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The Extraction of Selected Transplutonium(III) and Lanthanide(III) Ions by Dihexyl-*N*,*N*-diethylcarbamoylmethylphosphonate from Aqueous Nitrate Media

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Abstract

The extraction behavior of selected transplutonium(III) and lanthanide(III) ions from nitrate solution was studied using relatively pure dihexyl-*N*,*N*-diethylcarbamoylmethylphosphonate (DHDECMP). The data obtained for Am(III) and Eu(III) using DHDECMP were compared with analogous measurements obtained with dibutyl butylphosphonate (DB[BP]) and in certain cases with dihexyl-*N*,*N*-diethylcarbamoylethylphosphonate (DHDECEP). It was found that both the nitrate and extractant concentration dependencies were third power. The K_d's for Am(III) and for Eu(III) measured from low acid $LiNO_3$ solutions were similar for DHDECMP, DHDECEP, and DB[BP], thus giving no evidence for any significant chelation effect for DHDECMP. Significant differences among DHDECMP, DHDECEP, and DB[BP] are found for the extraction of Am(III) and Eu(III) from 1 to 5 *M* HNO_3. These differences are explained by the ability of DHDECMP (and to a lesser extent, DHDECEP) to buffer itself against HNO_3 by protonation of the amide group. The K_d's for Am(III) through Fm(III) and for La(III) through Lu(III) measured from $LiNO_3$ and HNO_3 using DHDECMP show a definite tetrad effect when plotted as a function of Z. The K_d's for the lanthanides generally decrease with Z whereas the K_d's for the transplutonium elements change very little with Z.

INTRODUCTION

The preceding paper by the authors (*1*) focused on the extraction behavior of Th(IV) and U(VI) with dihexyl-*N*,*N*-diethylcarbamoylmethylphosphonate (DHDECMP) (current nomenclature used by *Chemical*

Abstracts). The extraction behavior of trivalent actinides from nitric acid is of importance in the removal of actinides from high level liquid waste because of the presence of americium and curium isotopes.

Since the trivalent actinides are much more difficult to extract from an acidic solution using a neutral organophosphorus extractant, the enhanced extractability of Am(III) and Cm(III) from nitric acid using neutral bifunctional organophosphorus extractants such as DHDECMP is very significant (*2*). Our previous study (*1*) showed that the bidenticity of the DHDECMP did not appear to be the key factor in the ability of this compound to extract Th and U from acid solution. Rather, the ability of the DHDECMP to "buffer" itself from the influence of hydrogen ion in nitric acid solution appears to bring about its superiority over the monodentate extractants such as dibutyl butylphosphonate (DB[BP]).

Our objectives in this investigation are to determine the stoichiometries and thermodynamic constants of extraction for Am(III) and Eu(III) and to elucidate the denticity of the DHDECMP for these ions. As in our preceding study, the latter objective will be approached by comparing the extraction behavior of DHDECMP with DB[BP]. In addition, studies will be performed on a similar bifunctional extractant having an ethylene bridge between the phosphoryl and the carbonyl groups to help elucidate the importance of chelation in the extraction of Am(III).

EXPERIMENTAL

Materials

The source and purification of DHDECMP and DB[BP] were described in the preceding paper (*1*).

Dihexyl-*N*,*N*-diethylcarbamoylethylphosphonate (DHDECEP) was prepared by addition of the stoichiometric quantity of *N*,*N*-diethyl-3-chloropropionamide (*3*) to a solution of the sodium salt of dihexyl phosphonate in heptane, refluxing for 7 h. The product, obtained in 47% yield, was contaminated with about 25% of dihexyl hexylphosphonate, the only significant impurity detected by gas chromatography (GC). Purification was effected, albeit with considerable loss, by treatment with 3 volumes of heptane and 2 volumes of 8 *M* HNO_3. Under these conditions, three phases are formed. The middle phase, which contains the purified DHDECEP, was separated and mixed with water and heptane. The resultant heptane, which contains the product, was washed with 1 *M* NaOH and H_2O, and pumped to constant weight, finally at 100° and 2 mm pressure. GC analysis showed 2% residual impurity. The spectral properties were fully consistent with the assigned structure. M.S.: small parent peak at m/e 377; base peak 72; other intense peaks at 137, 128, 111, 210, 294. UV: λ_{max} 201 nm; ε_{max} 7600. NMR: quartet at $\delta = 4.01$ ppm (relative to TMS), 4 H, $J = 7$ Hz (OCH_2); quartet at 3.39 ppm, 4 H, $J = 7$ Hz ($N—CH_2$); remaining resonances at 0.8 to 2.8 ppm, 32 H. IR: strong bands at 2860–2960 cm^{-1}, C—H str; 1648, C=O str; 1462 and 1432, C—H bend; 1266, 1244, P=O str; 1000, POC str.

DHDECMP labeled with tritium at the methylene hydrogen positions was prepared by mixing 1.0 g (2.75 mmol) of DHDECMP with 0.4 Ci [400 μL of $H_2O(THO)$] in 3 mL of dimethylformamide containing 0.53 g (3 mmol) of $(CH_3)_4NOH \cdot 5H_2O$ at 54°C for 42 h. The resultant mixture was then neutralized with 3 mL of 1 M HCl and extracted with hexane. The hexane extract was scrubbed successively with three equal volumes of 0.25 M Na_2CO_3 and 0.5 M HNO_3. Scintillation counting of the organic phase showed that ~25 mCi of tritium was present. Theoretical yield was ~26 mCi.

The radionuclides ^{241}Am, ^{244}Cm, ^{249}Cf, and ^{253}Es were obtained from ANL stocks and were purified by extraction chromatographic procedures (*4–6*). ^{249}Bk and ^{255}Fm daughters were separated from a 6-μg sample of ^{253,254,255}Es and from each other using a high efficiency HDEHP column (*5*). The radiotracer rare earth elements used were ^{144}Ce, ^{147}Pm, ^{151}Sm, ^{152,154}Eu, ^{153}Gd, ^{160}Tb, ^{170}Tm, ^{169}Yb, and ^{88}Y. All tracers were obtained as >99% radiochemical purity and were dissolved in nitric acid or lithium nitrate solutions.

