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The Extraction of Th(IV) and U(VI) by Dihexyl-*N*,*N*-diethylcarbamoylmethylphosphonate from Aqueous Nitrate Media

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Abstract

The extraction behavior of Th(IV) and U(VI) from nitrate media was studied using relatively pure dihexyl-*N*, *N*-diethylcarbamoylmethylphosphonate (DHDECMP). The data were compared with analogous measurements obtained with dibutyl butylphosphonate (DB[BP]). It was found that the extractant dependency is second power for U(VI) with both DHDECMP and DB[BP]. However, the extractant dependency for Th(IV) is third power for DB[BP] but varied from 2.5 to 2.0 power for DHDECMP depending on the total nitrate concentration. The K_d data do not support the theory that DHDECMP is an effective chelating agent for actinide ions. Significant differences between DHDECMP and DB[BP] do appear in the extraction behavior of Th(IV) from 1 to 5 *M* HNO_3. These differences are explained by the ability of DHDECMP to buffer itself against the effects of HNO_3 by protonation of the amide group.

INTRODUCTION

During the last 10 years there has been a great deal of interest in the solvent extraction behavior of neutral bifunctional (usually referred to as bidentate) organophosphorus compounds (*1–10*). This interest stems primarily from the ability of neutral bifunctional organophosphorus compounds to extract nitrato complexes of trivalent actinides, e.g., Am(III) and Cm(III), from nitric acid solutions. Since spent nuclear fuel reprocessing is performed in nitric acid media and the resultant high level liquid waste is also a nitric acid solution, the selective extraction of actinide(III) ions over fission products from nitrate media has always been an important and challenging problem.

Although a number of bifunctional neutral organophosphorus compounds have been shown to extract trivalent actinides from nitric acid solutions (*1*), only the carbamoylmethylphosphonates (CMP's) (current nomenclature used by *Chemical Abstracts* is employed throughout) have been studied for use in the recovery of actinides from waste in a plant-scale operation (*3, 5*). Currently, dihexyl-*N*,*N*-diethylcarbamoylmethylphosphonate (DHDECMP) has received the most attention (*3*). DHDECMP combines many favorable properties which make it the choice extractant for actinide removal from nitric acid media. For example, favorable solubilities with and without actinide loading can be achieved in acceptable diluents, and favorable distribution ratios and selectivities can be achieved without significantly altering the composition of the high level liquid waste.

In spite of the many studies carried out on the properties of DHDECMP, the extraction stoichiometries and equilibria for tri-, tetra-, and hexavalent actinides are not well defined and practically all previous studies have been performed with relatively impure (65%) extractant (*3*). In addition, no previous study has established that CMP extractants actually behave as bidentate ligands. Our objectives in this investigation were twofold: (a) to determine the stoichiometries and thermodynamic constants for the extraction of a tetravalent and a hexavalent actinide, Th(IV) and U(VI), from nitrate media using much higher purity DHDECMP; and (b) to elucidate the denticity of the extractant. The latter objective will be approached by comparing the extraction behavior of DHDECMP with a typical monodentate neutral phosphonate, dibutyl butylphosphonate, DB[BP].

EXPERIMENTAL

Materials

Crude (65%) DHDECMP (Wateree Chemical Co.) was kindly provided by L. D. McIsaac of Exxon Nuclear Idaho, Inc. Purification of this extractant was effected using the technique of precipitation by $Hg(NO_3)_2$ (*11*). Regeneration of the DHDECMP from the mercury salt with KCN/Na_2CO_3 has been reported to yield the extractant with a purity of about 98% (*11*). Analyses (Microtech Laboratory, Skokie, Illinois) of two separately prepared batches of the compound purified in this manner gave the results shown in Table 1 after two crystallization cycles.

The major impurity remaining after the mercury–DHDECMP salt crystallization is a neutral phosphonate.

DB[BP] was obtained from Virginia-Carolina Chemical Corp. and

TABLE 1

	% C	% H	% N	% P
1	60.31	10.92	4.19	8.50
2	61.18	11.23	3.99	8.42
Theoretical	59.48	10.54	3.85	8.52

was purified by a modification of the literature procedure (*12*) for the purification of TBP (*13*). *N*,*N*-Dihexyloctanamide [$(C_6H_{13})_2NC(O)C_7H_{15}$, DHOA] was prepared by the method of Gasparini and Grossi (*14*).

