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V. N. Romanovskiy[a]; V. A. Babain[a]; M. Yu. Alyapyshev[a]; I. V. Smirnov[a]; R. S. Herbst[b]; J. D. Law[b]; T. A. Todd[b]
[a] RPA "V.G. Khlopin Radium Institute", St. Petersburg, Russia [b] Idaho National Laboratory, Idaho Falls, ID, USA

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Radionuclide Extraction by 2,6-Pyridinedicarboxylamide Derivatives and Chlorinated Cobalt Dicarbollide

V. N. Romanovskiy, V. A. Babain, M. Yu. Alyapyshev, and I. V. Smirnov
RPA "V.G. Khlopin Radium Institute", St. Petersburg, Russia

R. S. Herbst, J. D. Law, and T. A. Todd
Idaho National Laboratory, Idaho Falls, ID, USA

Abstract: The extraction properties of diamide derivatives of dipicolinamide (2,6-pyridinedicarboxylamide or DPA, $(R'R''NCO)_2C_5NH_3$) in mixtures containing chlorinated cobalt dicarbollide in the acid form (HCCD), with and without a substituted polyethylene glycol (PEG), have been investigated. Distribution ratios of Cs, Sr, U, Eu and Am have been measured for various concentrations of diamide, PEG, aqueous phase nitric acid, with various HCCD:diamide ratios, and using different organic diluents. In the absence of HCCD, the diamides show little affinity for the extraction of Am or Eu from nitric acid solutions (distributions typically <1). Addition of HCCD with the diamide extractants indicates a pronounced synergistic effect with regard to actinide and lanthanide extraction; the observed Am and Eu distribution ratios typically increase by several orders of magnitude. Cesium is also appreciably extracted by the HCCD in the presence of the various diamides. Addition of PEG (to simultaneously extract Sr) with HCCD and diamide has minimal impacts on the Eu and Am distribution ratios. The initial data indicate that alkyl substituted DPA derivatives weakly affect the extraction properties with regard to actinides and lanthanides, while aryl substituents decrease extraction ability of the mixture. The results of this preliminary work indicate that numerous HCCD-PEG-DPA systems

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Address correspondence to R. S. Herbst, Idaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83415-2208, USA. Fax: (208)526-8541; E-mail: r.herbst@inl.gov

are promising and effective for the simultaneous extraction Cs, Sr, Am, and Eu from acidic solutions.

Keywords: Cobalt dicarbollide, diamides of dipicolinamide, extraction, cesium, strontium, actinides, lanthanides

INTRODUCTION

The acid form of chlorinated cobalt dicarbollide (HCCD) in an appropriate polar, organic diluent, such as nitrobenzene, is a well-studied Cs extractant from acidic, aqueous media (1). Different synergistic extractants used in conjunction with HCCD strongly affect the extraction properties of the system. Addition of polyethylene glycols (PEG) or crown ethers affords simultaneous extraction of both cesium and alkali earth elements (2). By incorporating bidentate organophosphorus compounds in the organic phase, the simultaneous extraction of the actinide (AN) and lanthanide (LN) elements is possible (3). Mixtures of various carbamoylmethylphosphine oxides (CMPO) with HCCD make it possible to simultaneously obtain very high distribution ratios for cesium, AN, and LN. These synergistic effects with HCCD are prevalent in acidic medium.

The Universal Extraction (UNEX) process has been developed for simultaneous extraction of cesium, strontium, and actinides from acidic solutions (4). This process utilizes an extractant consisting of 0.08 M HCCD, 0.007–0.02 M PEG-400, and 0.02 M diphenyl-*N,N*-di-*n*-butyl-carbamoylmethylphosphine oxide (Ph_2Bu_2CMPO) in the diluent phenyltrifluoromethyl sulfone ($C_6H_5SO_2CF_3$, designated FS-13) and provides simultaneous extraction of all major radionuclides (Cs, Sr, AN, and LN) from aqueous HNO_3 solutions up to ~2 M HNO_3 and ~4 M total nitrates. The process was initially developed for the treatment of acidic aqueous radioactive wastes, which contain relatively low concentrations of the radionuclides, to minimize the volume of material requiring long-term geological disposal (5). The UNEX process is of limited utility for processing aqueous, acidic solutions containing large quantities of LN and/or AN elements, such as present in dissolved spent nuclear fuel solutions. These constraints are primarily attributed to the limited solubility of CMPO (a maximum of ~0.02 M) and the CMPO-metal complexes in the organic phase. As a result, alternative actinide and lanthanide extractants are being investigated for use with HCCD as an improvement for waste processing and for applications where higher concentrations of the LN elements are prevalent. The objective of the present work was to evaluate dipicolinamide (DPA) derivatives as potential substitutes for CMPO in the UNEX process and determine if higher solubility of the extractant could be realized while maintaining substantial extraction of the LN and AN elements in the presence of HCCD.