Inactive lanthanum, praseodymium, neodymium, dysprosium, holmium, erbium, and lutetium nitrate solutions were prepared from a weighed amount of the appropriate oxides of 99.9% or better purity by dissolution in hot concentrated nitric acid and dilution to a known volume.

The source and purity of the water, nitric acid, and lithium nitrate used in this study were described in the preceding paper (*1*). The *p*-diisopropylbenzene (DIPB) was 99% purity from Aldrich Chemical Co.

Measurement of Distribution Coefficients, K_d's

The distribution coefficients of the various metal ions using DHDECMP and DB[BP] were determined as described previously (*1, 7*). Distribution coefficient measurements for Am and Eu using DHDECEP were performed with aqueous phases containing 10^{-3} M $Lu(NO_3)_3$. The lutetium was used to minimize the effect on the K_d which would be caused by the presence of any acidic impurity in the DHDECEP. Liquid scintillation counting was performed using a Beckman CPM 100 and Beckman HP Cocktail in plastic vials. Gamma counting was accomplished with a Beckman Biogamma 3-channel analyzer (NaI detector). Alphaspectroscopy was performed using an Ortec surface-barrier detector in conjunction with a DSD Co. Multichannel Analyzer, Model 1056 A. Thermodynamic parameters were measured as described elsewhere (*8*).

The pH's of aqueous phases in the pH-variation experiment were measured before and after equilibration with the organic phase with a Sargent combination electrode (S-30070-10) and a Beckman Model 4500 digital pH meter.

Z-Curve K_d Measurements

The effect of atomic number on the distribution coefficients of transplutonium elements and rare earth elements was determined using ^{241}Am as an internal normalizing nuclide. The separation factors ^{241}Am/^{244}Cm, ^{241}Am/^{253}Es, and ^{241}Am/^{255}Fm were measured using alpha pulse height analysis of aliquots of each phase evaporated on platinum plates. Those aqueous phases containing lithium nitrate were extracted with 0.4 *F* HDEHP and aliquots of this extract were evaporated. No corrections for the decay of ^{255}Fm ($t_{1/2}$ = 20 h) were necessary since plates containing aliquots of the organic and aqueous phases were counted within a few minutes of one another.

The separation factors ^{241}Am/^{249}Cf, ^{241}Am/^{152,154}Eu, ^{241}Am/^{144}Ce, ^{241}Am/^{153}Gd, and ^{241}Am/^{88}Y were determined using the appropriate window setting in two different channels of the Biogamma system. Corrections were made for any overlap of the γ-spectra of the second nuclide on that of ^{241}Am.

The separation factors ^{241}Am/^{249}Bk, ^{241}Am/^{147}Pm, ^{241}Am/^{151}Sm, ^{241}Am/^{160}Tb, ^{241}Am/^{170}Tm, and ^{241}Am/^{169}Yb were measured using the Beckman CPM-100 liquid scintillation counter to count the α-peak separately from low-energy β-peaks. Again, corrections for the overlap of the ^{241}Am α-spectrum on β-spectra were made.

Since radiotracers for the remaining lanthanides were not readily available, the separation factors of ^{241}Am to La, Pr, Nd, Dy, Ho, Er, and Lu were determined as described below. A given lanthanide nitrate solution was evaporated to dryness and redissolved in 1 *M* HNO_3 or 1 *M* $LiNO_3$. The amount of lanthanide was chosen so that less than 1% of the DHDECMP available in the organic phase was complexed. About 10^5 cpm of ^{241}Am tracer was added to the aqueous phase. After equilibration with the organic phase, the K_d of Am was determined radiometrically. A known volume of the organic phase was then washed three times with 0.01 *M* HNO_3 and the washes collected. An equal volume of the aqueous phase and the washings from the organic phase were each analyzed for total lanthanide content by the ANL Analytical Division using spectrophotometric determination of xylenol orange complexes.

Infrared Studies

Infrared studies were carried out as described previously (*1*). Organic phases of the appropriate extractant, either undiluted or diluted with *o*-xylene, were saturated with lanthanum(III), thorium(IV), or uranium(VI) from 2 *M* HNO_3.

RESULTS AND DISCUSSION

pH and Extractant Dependencies

The preceding paper by the authors showed that the methylene hydrogens in the DHDECMP molecule were not liberated during the extraction of Th(IV) (*1*). A similar study was performed for the extraction of Am(III) by measuring the dependency of K_d for Am on pH at a constant total nitrate concentration. Using 0.695 *M* DHDECMP and 1 *M* (H, Li)NO_3 at $T = 25°$, the K_d for Am varied from 1.10 to 1.23 in the pH range 1.13 to 3.82, a dependency of <0.02 of log K_d on pH. Thus there is no evidence for the ionization of a methylene proton from the DHDECMP molecules extracting Am(III), as suggested by McIsaac et al. (*9*). The small decrease of K_d with increasing hydrogen ion concentration may be explained by the complexation of DHDECMP by HNO_3. Also, the lack of dependency on pH in this range shows there are no appreciable acidic impurities in the DHDECMP.

Figure 1 shows the third power dependence of K_d for Am and Eu on DHDECMP and DHDECEP concentration in the extraction of Am(III) and Eu(III) from 2 *M* $LiNO_3$ (pH = 1.7), $T = 25°$. A third power extractant dependency was also found for DB[BP] using the same conditions. This study confirms the observations of several authors that CMP compounds and monodentate neutral organophosphorus extractants (TBP) extract trivalent actinides and lanthanides in a 3:1 stoichiometry (*9–13*).