Uranium-233 and thorium-230 tracer samples were obtained from ANL stocks and were purified of daughter activity prior to use by standard radiochemical procedures.

Aqueous solutions of HNO_3 and $LiNO_3$–HNO_3 were prepared using ultrapure water obtained from a Milli-Q2 system water purifier (Millipore Corp.), Ultrex grade nitric acid (J. T. Baker Chemical Co.), and Suprapur lithium nitrate (E M Laboratories). The diluent for all extractants, *o*-xylene, was distilled-in-glass grade obtained from Burdick and Jackson Laboratories.

K_d Measurements

Distribution ratios (K_d's) were determined by equilibration of the aqueous and organic phases in 13 × 100 mm Pyrex culture tubes with Teflon-lined screw caps. Prior to the distribution ratio measurement, the organic phase was preconditioned three successive times with aqueous HNO_3 or $LiNO_3$–HNO_3 solution of the concentration used for the measurement. The preconditioned organic phase was then added to an equal volume of the aqueous phase containing the appropriate tracer. Chemical equilibrium was attained by vigorous mixing of the two phases for 1 min by means of a vortex mixer. The K_d values were obtained either at ambient temperature or, in the case of the thermodynamic studies, at temperatures in the range of 0–50°C (controlled to ±0.1°C) by means of thermostatically controlled, jacketed culture tubes, as described previously (*15*).

Radiometric assays were performed using conventional liquid scintillation counting techniques using a Beckman CPM 100 scintillation counter and Beckman Ready-Solv GP or HP scintillation cocktail solutions.

The extent of extraction of nitric acid into the organic phase was determined by back-extraction of the organic phase into a pure aqueous phase and titration of the resulting aqueous phase with 0.01 *M* NaOH, using a pH meter to ascertain the end point.

Infrared Studies

Infrared spectra were recorded with a Beckman Acculab 4 spectrophotometer and calibrated with polystyrene. Samples were prepared by equilibrating the neat extractants with solutions of the appropriate metal ion ($\sim 2\ M$) in 2 *M* nitric acid for several hours. After centrifugation, a drop of the resultant organic phase was placed between sodium chloride plates for spectral analysis. Additional experiments using samples prepared by the saturation of the extractants with the solid metal nitrate salts or by contacting 0.25 *M* solutions of the extractants in *o*-xylene with the metal ions in 0.25 *M* HNO_3 gave the same results.

Samples of the extractants which had been contacted with HNO_3 solution containing no metal ions were also prepared to examine the effect of extracted nitric acid on the spectra.

RESULTS AND DISCUSSION

Distribution Ratio of Th(IV) as a Function of pH

In order to determine if DHDECMP is behaving as a neutral extractant, measurement of the K_d for Th(IV) extraction by 0.125 *M* DHDECMP was carried out from an aqueous medium in which the ionic strength and nitrate concentration were held constant at 2.00 by varying the relative concentrations of HNO_3 and $LiNO_3$. It was found that the K_d values were constant (within the experimental error of $\pm 5\%$) in the range of nitric acid concentrations of 0.01 to 0.20 *M*, with only a slight decrease (on the order of 50%) in the distribution ratio when the acid concentration was increased to as high as 1.00 *M*. This small lowering of the K_d values at higher acidity can be satisfactorily explained in terms of the decrease in the free extractant concentration due to the extraction of nitric acid. The constant values for the distribution ratio with variations of hydrogen ion concentration over two orders of magnitude indicate that the extractant is behaving as a neutral, rather than acidic, extractant. The lack of acid dependency shows conclusively that the ionization of a methylene hydrogen from the DHDECMP, as was found in the case of the reaction with Hg(II) (*11*) and was suggested in the extraction of Am(III) (*3*), is not occurring to any extent in this system. These results also show that there are no acidic impurities in the DHDECMP preparation.

Extractant Dependency

The variation of the distribution ratios of Th(IV) and U(VI) from 0.25

M HNO_3 as function of DHDECMP concentration in *o*-xylene diluent is shown in Fig. 1. For comparison, the extractant dependency data for DB[BP] with these metal ions under the same conditions are plotted in Fig. 2. Both DHDECMP and DB[BP] give good second-order dependencies for U(VI) with extractant concentrations of 0.20 *M* or less, indicating that the extraction stoichiometry for U(VI) is

$$UO^{2+}_{2(a)} + 2NO^-_{3(a)} + 2E_{(o)} \rightleftharpoons UO_2(NO_3)_2 \cdot 2E_{(o)} \qquad (1)$$

where the subscripts *a* and *o* represent the organic and aqueous phases, respectively, and E represents either of these extractants.

