Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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E. P. Horwitz[a]; D. G. Kalina[a]; L. Kaplan[a]; G. W. Mason[a]; H. Diamond[a]
[a] CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

To cite this Article Horwitz, E. P. , Kalina, D. G. , Kaplan, L. , Mason, G. W. and Diamond, H.(1982) 'Selected Alkyl(phenyl)-*N,N*-dialkylcarbamoylmethylphosphine Oxides as Extractants for Am(III) from Nitric Acid Media', Separation Science and Technology, 17: 10, 1261 — 1279

To link to this Article: DOI: 10.1080/01496398208060649

URL: http://dx.doi.org/10.1080/01496398208060649

SEPARATION SCIENCE AND TECHNOLOGY, 17(10), pp. 1261-1279, 1982

Selected Alkyl(phenyl)-*N,N*-dialkylcarbamoylmethylphosphine Oxides as Extractants for Am(III) from Nitric Acid Media

E. P. HORWITZ, D. G. KALINA, L. KAPLAN, G. W. MASON,
and H. DIAMOND

CHEMISTRY DIVISION
ARGONNE NATIONAL LABORATORY
ARGONNE, ILLINOIS 60439

Abstract

A new series of neutral bifunctional extractants, alkyl(phenyl)-*N,N*-dialkylcarbamoylmethylphosphine oxides, has been prepared and studied as extractants for Am(III) from nitric acid media. Two types of alkyl(phenyl)-*N,N*-dialkyl CMPO compounds were prepared, one containing *N,N*-diethyl groups and the other containing *N,N*-diisobutyl groups. The *N,N*-diethyl series contained hexyl(phenyl) and 6-methylheptyl(phenyl) derivatives, abbreviated HϕDECMPO and 6-MHϕDECMPO, respectively. The *N,N*-diisobutyl series contained the *n*-octyl(phenyl), 6-methylheptyl(phenyl), and the 2-ethylhexyl(phenyl) derivatives, abbreviated OϕD[IB]CMPO, 6-MHϕD[IB]CMPO, and 2-EHϕD[IB]CMPO, respectively. Third power extractant dependencies for the extraction of Am(III) from 0.5 and 3 *M* HNO_3 were obtained at low (<0.25 *M*) concentrations of extractant, but higher power dependencies were obtained above 0.25 *M* extractant from 3 *M* HNO_3. The HϕDECMPO, 6-MHϕDECMPO, 6-MHϕD[IB]CMPO, and Oϕ*D*[IB]CMPO [all 0.5 *M* in diethylbenzene (DEB)] are significantly better extractants than DHDECMPO for Am(III) from 1 to 6 *M* HNO_3. These same extractants have lower D_{Am} values than DHDECMPO at low acidities. HϕDECMPO and OϕD[IB]CMPO also have better selectivity for Am(III) over Fe(III) than DHDECMPO. HϕDECMPO in DEB has a strong tendency toward the formation of a second liquid organic phase on extracting macroconcentrations of Nd(III) and U(VI) from 3 *M* HNO_3; however, this behavior is substantially diminished with the OϕD[IB]CMPO and 6-MHϕD[IB]CMPO compounds.

INTRODUCTION

During the last few years we have studied a number of compounds containing the carbamoylphosphoryl moiety as extractants for actinides from nitrate (*1–3*) and thiocyanate (*4*) media. This work was motivated by earlier studies at other laboratories (*5–14*) on various neutral bifunctional organophosphorus compounds, particularly dihexyl *N,N*-diethylcarbamoylmethylphosphonate (DHDECMP), as extractants for Am(III) and Cm(III) from the acidic solutions generated by reprocessing spent nuclear fuel.

A portion of our recent investigations in this area has involved the study of the extractant behavior of a series of compounds containing the carbamoylmethylphosphoryl (CMP) moiety in which the basicity of the phosphoryl group and the steric bulk of the substituent groups were varied (*3*). The effect of these changes on the extraction of Am(III) and Fe(III) were studied to evaluate if modifications in the CMP structure would result in an extractant with higher Am(III) distribution ratios (*D*'s) than obtained with DHDECMP while maintaining comparable selectivities. We found that the phosphine oxide analog dihexyl *N,N*-diethylcarbamoylmethylphosphine oxide (DHDECMPO) was indeed a stronger extractant (higher *D*'s) than DHDECMP for all of the actinides. In addition, the replacement of alkoxy by alkyl groups should improve the stability of the DHDECMPO toward hydrolysis. However, DHDECMPO lacked the selectivity for actinide(III) ions over some important fission products, e.g., Zr(IV), and corrosion products, e.g., Fe(III). This same study showed that the phosphinate analog hexyl hexyl-*N,N*-diethylcarbamoylmethylphosphinate (HHDECMP) had the best combination of high *D*'s for Am(III) and high selectivity over Fe(III). But HHDECMP formed an insoluble complex with Pd(II), has the potential of hydrolyzing at the alkoxy group, and was difficult to synthesize (*15*).

The objective in this investigation was to study further the effect of structural modifications of compounds containing the CMP moiety to see if we could prepare an extractant that had both high *D*'s for actinide(III) ions as well as high selectivity over fission products and favorable solubility properties on loading.