Nitrate Dependency

Since DHDECMP does not ionize when extracting trivalent transplutonium elements or rare earth elements, three nitrate ions must be extracted along with the metal ion to maintain electroneutrality. Hence, the equation for extraction can be written

$$Am^{3+} + 3NO_3^- + 3\overline{DHDECMP} \rightleftharpoons \overline{Am(NO_3)_3(DHDECMP)_3} \quad (1)$$

and the equilibrium constant including activity coefficients of all species is

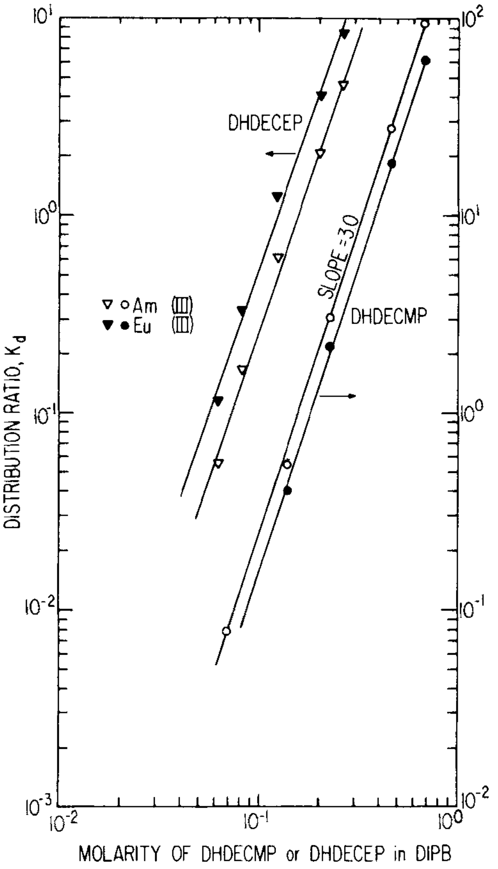


FIG. 1. Distribution ratios of Am(III) and Eu(III) versus molarity of DHDECMP and DHDECEP in DIPB. Aqueous phase = 2.00 *M* $LiNO_3$ (pH = 1.7), *T* = 25 °C.

$$K_{\mathrm{EQ}}^{\mathrm{CMP}} = \frac{\overline{[\mathrm{Am(NO_3)_3(CMP)_3}]}\gamma_{\overline{\mathrm{Am(NO_3)_3(CMP)_3}}}}{[\mathrm{Am}^{3+}]\gamma_{\mathrm{Am}^{3+}}[\mathrm{NO^-}_3]^3\gamma^3_{\mathrm{NO_3}^-}[\overline{\mathrm{CMP}}]^3\gamma^3_{\overline{\mathrm{CMP}}}} \tag{2}$$

where a bar denotes a species in the organic phase and CMP is an abbreviation for DHDECMP. It is necessary to include activity coefficients since the ionic strength of the aqueous phase cannot be held constant when the nitrate concentration is varied because neutral complexes of Am(III) with other anions, e.g., ClO_4^-, will also be extracted.

To further confirm this stoichiometry, the dependency of K_d for Am and Eu on total lithium nitrate activity at constant extractant concentration and pH was determined. The lower two lines in Fig. 2 show that plots of

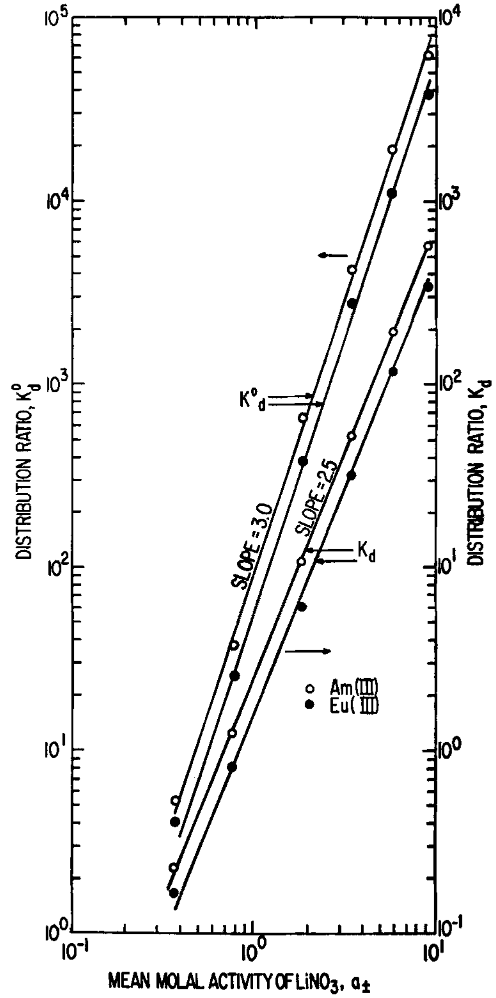


FIG. 2. Distribution ratios of Am(III) and Eu(III) versus the mean molal activity of nitrate ion. Organic phase = 0.694 M DHDECMP in DIPB. Aqueous phase = $LiNO_3$ (pH = 1.8), $T = 25\,^{\circ}C$. K_d and $K_d{}^{\circ}$ are the observed and corrected distribution ratios, respectively.

log K_d for Am and Eu vs log a_{LiNO_3} each have a slope of 2.5. However, one may not conclude that this is the dependency of the distribution coefficient, $K_d{}^{\circ}$, on nitrate concentration since the metal ions are complexed by nitrate ions in the aqueous phase as well as in the organic phase. The distribution coefficient of the metal ion, Am(III), is

$$K_d^{\circ} = \frac{[\overline{\mathrm{Am}}]}{[\mathrm{Am}^{3+}]} \qquad (3)$$

whereas the measured distribution coefficient is

$$K_d = \frac{[\overline{\mathrm{Am}}]}{[\mathrm{Am}^{3+}] + [\mathrm{Am(NO_3)}^{2+}] + [\mathrm{Am(NO_3)_2}^{+}]} \qquad (4)$$

Therefore

$$K_d = \frac{K_d^{\circ}}{1 + \beta_1[\mathrm{NO_3}^-] + \beta_2[\mathrm{NO_3}^-]^2} \qquad (5)$$

where β_1 and β_2 are the overall stability constants for the first and second nitrate complexes of Am(III), respectively, and $\beta_2 = K_1K_2$.