Th(IV), however, gives an approximately third-order dependence for for the extraction by DB[BP], but a dependency of 2.4 power with DHDECMP over a very wide concentration range. It appears that the limiting stoichiometry for Th(IV) is

$$Th^{4+}_{(a)} + 4NO^-_{3(a)} + 3E_{(o)} \rightleftharpoons Th(NO_3)_4 \cdot 3E_{(o)} \qquad (2)$$

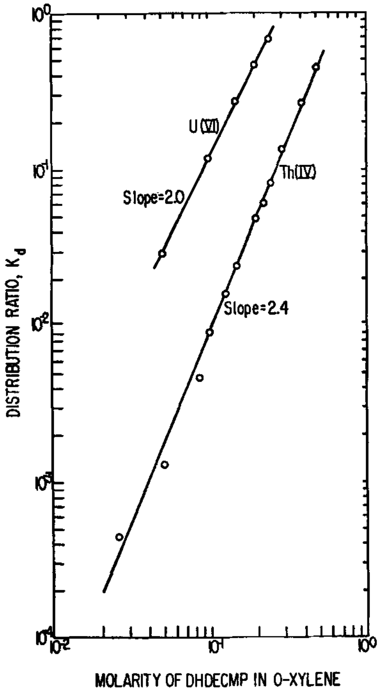


FIG. 1. Distribution ratios of U(VI) and Th(IV) versus molarity of DHDECMP in *o*-xylene, 0.25 *M* HNO_3. T = 22–25°C.

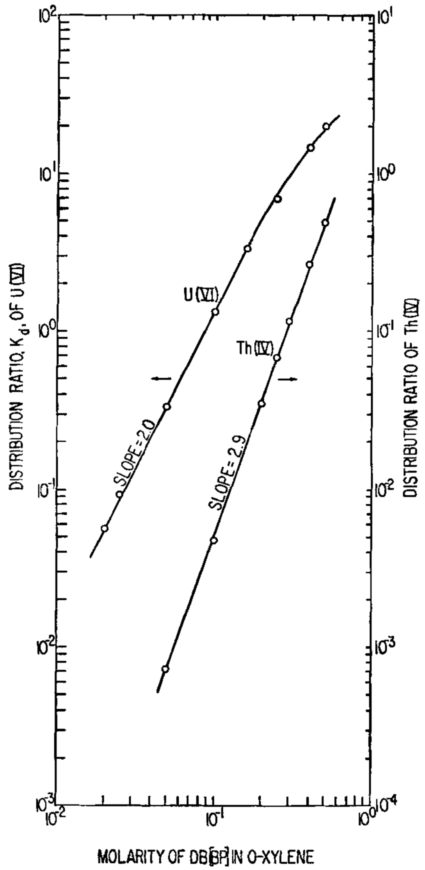


FIG. 2. Distribution ratios of U(VI) and Th(IV) versus molarity of DB[BP] in *o*-xylene, 0.25 *M* HNO_3. $T = 22\text{–}25\,°C$.

The nonintegral extractant dependence for the extraction of thorium from 0.25 *M* HNO_3 led us to study the extraction from aqueous phases of different ionic strength and acidity. The extractant dependency varied from 2.5 power for an aqueous phase composed of 0.1875 *M* $LiNO_3$ and 0.0625 *M* HNO_3 to 2.2 when the aqueous phase was 0.50 *M* HNO_3/0.50 *M* $LiNO_3$ or 0.025 *M* HNO_3/0.975 *M* $LiNO_3$ to 2.0 for the extraction from 2.00 *M* HNO_3. Thus the general trend is toward a lower extractant dependency when the ionic strength of the aqueous phase is increased, irrespective of the acid concentration. One possible explanation for this phenomenon may be that the Th(IV) ion is unable to easily accommodate three of the sterically bulky DHDECMP molecules in its coordination sphere. As the nitrate ion concentration is increased, increased competition of nitrate ions for coordination sites may result in the lowered extractant dependency.