Rationale for the Alkyl(phenyl)-*N,N*-dialkyl CMPO Series

Our previous study (*3*), in which we systematically varied the phosphoryl oxygen (P=O) donor strength, revealed that one of the important features of extractants containing the CMP moiety is that much of the gain in P=O basicity is not realized in achieving high D_{Am} at high acidities because of corresponding increases in the affinity of HNO_3 for the same basic donor group. For example, the ratio D_{Am}(DHDECMPO)/D_{Am}(DHDECMP) is ~10^3 from 0.1 to 0.5 *M* HNO_3 but only ~10 from 4 to 6 *M* HNO_3. Since selectivity decreases with increasing basicity of P=O, but is adequate for the phosphinate analog, we reasoned that a superior CMP extractant should have less P=O basicity than is present in DHDECMPO, but should be achieved without introducing a P—O—C bond, which is subject to hydrolysis. Replacement of one of the alkyl groups bonded to the P=O with a phenyl group would decrease the basicity of oxygen because of the greater inductive effect of the benzene ring. Furthermore, this type of extractant could be conveniently synthesized from commercially available starting materials.

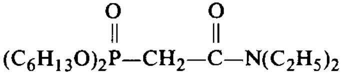
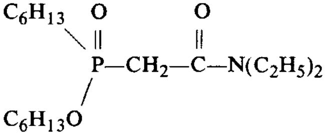
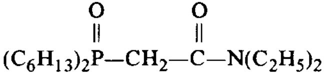
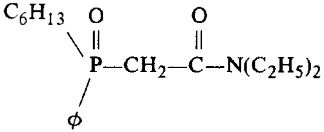
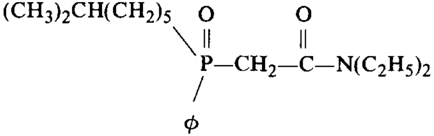
Because of these possible advantages, we began an investigation into the synthesis and purification of a series of alkyl(phenyl)-*N,N*-dialkylcarbamoylmethylphosphine oxides and their evalaution as extractants for HNO_3, Am(III), Eu(III), and Fe(III).

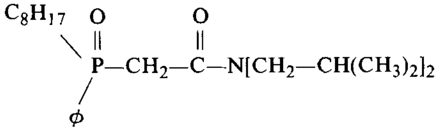
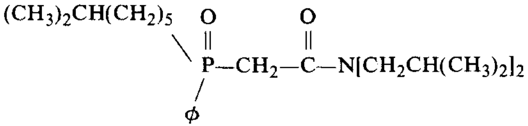
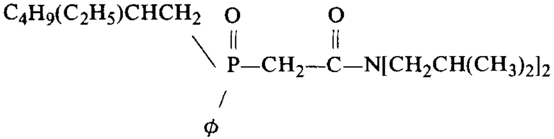
EXPERIMENTAL

The preparation and purification of DHDECMP, HHDECMP, and DHDECMPO have been described in earlier publications (*1–3*). (See Table 1 for an explanation of abbreviations.) Crude HϕDECMPO was synthesized by reaction of butyl phenylphosphinate (*16*) with two equivalents of hexylmagnesium bromide in ether followed by treatment (after addition of benzene to raise the boiling point and solubilities) with one equivalent of *N,N*-diethyl-2-chloroacetamide (*17*). After removal of volatile impurities by heating *in vacuo*, the product was converted to an insoluble mercury salt (*18*) which was washed well with warm benzene in lieu of recrystallization. Regeneration (*18*) gave a product of 99% purity (by GC) in 55% overall yield. 6-MHϕD[IB]CMPO was prepared and purified similarly (99% purity, 56% overall yield) using ethyl phenylphosphinate (from tranesterification of phenylphosphinic acid with triethyl phosphite), 1-bromo-6-methylheptane (Wiley Organics), and *N,N*-diisobutyl-2-chloroacetamide (*17*). The other alkyl(phenyl)-*N,N*-dialkyl CMPO extractants were prepared and purified analagously; all were over 97% pure. The spectral properties of these phenyl CMPO compounds were consistent with the assigned structures shown in Table 1. The mass spectrum of HϕDECMPO exhibited a parent peak at *m/e* 323, with the largest peaks at 72 and 154. All showed characteristic benzenoid absorption in the UV with λ_{max} 271, 264 (ε_{max} ~ 650), 258, and ~252 mm. The IR spectra each exhibited a band at ~3050

TABLE 1

Abbreviations, Structures, and Nomenclature of CMP and CMPO Extractants Employed in This Work

Abbreviations	Extractant	Nomenclature
DHDECMP	 $(C_6H_{13}O)_2P(=O)-CH_2-C(=O)-N(C_2H_5)_2$	Dihexyl *N,N*-diethylcarbamoylmethylphosphonate
HHDECMP	 $(C_6H_{13})(C_6H_{13}O)P(=O)-CH_2-C(=O)-N(C_2H_5)_2$	Hexyl hexyl-*N,N*-diethylcarbamoylmethylphosphinate
DHDECMPO	 $(C_6H_{13})_2P(=O)-CH_2-C(=O)-N(C_2H_5)_2$	Dihexyl-*N,N*-diethylcarbamoylmethylphosphine oxide
HϕDECMPO	 $(C_6H_{13})(\phi)P(=O)-CH_2-C(=O)-N(C_2H_5)_2$	Hexyl(phenyl)-*N,N*-diethylcarbamoylmethylphosphine oxide
6-MHϕDECEMPO	 $((CH_3)_2CH(CH_2)_5)(\phi)P(=O)-CH_2-C(=O)-N(C_2H_5)_2$	6-Methylheptyl(phenyl)-*N,N*-diethylcarbamoylmethylphosphine oxide