These stability constants have been determined previously at various ionic strengths using solvent extraction methods employing acidic extractants. For the equilibrium

$$\mathrm{Am}^{3+} + n\mathrm{NO_3}^- \rightleftharpoons \mathrm{Am(NO_3)}_n{}^{3-n} \qquad (6)$$

the equilibrium constant is

$$K_{\mathrm{EQ}} = \beta_n{}^{\circ} = \frac{[\mathrm{Am(NO_3)}_n{}^{3-n}]\gamma_{\mathrm{Am(NO_3)}_n{}^{3-n}}}{[\mathrm{Am}^{3+}]\gamma_{\mathrm{Am}^{3+}}[\mathrm{NO_3}^-]^n\gamma^n_{\mathrm{NO_3}^-}} \qquad (7)$$

The equilibrium for a typical acidic extractant is

$$\mathrm{Am}^{3+} + 3\overline{\mathrm{HD}} \rightleftharpoons \overline{\mathrm{AmD_3}} + 3\mathrm{H}^+ \qquad (8)$$

and the corresponding equilibrium constant is

$$K_{\mathrm{EX}}{}^{\mathrm{HD}} = \frac{[\overline{\mathrm{AmD_3}}]\gamma_{\overline{\mathrm{AmD_3}}}[\mathrm{H}^+]^3\gamma_{\mathrm{H}^+}{}^3}{[\mathrm{Am}^{3+}]\gamma_{\mathrm{Am}^{3+}}[\overline{\mathrm{HD}}]^3\gamma_{\overline{\mathrm{HD}}}{}^3} \qquad (9)$$

Equation (3) and, in the presence of nitrate, Eq. (4) also apply to extraction with HD; therefore Eq. (9) may be rewritten

$$K_d{}^{\mathrm{HD}} = \frac{K_d{}^{\circ,\mathrm{HD}}}{1 + \sum_1^n \beta_n{}^{\circ}[\mathrm{NO_3}^-]^n\gamma^n_{\mathrm{NO_3}^-}\gamma^{-1}_{\mathrm{Am(NO_3)}_n{}^{3-n}}} \qquad (10)$$

Consequently, the usual plot of $(K_d{}^{\circ,\mathrm{HD}}/K_d{}^{\mathrm{HD}} - 1)$ vs $[\mathrm{NO_3}^-]$ fits a quadratic equation whose coefficients are

$$\beta_1 = \beta_1{}^{\circ}\gamma_{\mathrm{Am}^{3+}}\gamma_{\mathrm{NO_3}^-}\gamma^{-1}_{\mathrm{Am(NO_3)}^{2+}} \qquad (11)$$

and

$$\beta_2 = \beta_2{}^{\circ}\gamma_{\mathrm{Am}^{3+}}\gamma^2_{\mathrm{NO_3}^-}\gamma^{-1}_{\mathrm{Am(NO_3)}^{2+}} \qquad (12)$$

Theorefore, the β's reported for nitrate complexation vary with ionic strength because of variations in activity coefficients of the reacting species.

Rewriting Eq. (2) and including nitrate complexation, Eq. (5), gives

$$K_{\mathrm{EQ}}^{\mathrm{CMP}} = \frac{K_d^{\mathrm{CMP}}\left(1 + \sum_{1}^{n} \beta_n[\mathrm{NO_3}^-]^n\right)\gamma_{\overline{\mathrm{Am(NO_3)_3(CMP)_3}}}}{\gamma_{\mathrm{Am^{3+}}}\gamma_{\mathrm{NO_3^-}}^{3}[\mathrm{NO_3}^-]^3[\overline{\mathrm{CMP}}]^3\gamma_{\overline{\mathrm{CMP}}}^{3}} \tag{13}$$

Rearranging and taking logarithms gives

$$\log\left\{\frac{K_d^{\mathrm{CMP}}\left(1 + \sum_{1}^{n} \beta_n[\mathrm{NO_3}^-]^n\right)}{\gamma_{\mathrm{Am^{3+}}}}\right\} = 3\log(\gamma_{\mathrm{NO_3^-}}[\mathrm{NO_3}^-]) + \log\left\{\frac{K_{\mathrm{EQ}}^{\mathrm{CMP}}[\overline{\mathrm{CMP}}]^3\gamma_{\overline{\mathrm{CMP}}}^{3}}{\gamma_{\overline{\mathrm{Am(NO_3)_3(CMP)_3}}}}\right\} \tag{14}$$

The second term on the right of Eq. (14) is a constant since the activity coefficients of $\overline{\mathrm{Am(NO_3)_3(DHDECMP)_3}}$ and $\overline{\mathrm{DHDECMP}}$ should not vary with aqueous phase ionic strength and since $\overline{\mathrm{DHDECMP}}$ concentration is held constant.

Therefore, a plot of

$$\log\frac{K_d^{\mathrm{CMP}}\left(1 + \sum_{1}^{n} \beta_n[\mathrm{NO_3}^-]^n\right)}{\gamma_{\mathrm{Am^{3+}}}}$$

(which is K_d°) vs $\log(\gamma_{\mathrm{NO_3^-}}[\mathrm{NO_3}^-])$ should be a straight line with a slope of 3.0 and an intercept of

$$\log\left\{\frac{K_{\mathrm{EQ}}^{\mathrm{CMP}}[\overline{\mathrm{CMP}}]^3\gamma_{\overline{\mathrm{CMP}}}^{3}}{\gamma_{\overline{\mathrm{Am(NO_3)_3(CMP)_3}}}}\right\}$$

The values of $\gamma_{\mathrm{NO_3^-}}[\mathrm{NO_3}^-]$ were obtained from tables in Kertes and Marcus (*14*). The values of β_1 or K_1 for both Am(III) and Eu(III) were obtained in most cases from Martell and Smith (*15*). At ionic strengths for which β_1 was not available, values were obtained from the curve resulting from a plot of β_1 vs ionic strength. For both Am(III) and Eu(III), the values of $\gamma_{\mathrm{Nd^{3+}}}$ and K_2 ($K_2 = \beta_2/K_1$) for $\mathrm{Nd(NO_3)_2}^+$ given by O'Brien and Bautista (*16*) were used as an approximation. The values for β_1 and β_2 for Am(III) and Eu(III) and for $\gamma_{\mathrm{Nd(III)}}$ used in the calculation of K_d° are shown in Table 1. The upper two curves in Fig. 2 show the results. Straight lines are obtained as expected with slopes of 3.0, confirming the extraction stoichiometry shown in Eq. (1).

