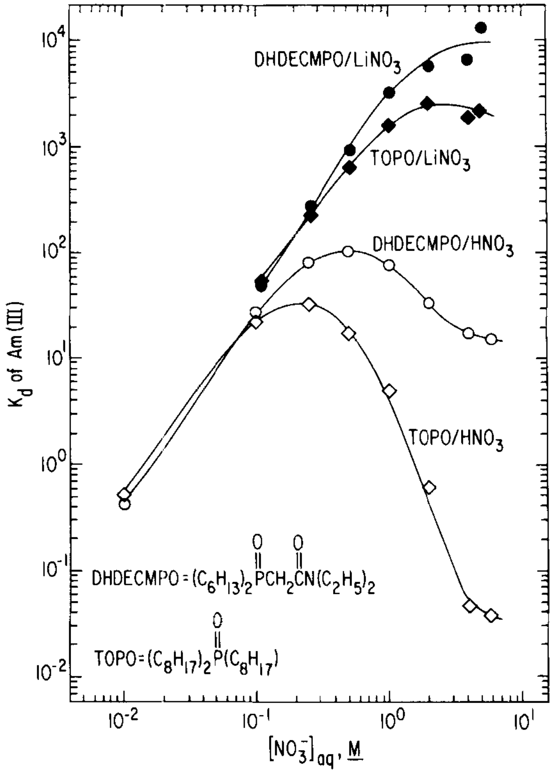

FIGURE 9. Comparison of the extraction of Am(III) from HNO_3 and $LiNO_3$ by 0.50 M DHDECMPO and TOPO.

and was attributed to the ability of DHDECMP to act as an intramolecular acid buffer, which protects the phosphoryl oxygen-metal bond from attack by hydrogen ions, resulting in significantly larger K_d values for the extraction from acidic media as compared to DB[BP] (1,2). Since there was no significant difference between DHDECMP and DB[BP] for the extraction of Am^{3+} from $LiNO_3$ solution, chelation or bidentate coordination of the DHDECMP was ruled to be an unimportant factor in extraction (2).

For the extractants HHDECMP and DHDECMPO, when compared to the monofunctional compounds B[DBP] and TOPO, respectively, similar behavior is observed. The monofunctional extractants are equally as effective as their bifunctional counterparts for the extraction of Am(III) from $LiNO_3$, indicating bidentate behavior of the bifunctional compounds (which would be expected to result in greatly enhanced distribution ratios relative to monodentate coordination (3)) is not an important factor. The differences in the distribution ratios as a function of HNO_3 concentration parallel quite closely those observed for Am^{3+} extraction by DHDECMP and DB[BP] (2), indicating a similar buffering effect is operational.

It can be noted from the data in Figs. 5 and 7-9 that the change in distribution ratio as a function of aqueous phase acidity also varies depending upon the basicity of the phosphoryl group. Whereas the K_d values for Am(III) extraction by the most basic bifunctional extractant, DHDECMPO, reach a maximum at approximately 0.50 $\underline{M}$ HNO_3, the maximum occurs at *ca.* 3-4 $\underline{M}$ HNO_3 for HHDECMP while no maximum is observed for extraction by DHDECMP. This behavior, which is also observed to a lesser degree for the extraction by the monofunctional extractants, reflects the greater affinity of hydrogen for the phosphoryl oxygen as the basicity of this group is increased. This increased affinity apparently counteracts the buffering effect of the amide group, resulting in a greater influence of the acidity on extraction in the more basic extractants.

SUMMARY AND CONCLUSIONS

The study of the extraction of Am(III) and Fe(III) from aqueous media by a series of mono- and bifunctional extractants reveals the importance of steric and inductive effects in the selectivity and efficiency in this process. The use of bifunc-

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tional extractants permits the extraction of Am(III) from a wide range of aqueous acidity through the ability of these compounds to buffer the effects of high hydrogen ion concentrations, rather than through bidentate coordination. Substitution of R-O-P groups by R-P should increase the stability of these compounds towards hydrolysis, in addition to increasing the extracting capability by increasing the basicity of the coordinating group. This has the effect, however, of diminishing the selectivity of the extractants. The selectivity can be increased somewhat by the introduction of branched alkyl groups in the amide moiety. Branching near the phosphoryl group decreases the extent of extraction without increasing selectivity.

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The HHDECMP and the DHDECMPO compounds show promise for actinide(III) purifications. The high K_d's for Am(III) from nitric acid solutions ranging in concentrations from 0.1 to 3 M HNO_3 using DHDECMPO may be the basis for a general actinide(III) "clean-up" procedure. In addition, the stability of the phosphine oxide compound to hydrolysis is an advantage. The HHDECMP compound has potential as an improved extractant for actinide(III) ion recoveries from high level liquid waste. However, as observed in the studies of DHDECMP (4), scrubbing with 3 M HNO_3/0.05 M oxalic acid solution is necessary to achieve decontamination from certain fission products; e.g., zirconium. Both of these applications are being investigated.

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