OφD[IB]CMPO		*n*-Octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide
6-MHφD[IB]CMPO		6-Methylheptyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl-phosphine oxide
2-EHφD[IB]CMPO		2-Ethylhexyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl-phospine oxide

cm^{-1} (phenyl) and stronger bands at 2960–2850 (C—H str), 1630 (C=O str), 1468–1435 (C—H bend) and 1200–1190 (P=O str). The NMR spectra at 200 MHz in $CDCl_3$ solution displayed resonances at ~7.80 ppm (relative to TMS) for the ortho hydrogens, ~7.50 (meta and para), 3.3 to 3.0 (N—CH_2 and $OPCH_2CO$), ~2.3 (C—C—CH_2—PO), ~1.85 (CH where present), 1.6–1.0 (other CH_2), ~1.03 (CH_3 in N—C_2H_5 where present), and 0.87–0.81 (other CH_3). The relative GC retentions on an Apiezon L column at 250° of the compounds listed in Table 1, in the order listed, were 1, 1.08, 1.41, 1.70, 2.81, 5.27, 4.74, 2.92.

Extractant solutions were prepared using distilled-in-glass grade *o*-xylene (Burdick and Jackson Laboratories) and diethylbenzene (DEB) (mixture of isomers, Aldrich Chemical Co.). Aqueous solutions were prepared using ultrapure water obtained from a Milli-Q2 system water purifier (Millipore Corp.) and Ultrex grade nitric acid (J. T. Baker Chemical Co.). Extraction studies were performed using ^{241}Am, $^{152,154}Eu$, and ^{55}Fe.

All distribution ratio measurements were performed at 25°C using the procedure described previously for Am(III) and Eu(III) (*1*) and for Fe(III) (*3*). Radiometric assays of ^{241}Am and $^{241}Am–^{152,154}Eu$ mixtures were accomplished using a Beckman Biogamma 3-channel analyzer (NaI detector). Radiometric assays of ^{55}Fe were accomplished by liquid scintillation counting using a Beckman CPM 100 counter and Beckman MP Cocktail. Duplicate assays of each phase were performed for both ^{55}Fe and $^{241}Am–^{152,154}Eu$. Distribution ratios were reproducible within ±5%. In some distribution ratio measurements performed with HNO_3 solutions in the 10^{-2} to 10^{-1} *M* range, the aqueous phase was made 10^{-3} *M* in $Lu(NO_3)_3$ to minimize the effect of acidic extractant impurities on D_{Am} and D_{Fe}. This was found to be necessary with 6-MHD[IB]CMPO for Am(III) and for all extractants with Fe(III).

The nitric acid extractions were performed by equilibrating a given organic phase four successive times with an equal volume of nitric acid solution. The nitric acid in the resultant organic phase was then back-extracted and titrated. Measurements of $[HNO_3]_o$ were reproducible within ±1% when the $(HNO_3]_a$ was $\geqq$ 0.50 *M*. Loading measurements of a given extractant with Nd(III) and U(VI) were performed by closely examining a centrifuged organic–aqueous phase mixture for third phase or precipitate formation after successive equilibrations with an equal volume of 3 *M* HNO_3 containing increasing concentrations of $Nd(NO_3)_3$ or $UO_2(NO_3)_2$. Essentially quantitative extraction of Nd(III) and U(VI) was observed after each incremental addition of metal ion until either third phase formation occurred or 75% of saturation of the extractant was achieved.

RESULTS AND DISCUSSION

Nitric Acid Extraction

Table 2 shows a comparison of the extraction of nitric acid from a range of aqueous HNO_3 concentrations by the phosphonate DHDECMP, the phosphinate HHDECMP, and the phosphine oxides DHDECMPO and HϕDECMPO in *o*-xylene diluent. The expected increase in extraction of HNO_3 by the compounds with the more basic phosphoryl groups is readily apparent when the mole ratio of HNO_3 to extractant in the organic phase is less than 1 ($[HNO_3]_o < 0.5$). From these data it seems apparent that the basicity of the phosphoryl oxygen of HϕDECMPO is intermediate between those of HHDECMP and DHDECMPO.

Differences in the basicity of the four extractants in Table 2 are less apparent when the HNO_3 to extractant ratio is greater than 1. This is probably due to the extraction of HNO_3 by the amide group once the more basic phosphoryl oxygen is protonated. The extraction of HNO_3 beyond a 1-to-1 stoichiometry does not necessarily prove involvement of the amide group since the extraction of HNO_3 by monofunctional neutral phosphorus esters, e.g., TBP, also exceeds a stoichiometry of 1 (*19*). However, Mrochek and Banks (*20*) showed that the extraction of nitric acid for a series of diphosphine oxides increased the greater the distance between the two basic groups. This behavior is expected (from electrostatic considerations) if both

TABLE 2

Extraction of HNO_3 by 0.5 *M* Extractant in *o*-Xylene

	$[HNO_3]_o$			
$[HNO_3]_a$	DHDECMP (phosphonate)	HHDECMP (phosphinate)	DHDECMPO (phosphine oxide)	HϕDECMPO (phosphine oxide)
0.10	0.00260	0.00847	0.0377	0.0201
0.25	0.0135	0.0353	0.136	0.0667
0.50	0.0434	0.0983	0.268	0.159
1.0	0.139	0.237	0.424	0.305
2.0	0.344	0.464	0.552	0.466
3.0	0.533	0.611	0.650	0.602
4.0	0.694	0.694	0.726	0.689
6.0	0.921	0.936	0.943	0.939

basic groups are involved in bonding to HNO_3. We feel that protonation of the amide portion of the CMPO molecule does occur and is important in the extraction of actinides from moderate to high HNO_3 concentrations (*1–4*). The amide group lessens the direct attack on the metal-phosphoryl oxygen bond by hydrogen ions and thus behaves as an intramolecular buffer.