Figure 3 shows the results of similar plots for extraction of Am(III) by equal concentrations of DHDECMP and DB[BP]. Slopes of approximately 2.8 to 3.0 can be drawn for both extractants at low nitrate concentrations, but the slope in the case of DB[BP] changes to 3.3 at higher nitrate concentrations. The increase in slope may be explained by the

TABLE 1

Data Used for Nitrate Concentration Dependency Calculations

Ionic strength	β_1^{Am}	β_2^{Am}	β_1^{Eu}	β_2^{Eu}	$\gamma_{Nd(III)}$
0.5	2.45	0.60	2.75	0.60	0.103
1.0	1.82	0.38	2.04	0.38	0.108
2.0	1.58	0.30	1.82	0.30	0.094
3.0	1.48	0.26	1.66	0.26	0.097
4.0	1.41	0.25	1.58	0.25	0.111
5.0	1.35	0.25	1.51	0.25	0.131

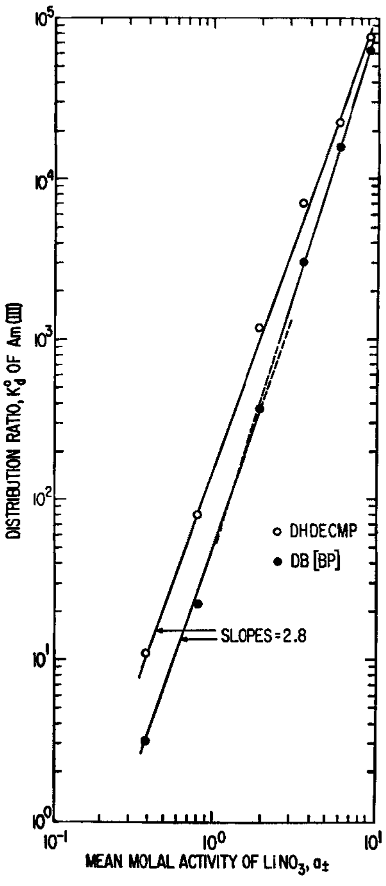


FIG. 3. Comparison of the distribution ratios of Am(III) versus $a_\pm$ for $LiNO_3$ using 0.817 *M* DHDECMP and DB[BP] in DIPB, *T* = 25°C.

extraction of higher nitrate complexes of the metal ion plus lithium cation, such as $Li[Am(NO_3)_4]\cdot 3E$. Analogous behavior is exhibited by U(IV) in its extraction by TBP from lithium nitrate solution (*17*).

The similarities in the extractant and nitrate dependencies for both bifunctional and monofunctional extractants do not indicate that chelation is occurring with the bifunctional extractants, unless the coordination number of the Am(III) and Eu(III) ions is expanding with these extractants. In addition, the fact that there are no significant differences in the K_d's of Am(III) or of Eu(III) from $LiNO_3$ with the three extractants does not support the chelation theory. One might also expect the K_d's for DHDECMP to be larger than those for DHDECEP if chelation were important since it is well established that six-membered chelate rings are more stable than seven-membered rings (*15*). The data in Fig. 1 show slightly higher K_d's for DHDECEP than for DHDECMP.

Thermodynamic Studies

In order to investigate further the importance of the chelation process in the extraction of Am(III) and Eu(III) by DHDECMP, variable temperature extraction studies were performed with both DHDECMP and DB[BP] to determine the thermodynamic parameters of extraction. Figure 4 shows the effect of temperature on the K_{eq}. The thermodynamic values and equations for the variation of K_d and K_{eq} [using the same corrections as described previously (*8*)] are compiled in Table 2. The significant feature of these data is the small differences in the entropy terms for DHDECMP and DB[BP], especially in the case of Am(III) extraction. One would expect that an extractant behaving in a bidentate fashion would have a larger entropy effect than a monodentate extractant (*18*). In addition, the enthalpy of extraction should also be larger for DHDECMP due to the formation of coordinate bonds to carbonyl as well as phosphoryl oxygens by the Am(III) or Eu(III) ion. Since the data in Table 2 show only small differences in these terms, chelation does not appear to be important when Am(III) and Eu(III) are extracted by DHDECMP from $LiNO_3$ media. Similar results were found for the extraction of Th(IV) and U(VI) by DHDECMP from low nitric acid concentrations (*1*).

Infrared Studies

Phosphoryl and carbonyl stretching vibrations were obtained for DHDECMP, DHDECEP, DB[BP], and *N*,*N*-dihexyloctanamide (DHOA) solutions saturated with lanthanum(III) nitrate. Similar data were obtained

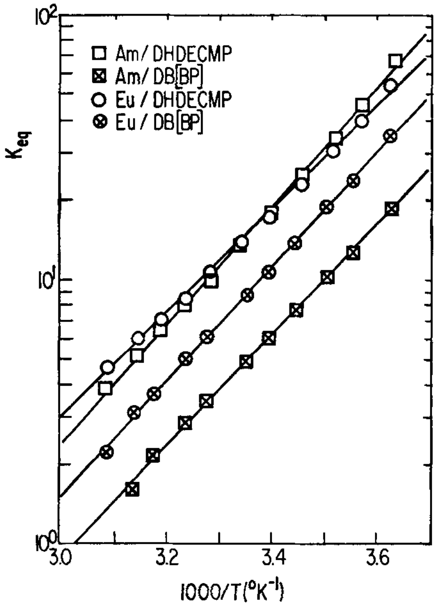


FIG. 4. Effect of temperature on K_{eq} for the extraction of Am(III) and Eu(III) by 0.25 *M* DB[BP] and DHDECMP in *o*-xylene from 2 *M* $LiNO_3$ (pH = 1.8).