More support for the inability of Th(IV) to easily coordinate three DHDECMP extractant molecules is given in Fig. 3. When the composition of the organic phase was continuously varied from 0.25 *M* DB[BP] to 0.25 *M* DHDECMP, the distribution ratio for the extraction of Th(IV) from 0.25 *M* HNO_3 was found to increase with increasing DHDECMP, reaching a maximum at ~65 mol-% DHDECMP, then decrease as the composition was further changed. Each data point in Fig. 3 is the average of at least two determinations. A reasonable explanation for this behavior can be made on the basis of the inability to form a stable 1:3 complex with DHDECMP under these conditions, probably due to congestion about the metal. Such steric crowding has been found to be an important factor in the extraction of Th(IV) with neutral phosphonates (*15*). Apparently, a complex of the nature $Th(NO_3)_4 \cdot 2DHDECMP \cdot DB[BP]$ can be formed which relieves this crowding to form a more stable, well-extracted complex.

The data in Fig. 3 do not support the bidenticity of DHDECMP. It is unlikely that the monodentate DB[BP] would displace a DHDECMP molecule that is chelated to a Th(IV) ion. Also, the distribution ratio of Th(IV) with DB[BP] is only slightly smaller than the corresponding K_d

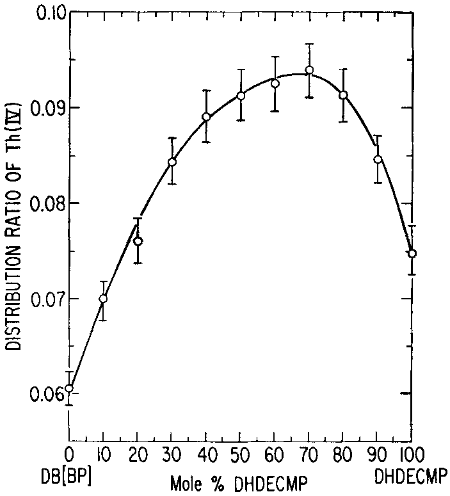
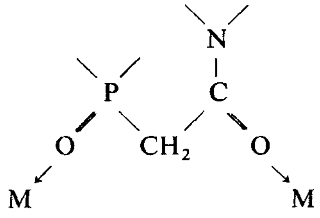


FIG. 3. Continuous variation study of the DHDECMP–DB[BP] system for the extraction of Th(IV). Total extractant concentration = 0.25 *M*. Aqueous phase = 0.25 *M* HNO_3. $T = 25°C$.

using DHDECMP. The chelation phenomenon usually results in much larger increases in K_d (*2*).

Because of the bifunctional nature of the DHDECMP, it was necessary to determine whether this extractant could act as a bridging ligand between two metals (*A*).



A

Such behavior could be invoked to explain the low extractant dependency for Th(IV). In order to test this possibility, the dependence of K_d as a function of Th(IV) concentration was studied. It was found that over a 50-fold increase in the Th(IV) concentration [~15–750 μg/mL ^{230}Th(IV)], the distribution ratio remained invariant. Therefore, the possibility of dimeric or higher polynuclear species can be ruled out.

Thermodynamic Studies

In order to determine the effect of the carbamoyl moiety on the extraction of these metals, variable temperature extraction studies with DB[BP] and DHDECMP were performed for U(VI) and Th(IV), analogous to those previously performed with a variety of monofunctional neutral organophosphorus extractants in dodecane (*15*), in order to determine the thermodynamic parameters for extraction. Because of the poorly defined extractant dependency for Th(IV), calculation of the equilibrium constant, and hence, the thermodynamic values, was not possible. It was found that in the range 0–50° DHDECMP was a slightly better extractant than DB[BP] with less of a temperature dependency, which would imply a less negative value for the enthalpy of extraction with DHDECMP. With U(VI), however, we were able to obtain meaningful thermodynamic values from the variable temperature measurements (Fig. 4). The thermodynamic values and the equations for the variation of K_d and K_{eq} [using the same corrections described previously (*15*)] for the extraction of U(VI) by these two extractants as a function of temperature are compiled in Table 2. The surprising features of these data are the small differences in the entropy terms for the two different extractants, the more negative enthalpy for the extraction by DB[BP], and the significantly lower K_{eq}