Nitric Acid Dependency of D_{Am}

A comparison of D_{Am} as a function of aqueous HNO_3 concentration for 0.50 *M* solutions of HφDECMPO and DHDECMPO in *o*-xylene is shown in Fig. 1. The hexylphenyl compound shows significantly higher D_{Am}'s at high acidities and significantly lower D_{Am}'s in the low acid range. Both the shift in the maximum D_{Am} to a higher HNO_3 concentration and the lower *D*'s in dilute acid for HφDECMPO are expected based on the diminution in P=O basicity for the hexylphenyl compound. However, the much higher D_{Am} values at high acidities shown by HφDECMP are somewhat surprising

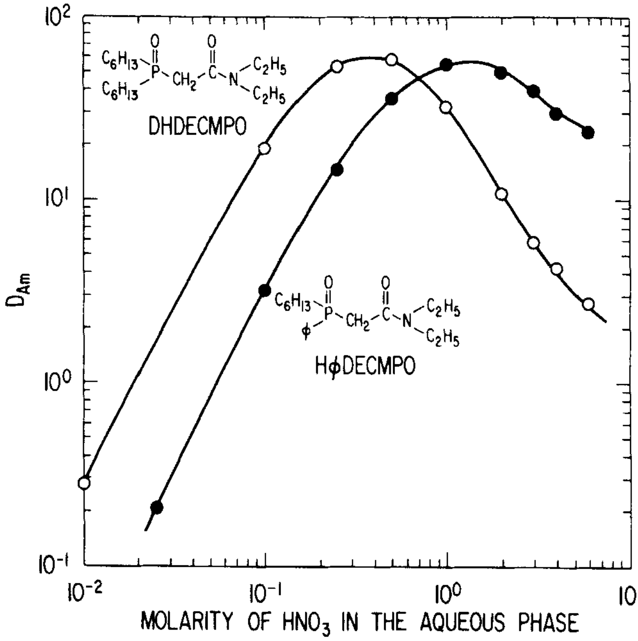


FIG. 1. Comparison of the D_{Am} vs HNO_3 concentration for 0.5 *M* solutions of DHDECMPO and HφDECMPO in *o*-xylene, 25°C.

in view of the rationale for introducing the phenyl group into the CMPO structure. The D_{Am} vs HNO_3 curve for HφDECMPO resembles to some extent the corresponding curve for the phosphinate analog HHDECMP (see Fig. 5 in Ref. *3*), which has a maximum D_{Am} at 2.5 to 3.0 *M* HNO_3, although the maximum is more pronounced for the phosphine oxide.

Although the HφDECMPO appears to be a better extractant for Am(III) than the DHDECMPO, the hexylphenyl compound in *o*-xylene readily forms a second liquid organic phase, which is heavier than the aqueous phase, when less than 5% of its capacity is consumed by UO_2^{2+} or Nd^{3+}. Solutions of HφDECMPO in DEB (diethylbenzene) or DIPB (diisopropylbenzene) form a second liquid organic phase when equilibrated with HNO_3 solutions above 1 *M*. To minimize or eliminate this problem, derivatives of alkyl(phenyl)-*N,N*-dialkyl CMPO were prepared in which the alkyl groups were lengthened and branched. (The effect of these structural modifications on third phase formation will be discussed in the section on loading studies below.)

The effect of replacing the two ethyl groups bonded to the amide nitrogen in the alkyl(phenyl) CMPO with isobutyl groups is shown in Fig. 2. (The hexyl group was replaced by 6-methyl-heptyl in both extractants and the diluent was changed to a higher boiling aromatic, DEB.) The D_{Am}'s for 6-methylheptyl(phenyl)-*N,N*-diethyl CMPO and HφDECMPO are essentially identical. (Differences in D_{Am} for HφDECMPO in Fig. 1 and for 6-MHφDECMPO in Fig. 2 are largely due to diluent effects.) Replacement of ethyl by isobutyl groups in the amide portion of the alkyl(phenyl) CMPO molecule shows no effect in the low acid range and only a small diminution in D_{Am} at high acidities. A similar effect was observed in the dihexyl-*N,N*-dialkyl CMPO series (*3*). This behavior may be explained by steric crowding about the amide group which would interfere with its protonation by HNO_3 and therefore reduce its intramolecular buffering properties, although no direct evidence is available to support this hypothesis.

Figure 3 shows a comparison of the D_{Am} vs aqueous HNO_3 concentration for three octyl isomers of phenyl *N,N*-diisobutyl CMPO. No difference in D_{Am} is observed between the *n*-octyl and 6-methylheptyl compounds since the branching of the octyl group is too far removed from the P=O group to influence bonding to Am(III). However, in the case of the 2-ethylhexyl isomer, a significant diminution in D_{Am} is found. In this case there is sufficient congestion around the metal center in the extracted complex to interfere with bonding (*3*). It is interesting to note that the decrease in D_{Am} with 2-EHφD[IB]CMPO is less at high acidities, possibly because the 2-ethylhexyl compound bonds less readily to HNO_3.

Although the magnitude of D_{Am} changes with the structural modifications described above, the general shape of the D_{Am} vs HNO_3 curves is the same.