TABLE 2

Thermodynamic Values and Equations for the Variable Temperature Extraction of Am(III) and Eu(III) from 2.0 *M* $LiNO_3$/0.01 *M* HNO_3 by 0.25 *M* Extractant

System	Eq. for ln K_d	Eq. for ln K_{eq}	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol °K)
Am/DB[BP]	$= \frac{4765}{T} - 17.90$	$= \frac{4765}{T} - 14.40$	−0.941	−9.469	−28.60
Am/DHDECMP	$= \frac{5092}{T} - 17.89$	$= \frac{5092}{T} - 14.39$	−1.593	−10.12	−28.59
Eu/DB[BP]	$= \frac{4969}{T} - 18.09$	$= \frac{4969}{T} - 14.49$	−1.289	−9.874	−28.79
Eu/DHDECMP	$= \frac{4495}{T} - 15.98$	$= \frac{4495}{T} - 12.38$	−1.597	−8.931	−24.60

for DHDECEP saturated with Th(IV) and U(VI) nitrates. These IR data together with the corresponding data for Th(IV) and U(VI) nitrates in DHDECMP, DB[BP], and DHOA from Ref. *1* are compiled in Table 3. The IR data show that the changes in the phosphoryl stretching frequency for DB[BP], DHDECMP, and DHDECEP are very similar and in general follow the expected trend of increasing $\Delta\nu$ in going from tri-, hexa-, to

TABLE 3

Phosphoryl and Carbonyl Frequencies for DB[BP], DHDECMP, DHDECEP, and DHOA Extractants and Complexes (cm^{-1})

	$\nu_{P=O}$	Shift[a] ($\Delta\nu_{P=O}$)	$\nu_{C=O}$	Shift[a] ($\Delta\nu_{C=O}$)
DB[BP]	1247			
HNO_3/DB[BP]	1233	−14		
La(III)/DB[BP]	1198	−49		
U(VI)/DB[BP]	1155	−92		
Th(IV)/DB[BP]	1150	−97		
DHDECMP	1255		1645	
HNO_3/DHDECMP	1228	−27	1639	−6
La(III)/DHDECMP	1209	−46	1608	−37
U(VI)/DHDECMP	1186, 1164	−69, −91	1600	−45
Th(IV)/DHDECMP	1183, 1160	−72, −95	1597	−48
DHDECEP	1266, 1244		1648	
La(III)/DHDECEP	1191	−64	1600	−48
U(VI)/DHDECEP	1167, 1142	−88, −113	1591	−57
Th(IV)/DHDECEP	1176, 1156	−79, −99	1583	−65
DHOA			1647	
HNO_3/DHOA			1639	−8
La(III)/DHOA			1591	−56
U(VI)/DHOA			1572	−75
Th(IV)/DHOA			1575	−72

[a] Defined as the $\nu_{P=O}$ or $\nu_{C=O}$ in complex minus the corresponding band in the unbound extractant.

tetravalent actinides. Thus the interactions between the metal ions and the oxygen of the phosphoryl groups of these three extractants are similar.

The data in Table 3 also show that the changes in carbonyl stretching frequencies are significantly smaller for DHDECMP and DHDECEP than for DHOA. This indicates either that the carbonyl–metal interaction is weaker in the CMP and CEP extractants or that coordination of the phosphoryl group lowers the bond order in the C—O linkage through inductive effects. The larger $\Delta\nu_{C=O}$ for DHDECEP than for DHDECMP supports the latter explanation. However, since DHOA is a very poor extractant for Am(III) and Eu(III) (K_d's are $<10^{-3}$) and since there is little or no support for strong bidentate behavior from other sources, is is possible that the observed spectral changes could be explained by both effects.

Comparison between the Am(III) Extraction from $LiNO_3$ and HNO_3 with DHDECMP, DHDECEP, and DB[BP]

Figure 5 shows a comparison between the extraction behavior of Am(III) as a function of the concentration of $LiNO_3$ and HNO_3 with

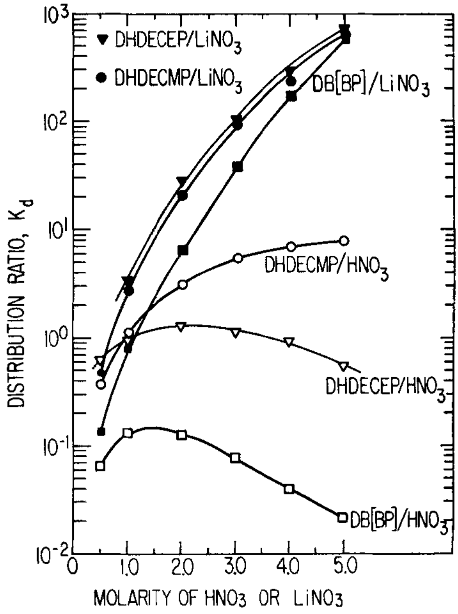


FIG. 5. Comparison of the distribution ratios of Am(III) from $LiNO_3$ and HNO_3 using 0.817 *M* DHDECMP, DHDECEP, and DB[BP] in DIPB, $T = 25°C$.

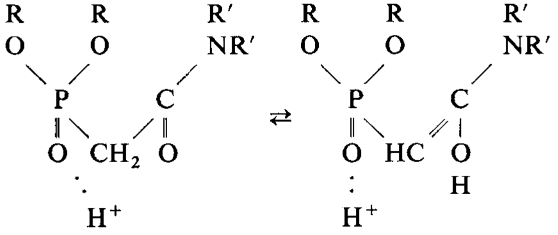
DHDECMP, DHDECEP, and DB[BP]. Using $LiNO_3$ solution (pH = 1.8 to 1.7), the K_d's are within a factor of five for the three extractants. However, using HNO_3 solutions, one finds significant differences in K_d's. A similar behavior was found for Th(IV) in the preceding paper by the authors (*1*). In our previous paper we explained the difference in the extraction behavior of Th(IV) from $LiNO_3$ and HNO_3 using DHDECMP and DB[BP] as due to the ability of the DHDECMP to protonate the amide group, either on the carbonyl oxygen or the amide nitrogen. This process protects the phosphoryl oxygen–metal ion bond from attack by hydrogen ions and thus behaves as sort of an intramolecular buffer.

The data in Fig. 5 lend additional support for the intramolecular buffering effect instead of chelation as the significant feature of the extraction of Am(III) and Eu(III) from acid solution by DHDECMP. Clearly, a case cannot be made for chelation in view of the similarity of the K_d's for Am(III) or for Eu(III) from low acidity $LiNO_3$ media using the three extractants. Not only are the K_d's (as well as the ΔH and ΔS of extraction) of Am(III) or of Eu(III) very similar for DHDECMP and DB[BP], but also the K_d's obtained with DHDECEP are larger than those obtained with DHDECMP, which is the reverse of what one would expect if chelation were important. Of course, the fact that chelation does not appear to be significant does not in itself support the intramolecular buffering theory. However, the comparison between DHDECMP and DHDECEP using HNO_3 aqueous phases is particularly significant since both of these extractants have amide groups. But in the case of the CEP extractant, the amide group is an extra —CH_2— removed from the phosphoryl group. Therefore, the electrostatic effect of the protonated amide group would be less effective in shielding the phosphoryl oxygen–metal ion bond from attack by hydrogen ions. Thus the K_d for Am(III) with DHDECEP is much more sensitive to increasing HNO_3 concentration than it is with DHDECMP, but is still higher than with the monofunctional extractant DB[BP]. In the case of DB[BP], HNO_3 competes with Am(III) ions for the only basic group available.