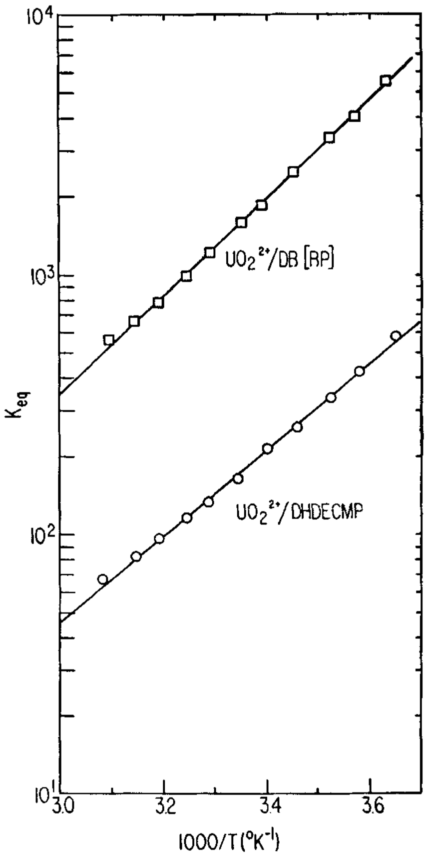


FIG. 4. Effect of temperature on K_{eq} for the extraction of U(VI) by 0.25 *M* DB[BP] in *o*-xylene and 0.25 *M* DHDECMP in *o*-xylene from 0.25 *M* HNO_3.

TABLE 2

Thermodynamic Values and Equations for the Variable Temperature Extraction of Th(IV) and U(VI) from 0.25 *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)
U(VI)/DB[BP]	$\frac{4194}{T} - 12.34$	$\frac{4261}{T} - 6.92$	−4.37	−8.48	−13.74
U(VI)/DHDECMP	$\frac{3740}{T} - 13.00$	$\frac{3755}{T} - 7.42$	−3.07	−7.46	−14.74
Th(IV)/DB[BP]	$\frac{4392}{T} - 17.37$	$\frac{4266}{T} - 6.34$	−4.64	−8.40	−12.60
Th(IV)/DHDECMP	$\frac{3822}{T} - 15.24$	[a]	[a]	[a]	[a]

[a] Not determined due to uncertainty in equilibrium stoichiometry.

for the extraction of U(VI) by DHDECMP. These data do not support the classification of DHDECMP as a bidentate extractant. The behavior of this extractant in a bidentate fashion should result in large differences in entropy due to the entropy of chelation (*16*) and in enthalpy due to the formation of coordinate bonds to carbonyl as well as phosphoryl oxygen atoms by the metal ion. These data actually show only slight differences in these terms, which are in the opposite direction that one would predict, giving no support to bidentate behavior for DHDECMP.

Infrared Studies

Since the thermodynamic measurements did not support a bidentate model for DHDECMP, it was felt that IR studies of metal complexes of this and other related extractants might yield information as to the bonding mode. Infrared data, compiled in Table 3, were obtained for U(VI) and Th(IV) complexes with DB[BP], DHDECMP, and DHOA. The study of the DB[BP] and DHOA extractants was undertaken to provide information regarding the effect of coordination of the phosphoryl group (DB[BP]) and the carbonyl functionality (DHOA) (*14*) on the stretching frequencies of these functional groups which could be used as models for DHDECMP. It is obvious that the changes in the stretching frequency of the phosphoryl group for DB[BP] and DHDECMP are very similar. We take this to be evidence for very similar interactions between the metal ions and the oxygen of the phosphoryl groups of these extractants. The changes in the carbonyl stretching frequencies were significantly smaller for DHDECMP than in DHOA, indicating either that the carbonyl–metal interaction is weaker in the DHDECMP or, possibly, that coordination of the phos-

TABLE 3

Phosphoryl and Carbonyl Frequencies in DB[BP], DHDECMP, 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		
U(VI)/DB[BP]	1155	−92		
Th(IV)/DB[BP]	1150	−97		
DHDECMP	1255		1645	
HNO_3/DHDECMP	1228	−27	1639	−6
U(VI)/DHDECMP	1186, 1164	−69, −91	1600	−45
Th(IV)/DHDECMP	1183, 1160	−72, −95	1597	−48
DHOA			1647	
HNO_3/DHOA			1639	−8
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 unbonded extractant.

phoryl group results in lowering of the bond order in the C–O linkage (through inductive effects resulting in electron withdrawal from the carbonyl group). Since there is little or no support from other sources for strong bidentate behavior, it seems likely that either (or both) of these effects could explain the observed spectral changes.