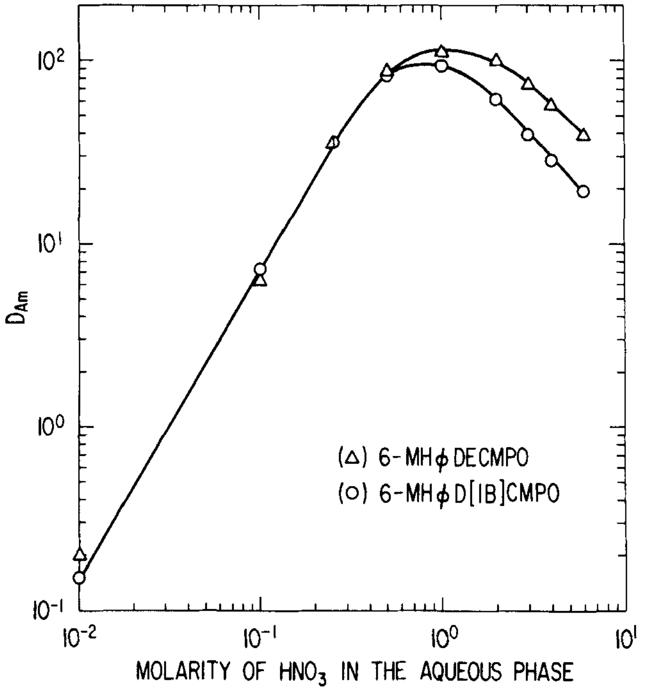


FIG. 2. Comparison of the D_{Am} vs HNO_3 concentration for 0.5 *M* solutions of 6-MHϕDECMPO and 6-MHϕD[IB]CMPO in DEB, 25°C.

The maximum in D_{Am} results from the increase in D_{Am} caused by the increase in nitrate ion concentration (*2*) and the decrease in D_{Am} caused by protonation of P=O group. The special feature of extractants containing the CMP moiety is that the decrease in distribution ratio at high HNO_3 concentrations is not nearly as abrupt as is the case with the corresponding monofunctional extractant. This property of CMP extractants is discussed in Refs. *1–4*.

Extractant Dependency

The variations in D_{Am} as a function of extractant concentration for HϕDECMPO, OϕD[IB]CMPO, and 2-EHϕD[IB]CMPO are shown in Figs. 4, 5, 6, respectively. Each extractant dependency was performed at low and high acidity. All three extractants show third-power dependencies at low

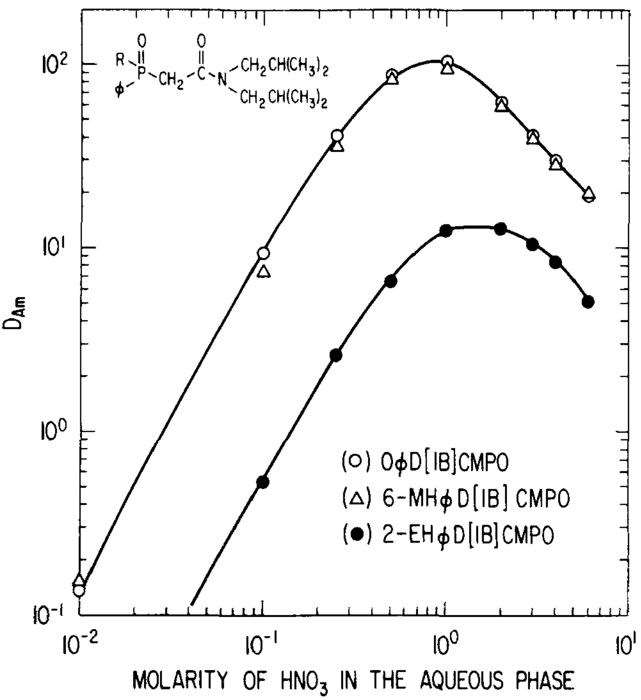


FIG. 3. Comparisons of the D_{Am} vs $\mathrm{HNO_3}$ concentration for 0.5 *M* solutions of octyl isomers of alkyl(phenyl)-*N,N*-diisobutyl CMPO in DEB, 25°C.

concentrations for both acidities. Thus the expressions for the extraction of Am(III) by the alkyl(phenyl)-*N,N*-dialkyl CMPO compounds are

$$\mathrm{Am}^{3+} + 3\mathrm{NO}_3^- + 3\bar{\mathrm{E}} \rightleftarrows \overline{\mathrm{Am(NO_3)_3 \cdot 3E}}$$

$$\mathrm{Am}^{3+} + \overline{3\mathrm{E}\cdot\mathrm{HNO_3}} \rightleftarrows \overline{\mathrm{Am(NO_3)_3 \cdot 3E}} + 3\mathrm{H}^+$$

where E is HφDECMPO, OφD[IB]CMPO, and 2-EHφD[IB]CMPO and the bar denotes the organic phase. The same dependency was found for DHDECMP (*2*) and DHDECMPO (*3*) for Am(III) extraction. However, when *n*-butyl, isobutyl, or *sec*-butyl groups were substituted for the ethyl groups in DHDECMPO, second-power dependencies were obtained (*3*).