The influence of the length of methylene bridging between two functional groups on the properties of extractants has been described in previous studies. For example, Siddall (*10*) and Mrochek and Banks (*19*) have shown the influence of the length of the bridging group between two phosphoryl groups on the extraction of HNO_3. Bifunctional extractants such as diphosphonates, diphosphine oxides, and CMP's are able to extract at least one molecule of HNO_3 for each phosphoryl and/or carbonyl group. As the bridging is varied from methylene to butylene, the ratio of HNO_3/extractant in equilibrium with a given aqueous HNO_3 concentration increases. These data show that the greater the separation of the basic groups, the less effect they have on each other and the more readily they extract HNO_3. These same investigators also found (with a few exceptions) that the K_d's of selected lanthanide(III) ions extracted from nitric acid with diphosphonates (*10*) and diphosphine oxides (*19*) decreased more rapidly with increasing acid as the length of the bridging group increases. However, as the acid concentration is lowered to 0.1 *M*, there is little difference in K_d's as a function of the length of the bridging group. In the case of the diphosphine oxides (*19*), the compound with an ethylene bridge gave higher K_d's than the corresponding compound with a methylene bridge when the aqueous phase was 0.1 *M* HNO_3. Thus the results described for these bifunctional extractants are qualitatively similar to the data shown in Fig. 5. Unfortunately, no data are available using low acid $LiNO_3$ solutions but the relative extraction properties found in 0.1 *M* HNO_3 probably parallel those in $LiNO_3$. These extraction properties of diphosphonates and diphosphine oxides suggest that acid buffering effects rather than chelation may also be of significance. However, in the case of the extraction of tripositive transplutonium ions from HNO_3 with tetraphenylmethylenediphosphine oxides (*20*), there appears little doubt that chelation is occurring because of the extraordidinarily high K_d's and the low extractant dependencies obtained with this extractant. Thus generalized statements concerning the denticity of bifunctional extractants which are based simply on one's ability to draw six-membered ring structures and on the fact that under specific conditions K_d's are higher than for monofunctional extractants should not be taken without question.

The quantitative effect of the length of methylene bridging between functional groups has also been investigated. In the case of dibasic acids the electrostatic influence of substitutents has been thoroughly studied by Westheimer and Shookhoff (*21*). These authors were able to quantitatively relate the difference in the first and second acidity constants (Δpk_a) to the intramolecular distance between carboxylic acid oxygens. The Δpk_a's for malonic (propanedioic) acid and succinic (butanedioic) acid are 2.63 and 1.24, respectively. This represents a 25-fold decrease in Δpk_a when the carboxylic groups are separated by an additional methylene group. The distances between the amide nitrogen and phosphoryl oxygen in DHDECMP and DHDECEP (4.7 and 6.0 Å, respectively) are comparable to the distances between the acidic hydrogens in malonic and succinic acids. (The intramolecular distances in the CMP and CEP molecules were measured using Leybold-Herans space filling molecular models.) The decrease in K_d for Am(III) from 5 *M* HNO_3 by the addition of the extra methylene group in DHDECEP is a factor of 15, which is in the general range expected for purely electrostatic effects.

Other structural features of the DHDECMP molecule, which are related to the intramolecular buffering capabilities of the CMP's, may contribute to its effectiveness as an extractant in acid solution. Equilibration experiments performed with the tritium-labeled DHDECMP in hexane showed that the methylene hydrogens are very labile, even when equilibrated with 0.5 *M* HNO_3 solution. The lability of the methylene hydrogens provides a mechanism for the transfer of protons in an organic medium from the phosphoryl oxygen to the carbonyl oxygen or amide nitrogen. Since the phosphoryl oxygen is the most basic group in the CMP molecule, it would preferentially hydrogen bond with HNO_3. The resultant complex would have two structures:



I II

An incoming metal ion would displace the hydrogen ion from the phosphoryl oxygen. In Structure II, the displaced hydrogen ion would be attracted to the carbon–carbon double bond, and the enol hydrogen could either remain in position or move to the amide nitrogen. Thus a low energy pathway is provided within the CMP structure for the protonation of the carbonyl oxygen or the amide nitrogen. Also, Structure II without the protonated phosphoryl oxygen accounts for the lability of the methylene hydrogens. In the case of the CEP extractant, enolization of the carbonyl oxygen would also occur but to a significantly smaller degree.

Effect of Ionic Strength on Separation Factors and of Atomic Number (Z) on K_d

Tables 4 and 5 show the effect of HNO_3 and $LiNO_3$ on the separation factors, α_x^{Am}, for a number of transplutonium(III) and lanthanide(III) ions with 0.817 *M* DHDECMP. Although the α_x^{Am} decreases in general with increasing ionic strength and with substituting $LiNO_3$ for HNO_3, the effects are small. These trends are probably due to aqueous phase phenomena, such as activity coefficients and the ease of dehydration of the tripositive ions as a function of the media, rather than due to some change in the basic structure of the extracted complex. The data for 1 *M* $LiNO_3$ and 1 *M* HNO_3 are plotted in Fig. 6 together with the corresponding data for 1 *M* $LiNO_3$ using DB[BP] in DIPB for comparison. The general trend of decreasing K_d with increasing Z in the lanthanide series is typical of nitrato complexes of these ions; similar trends have been reported with TBP (*22*) and with anion exchange and amine extraction from $LiNO_3$ media (*23*). This trend for lanthanides may be explained by

TABLE 4

Variation of the Separation Factor between Am(III) and Eu(III), α_{Eu}^{Am}, as a Function of Ionic Strength and Medium. Organic Phase: 0.817 *M* DHDECMP in DIPB. $T = 25°C$