Comparison between the Extraction of Th(IV) from $LiNO_3$ and HNO_3 Using DHDECMP and DB[BP]

A very revealing comparison between the extraction behavior of Th(IV) with DHDECMP and DB[BP] is shown in Fig. 5. In $LiNO_3$ media (0.01 *M* HNO_3) the K_d's for Th(IV) are within a factor of four for the two extractants. As was shown in Fig. 3, there is a very small difference between DHDECMP and DB[BP] at low acidities. This is not what one would expect if chelation was important in the extraction of Th(IV) by DHDECMP. However, significant differences in the extraction behavior of Th(IV) are found between the two extractants when the comparison is made using higher nitric acid concentrations. The diminution in the K_d with increasing acidity using DB[BP] is due to the competition between the Th(IV) ion and hydrogen ion for the phosphoryl oxygen. A similar competition must exist in the case of DHDECMP, and as the data in Fig. 5 show, the K_d's for Th(IV) using the bifunctional extractant are lower in HNO_3 than they are at the corresponding $LiNO_3$ concentration, although

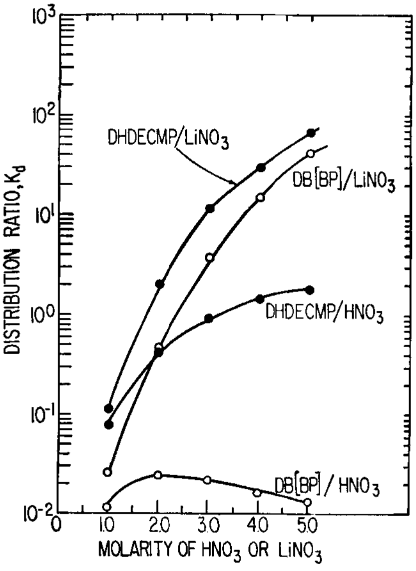


FIG. 5. Comparison of the distribution ratios of Th(IV) from $LiNO_3$ or HNO_3 by 0.05 *M* DHDECMP in *o*-xylene and by 0.05 *M* DB[BP] in *o*-xylene.

the effect is much smaller. Since earlier studies involving bifunctional extractants were performed almost invariably in the range of 1 to 8 *M* HNO_3, these differences between DHDECMP and typical monodentate neutral organophosphorus extractants like TBP and DB[BP] were used to support the supposition that DHDECMP (and similar CMP and carbamoyl phosphonate, CP, extractants) are forming stable chelate rings with the metal ion (*1*, *10*).

Obviously the DHDECMP molecule contains a special structural feature which enables it to function effectively as an extractant of metal ions from aqueous phases containing high concentrations of HNO_3. We do not believe this structural feature is a consequence of bidentate behavior, which would enable it to form a six-membered chelate ring between the metal ion and the phosphoryl and carbonyl oxygens, since the chelation effect should also be evident in $LiNO_3$ or in low HNO_3 media. Rather we believe that the protonation of the amide group, either on the carbonyl oxygen or amide nitrogen by HNO_3, is the key factor. The protonation of the amide group effectively protects or shields the phosphoryl oxygen–metal bond from attack by hydrogen ions. Thus the amide group behaves as a sort of intramolecular acid buffer. The above explanation is a hypothesis since the data in Fig. 5 and in the previous figures were rather indirect and do not in themselves prove that the proposed explanation is valid. A much stronger argument can be made that the chelation effect is not significant in DHDECMP extractions and thus some other effect must be taking place. However, additional supporting data for the intramolecular buffering effect hypothesis will be presented in the authors' following paper on the extraction of Am(III) by DHDECMP.

SUMMARY

DHDECMP behaves as a neutral extractant toward U(VI) and Th(IV). Although its denticity in the technical sense may be two, since there is IR evidence that the carbonyl oxygen in addition to the phosphoryl oxygen interacts with the metal ion, the carbonyl oxygen–metal interaction is weak and does not contribute significantly to the enthalpy and entropy of extraction. The greater effectiveness of DHDECMP as an extractant in nitric acid solution, compared to the monodentate extractant DB[BP], is probably due to its ability to reduce the direct attack of hydrogen ions on the metal–phosphoryl bond by the protonation of the amide group and not on a chelation effect.

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