Deviations from third power dependencies are evident in Figs. 4, 5, and 6 at high extractant concentrations. Increases in the slope occur when the

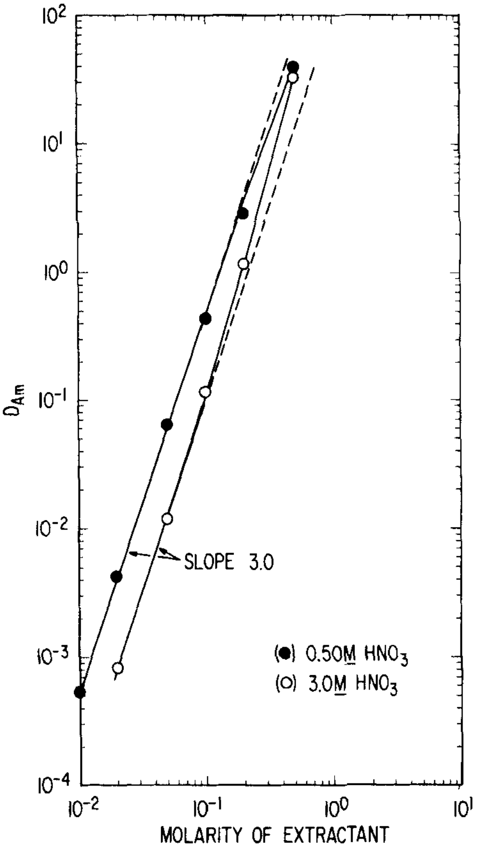


FIG. 4. Extractant dependency for Am(III) using HϕDECMPO in *o*-xylene, 25°C.

extraction is performed from 3 *M* HNO_3; decreases in slope occur when the extraction is performed at 0.5 *M* HNO_3. These changes in slope are similar for all three extractants but are the most pronounced for 2-EHϕD[IB]CMPO and least pronounced for HϕDECMPO. Such changes in dependency are not unique to this class of extractants. Peppard, Mason, and Maier (*21*) reported that the extraction of Th(IV) by 25–100% TBP in benzene was second power at 1.9 *M* HNO_3, third power at 6.1 *M* HNO_3, and fourth power at 10.1 *M* HNO_3. Shoun, McDowell, and Weaver (*8*) found a slope of 3.2 for the extraction of Am(III) from 6 *M* HNO_3 by DHDECMP in DEB ranging in concentration from 0.28 to 1.3.

It is likely that the decreases in slope at low acid are due to activity coefficient effects. Alcock, Grimley, Healy, and Kennedy (*22*) have shown

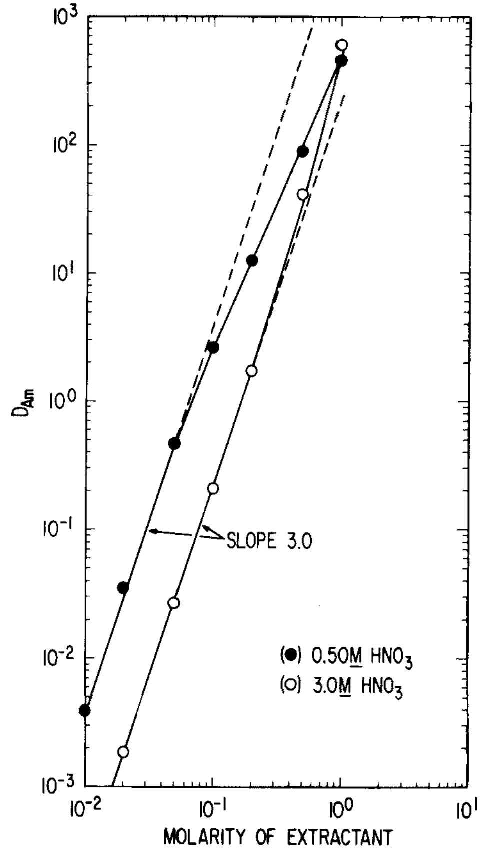


FIG. 5. Extractant dependency for Am(III) using OϕD[IB]CMPO in DEB, 25°C.

that the activity coefficient, γ, of TBP and TBP·HNO_3 decreases substantially as their concentration increases. Activity coefficients must also play a role in the dependencies at higher HNO_3 concentrations but other effects evidently more than compensate for the decrease in γ with increasing extractant concentrations. One possibility is the tendency of metal nitrato complexes in organic phases to form anionic species, which would require a protonated extractant molecule to neutralize the negative charge, e.g., $EH^+Am(E)_3(NO_3)_4^-$. A similar species containing Ce(III) has been postulated by Glueckauf to explain the extraction of cerium(III) nitrate from nitric acid by a neutral extractant (*23*). Another possibility is that the neutral americium nitrato-extractant complex is able to solvate extractant-HNO_3 molecules, thus forming a species with an extractant to metal ratio of >3.

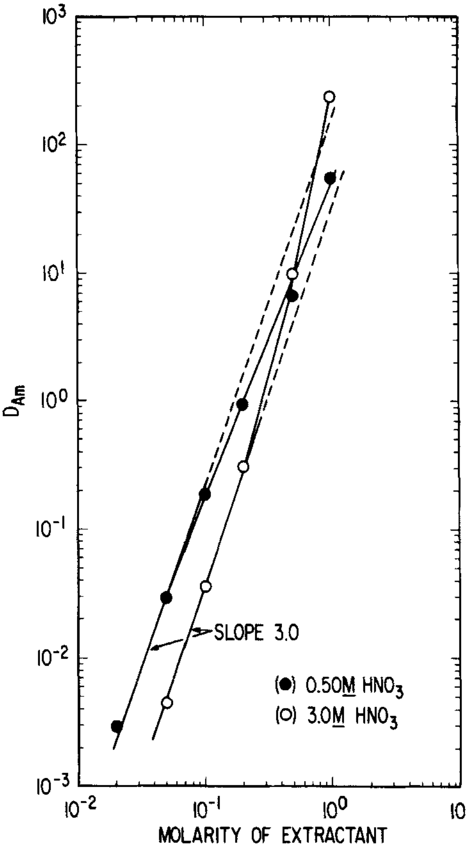


FIG. 6. Extractant dependency for Am(III) using 2-EHϕD[IB]CMPO in DEB, 25°C.