	α_{Eu}^{Am}	
[$LiNO_3$] or [HNO_3] (*M*)	HNO_3	$LiNO_3$
0.5	1.71	1.66
1.0	1.66	1.68
2.0	1.62	1.57
3.0	1.57	1.41
4.0	1.50	1.24
5.0	1.41	1.26

TABLE 5

Distribution Coefficients and Separation Factors with 0.817 *M* DHDECMP in DIPB, $T = 25°$

Element	K_d, 1 *M* $LiNO_3$	α_x^{Am}	K_d, 1 *M* HNO_3	α_x^{Am}	K_d, 5 *M* HNO_3	α_x^{Am}
Am	2.75	1.000	1.17	1.000	8.18	1.000
Cm	1.53	1.80	0.760	1.54	5.18	1.58
Bk	1.99	1.38	0.841	1.39	6.42	1.28
Cf	2.15	1.28	0.801	1.46	5.88	1.39
Es	1.83	1.50	0.696	1.68	4.62	1.77
Fm	1.83	1.50	0.672	1.74	3.90	2.10
La	4.24	0.648	1.65	0.708		
Ce	3.96	0.694	1.59	0.738	9.03	0.906
Pr	3.29	0.836	1.41	0.828		
Nd	2.79	0.986	1.12	1.04		
Pm	2.25	1.22	1.00	1.17	7.44	1.10
Sm	2.04	1.35	0.860	1.36	6.82	1.20
Eu	1.64	1.68	0.705	1.66	5.80	1.41
Gd	1.19	2.32	0.472	2.48	4.26	1.92
Tb	0.976	2.82	0.410	2.85	2.58	3.17
Dy	0.878	3.13	0.311	3.76		
Ho	0.663	4.15	0.218	5.37		
Er	0.511	5.38	0.156	7.50		
Tm	0.327	8.41	0.105	11.1	1.30	8.21
Yb	0.287	9.58	0.0786	14.9	1.02	9.68
Lu	0.180	15.3	0.0558	21.0		
Y	0.360	7.63	0.121	9.67	1.62	5.06

the increasing energy required to dehydrate the lanthanide(III) ion with increasing atomic number (*24*) combined with the spatial requirements in coordinating three nitrates and three extractant molecules to a progressively smaller ion. These two effects are only partially compensated for by the increasing charge density with increasing *Z*. Superimposed on these trends is the tetrad effect (*25*) which is evident in all three plots. It is interesting to note that Y(III) fits close to the expected position based on its hydration energy and ionic radius.

Figure 6 shows that the transplutonium(III) ions do not show the general decrease in K_d with increasing *Z*, and thus deviate significantly from the lanthanides curve at high *Z*. This deviation may be due to 5*f* orbital interactions which increase the stability of the organic phase complex, but spectral data are required to confirm this theory. It is interesting to note the transplutonium element K_d data using DB[BP] show a somewhat similar trend. Here again we see nothing to indicate that the DHDECMP complexes of the transplutonium(III) and lanthanide

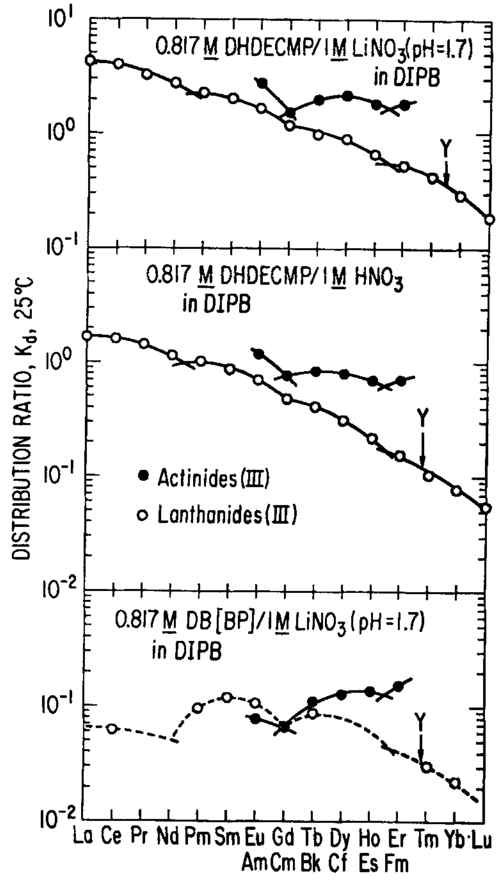


FIG. 6. Effect of atomic number (Z) on the K_d.

(III) ions are significantly different than the corresponding complexes formed with DB[BP], especially when one takes into account the differences in the sizes (volumes) of the two extractants and spatial considerations in coordination (*1*, *8*).

SUMMARY

DHDECMP behaves as a neutral extractant toward the transplutonium(III) and lanthanide(III) ions. Nitrate and extractant concentration dependencies for both Am(III) and Eu(III) ions are third power. When extracting Am(III) and Eu(III) from $LiNO_3$ media having low acidity, DHDECMP and the analogous DHDECEP behave very similarly to the monofunctional DB[BP]. Although IR data suggest that the carbonyl oxygen in both the CMP and CEP extractants is weakly bonded to the metal ion, and therefore in the technical sense these extractants may be bidentate, chelation does not appear to contribute significantly to the entropy of extraction or to the overall free energy of extraction.

The greater effectiveness of DHDECMP as an extractant of Am(III) and Eu(III) from nitric acid solution, compared to DB[BP], is attributed to the ability of DHDECMP, and to a lesser extent DHDECEP, to reduce the direct attack of hydrogen ions on the metal-phosphoryl oxygen bonds by the protonation of the amide group. This process resembles a buffering effect because it reduces the influence of HNO_3. The additional methylene bridge in DHDECEP makes it less effective than DHDECMP because of reduced electrostatic effects.

The distribution ratios of Am(III) through Fm(III) and of La(III) through Lu(III) extracted from $LiNO_3$ or HNO_3 media using DHDECMP show a definite tetrad effect. The K_d's for the lanthanides show a general decrease with increasing Z which is typical of the behavior of nitrato complexes of these elements. On the other hand, the K_d's for the transplutonium elements do not decrease appreciably with increasing Z, which indicates that $5f$ orbital effects may be taking place in the extracted complexes.

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