Selectivity

Table 3 shows the substantial improvement in selectivity of Am(III) over Fe(III) achieved with two alkyl(phenyl)-*N,N*-dialkyl CMPO extractants compared to DHDECMPO. The separation factors for the two alkyl(phenyl)-*N,N*-dialkyl CMPO's are comparable to those obtained with the phosphinate, HHDECMP (*3*). Although Fe(III) is only one of many constituents in high level radioactive waste, we found that if a given CMP or CMPO extractant does not have very good selectivity for Am(III) over Fe(III), it will not have sufficiently high selectivity for Am(III) over important fission products such as Zr(IV), Nb(V), and Mo(VI) (*15*). This was the case with DHDECMPO. Therefore, the substantially higher $\alpha_{\mathrm{Fe}}^{\mathrm{Am}}$values achieved with H$\phi$DECMPO and O$\phi$D[IB]CMPO are important to the potential of these compounds as selective actinide extractants.

TABLE 3

Separation Factor $\alpha_{\mathrm{Fe}}^{\mathrm{Am}}$ as a Function of Nitric Acid Concentration.[a] 0.5 M Extractant, 25°C

$[\mathrm{HNO_3}]_a$	DHDECMPO	HϕDECMPO	OϕD[IB]CMPO
0.50	6.1	2.8×10^2	1.1×10^2
1.0	5.2	2.4×10^2	1.4×10^2
2.0	1.8	1.0×10^2	7.6×10^1
4.0	1.0×10^{-1}	7.2	8.7
6.0	9.9×10^{-3}	0.60	1.2

[a] Separation factor, $\alpha_{\mathrm{Fe}}^{\mathrm{Am}} = D_{\mathrm{Am}}/D_{\mathrm{Fe}}$.

The separation factor $\alpha_{\mathrm{Eu}}^{\mathrm{Am}}$ is small in comparison to $\alpha_{\mathrm{Fe}}^{\mathrm{Am}}$. Am(III) and Eu(III) generally resemble each other closely with respect to their extraction behavior, except when soft donor groups are involved. The values of $\alpha_{\mathrm{Eu}}^{\mathrm{Am}}$ remain essentially constant in dilute acid up to 1 M $\mathrm{HNO_3}$, gradually increase until 4.0 M $\mathrm{HNO_3}$, and then decrease again at 6 M $\mathrm{HNO_3}$ (Table 4). Table 5 shows a small increase in $\alpha_{\mathrm{Eu}}^{\mathrm{Am}}$ with increasing extractant concentration.

Detectable changes in $\alpha_{\mathrm{Eu}}^{\mathrm{Am}}$ occur when a phenyl group replaces a hexyl group in DHDECMPO and when modifications are made in the alkyl(phenyl)-*N*,*N*-dialkyl CMPO structure. These results are summarized in Table 6 for $\alpha_{\mathrm{Eu}}^{\mathrm{Am}}$ measured at 3 M $\mathrm{HNO_3}$. It is interesting that in both cases where steric hindrance adjacent to the P=O group was increased, i.e., phenyl replacing hexyl and 2-ethylhexyl replacing n-octyl, $\alpha_{\mathrm{Eu}}^{\mathrm{Am}}$ increased. The decrease in $\alpha_{\mathrm{Eu}}^{\mathrm{Am}}$ when isobutyl groups replace ethyl groups in the amide moiety was also observed in the dihexyl CMPO series (*24*).

TABLE 4

Separation factor $\alpha_{\mathrm{Eu}}^{\mathrm{Am}}$ as a Function of Nitric Acid Concentration.[a] 0.5 M Extractant, 25°C

$[\mathrm{HNO_3}]_a$	DHDECMPO (in xylene)	6-MHϕDECMPO (in DEB)	6-MHϕD[IB]CMPO (in DEB)	2-EHϕD[IB]CMPO (in DEB)
0.10	1.06	1.54	1.02	1.14
0.25	1.02	1.56	1.03	1.11
0.50	1.01	1.67	1.04	1.16
1.0	1.12	1.76	1.12	1.39
2.0	1.25	1.73	1.31	1.70
3.0	1.32	1.70	1.42	1.73
4.0	1.28	1.52	1.42	1.70
6.0	1.05	1.31	1.21	1.41

[a] Separation factor, $\alpha_{\mathrm{Eu}}^{\mathrm{Am}} = D_{\mathrm{Am}}/D_{\mathrm{Eu}}$.

TABLE 5

Separation Factor α^{Am}_{Eu} as a Function of Extractant Concentration.[a] 25°C

	HφDECMPO, HNO_3		OφD[IB]CMPO, HNO_3		2-EHφD[IB]CMPO, HNO_3	
[E]	0.5 *M*	3.0 *M*	0.5 *M*	3.0 *M*	0.5 *M*	3.0 *M*
0.020	0.75	1.13	0.73	0.68		
0.050	0.79	1.02	0.75	0.75	1.04	0.95
0.10	0.86	1.16	0.78	0.82	1.03	1.20
0.20	0.97	1.41	0.84	0.99	1.04	1.41
0.50	1.42	1.69	1.07	1.41	1.20	1.70

[a] Separation factor, $\phi^{Am}_{Eu} = D_{Am}/D_{Eu}$.

Extractant Loading

The type of substituent groups bonded to the CMP moiety has a very striking effect on the quantities of lanthanides and actinides which may be extracted into the organic phase without the occurrence of third-phase formation. Extractant loading studies of several CMP and CMPO extractants were performed from 3 *M* HNO_3 using Nd(III), which is a good stand-in for Am(III), and U(VI). The results are expressed in Table 7 as the percent of the theoretical capacity of a given extractant which can be complexed by Nd(III) and U(VI) (UO_2^{2+}) before third-phase (second liquid organic phase) formation occurs. Several generalizations about loading CMP and CMPO extractants can be made based on these data. First, third-phase formation occurs much more readily with UO_2^{2+} than with Nd(III); second, replacement of alkoxy groups by alkyl groups enhances third-phase forma-

TABLE 6

Separation Factor, α^{Am}_{Eu}, as a Function of Structure.
3 *M* HNO_3, 25°C

DHDECMPO (in xylene)	1.32
HφDECMPO (in xylene)	1.69
6-MHφDECMPO (in DEB)	1.70
OφD[IB]CMPO (in DEB)	1.41
6-MHφD[IB]CMPO (in DEB)	1.42
2-EHφD[IB]CMPO (in DEB)	1.70

TABLE 7

Loading of CMP and CMPO Extractants with Nd(III) and U(VI), 0.5 *M* Extractant in DEB, 3 *M* HNO_3, 25°C

Extractant	% Loading	
	Nd(III)[a]	U(VI)[a]
DHDECMP	>75	100
HHDECMP	>75	80–85
DHDECMPO	65–70	30–35
HϕDECMPO	<5	<5
6-MHϕDECMPO	35–40	10–15
6-MHϕD[IB]CMPO	>75	40–45
2-EHϕD[IB]CMPO	>75	30–35
OϕD[IB]CMPO	>75	40–45

[a] Percent loadings are based on an extractant-to-metal ratio of 3 for Nd(III) and 2 for U(VI).

tion; and third, replacement of an ethyl group by an isobutyl group in the alkyl(phenyl)-*N*,*N*-dialkyl CMPO series drastically reduces third-phase formation. The substantial enhancement of third-phase formation that occurs when a phenyl group is substituted for a hexyl group is also striking and may be due to the increased polarity of the alkyl(phenyl) compound.

Additional loading studies performed on 0.5 *M* OϕD[IB]CMPO in DEB showed that the loading of UO_2^{2+} was increased to 50–55% of capacity at 50°C before third-phase formation appeared. A 1.0 *M* solution of OϕD[IB]CMPO in DEB can be loaded to full capacity with UO_2^{2+} at both 25 and 50°C without third-phase formation.

SUMMARY AND CONCLUSIONS

A new series of neutral bifunctional extractants, alkyl(phenyl)-*N*,*N*-dialkylcarbamoylmethylphosphine oxides, has been prepared and studied as extractants for Am(III) from nitric acid media. The rationale for preparing this class of compounds was to reduce the P=O basicity compared to dihexyl-*N*,*N*-diethylcarbamoylmethylphosphine oxide, DHDECMPO, to achieve better selectivity of Am(III) over Fe(III) and fission products and to preserve stability toward hydrolysis by eliminating alkoxy groups. We found that several alkyl(phenyl)-*N*,*N*-dialkyl CMPO compounds; namely, hexyl(phenyl)-*N*,*N*-diethyl CMPO, octyl(phenyl)-*N*,*N*-diisobutyl CMPO, and 6-methylheptyl-*N*,*N*-diisobutyl CMPO, were significantly better extractants for Am(III) from 1–6 *M* nitric acid concentrations than DHDECMPO and, in addition, had the desirable property of lower D_{Am} values at low acidities than obtained with DHDECMPO, thus enhancing the ease of Am(III) back-extraction. The HϕDECMPO and OϕD[IB]CMPO compounds also show substantially better selectivity of Am(III) over Fe(III) compared to DHDECMPO. Separation factors α_{Fe}^{Am} for HϕDECMPO and OϕD[IB]CMPO are similar in magnitude to those of the phosphinate, HHDECMP. The ratio of extractant to metal ion in the alkyl(phenyl)-*N,N*-dialkyl CMPO series appears to be 3 at dilute concentrations (<0.25 *M*) of extractant but may be higher at higher concentrations.

The HϕDECMPO compound shows a strong tendency toward third-phase formation on extracting macroconcentrations of Nd(III) and U(VI) from 3 *M* HNO_3. However, replacement of the hexyl group with either *n*-octyl or 6-methylheptyl and the ethyl groups with isobutyl groups significantly decreases this tendency.

The OϕD[IB]CMPO and 6-MHϕD[IB]CMPO compounds show considerable promise as improved extractants for actinide recoveries from high level liquid waste and for general actinide clean-up operations. Stability toward hydrolysis and ease of synthesis and purifications are additional favorable properties. However, as observed with our studies of HHDECMP (*15*) and with other investigators' studies of DHDECMP (*9, 10*), nitric acid–oxalic acid mixtures are necessary to achieve decontamination from Zr(IV), Nb(V), and Mo(VI). Although the *n*-octyl and 6-methylheptyl compounds are essentially identical in regard to their properties as extractants, the *n*-octyl compound would probably be less costly to synthesize because of the ready availability of the *n*-octyl halides. Therefore, our additional work on the above applications will focus on the OϕD[IB]CMPO compound.

Acknowledgment

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy under contract number W-31-109-ENG-38.

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Received by editor April 2, 1982