The available literature indicates research has been performed with systems containing both diamides and dicarbollide extractants. Dicarbollide mixtures with diamides of malonic acid, phenanthroline, and mixtures of phenanthroline with dibutylphosphoric acid (DBPA) were previously studied (6). Extraction from 0.1 M HNO_3 by a mixture of the sodium salt of dicarbollide, 0.05 M $Na^+BCl_6^-$, and 0.25 M *o*-phenanthroline in nitrobenzene resulted in an americium distribution ratio, D_{Am}, of 10.8 with a high separation from Eu^{3+} ($D_{Eu} = 0.316$, $D_{Am}/D_{Eu} = 34.1$). These metals were extracted when the initial aqueous phase was at pH ≥ 2, although the equilibrium pH is $\sim$4 due to neutralization of nitric acid by phenanthroline. At lower pH values (higher HNO_3 concentrations) in the aqueous phase, extraction was not observed. It was also noted that Am and Eu cannot be efficiently separated by extraction with *o*-phenanthroline when DBPA is included in the organic phase (6).

The prospects for using malonamides, picolinamides, and dipicolinamides have been considered for americium and LN extraction from HNO_3 solutions (7–10). The general structure of substituted 2,6-pyridinedicarboxamide, representing the dipicolinamides (DPA) under investigation in this study is indicated by the structure in Fig. 1. Dipicolinamides are weaker donors compared with malonamides (9). Furthermore, DPA are less basic compounds compared with picolinamides, since introduction of the second carboxamide group into the molecule further decreases the basicity of the pyridine nitrogen. Previous work suggested that diamides of dipicolinic acid extract Am and LN only from solutions with high salt and low acid concentrations ($D_{Am} = 8.82$ for an 0.4 M N,N′-dimethyl-N,N′dibutyl-2,6-pyridinedicarboxamide in C_6H_5CN from a 0.04 M $HNO_3 + 5$ M $LiNO_3$ aqueous phase) (7). These limited literature data also suggest that the extraction ability of diamides of DPA for Am and Eu is comparable to malonamides (7). Again, the postulated reason of this effect is a reduction in basicity of the diamides of dipicolinamide.

Picolinamides are capable of extracting the minor actinides from weakly acidic solutions. The extraction of actinides with mixtures of picolinamides and anionic surfactants has been investigated (8). Sodium bis(2-ethylhexyl)-sulphosuccinate was used as an anionic surfactant. It was shown that the introduction of the voluminous anion into the system considerably increases extraction ability and enables the extraction of trivalent metals from more acidic media. The best extraction properties were observed for substituted amides derived from picolinamide, containing a branched alkyl substituent in the pyridine ring and alkyl substitution at the amide nitrogen. However, even the mixture of picolinamide and anionic surfactant did not extract

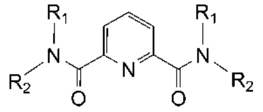


Figure 1. Structural formula of the DPA derivatives.

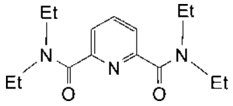
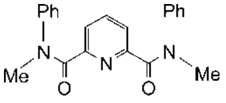
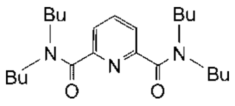
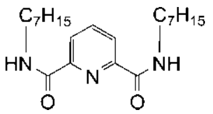
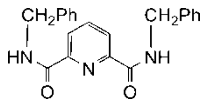
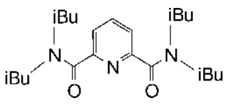
trivalent metals from aqueous solutions above 0.2 M HNO_3. This fact is most likely explained by protonation of picolinamides by the acidic medium. Finally, salts of picolinamides do not effectively extract metal ions.

A significant synergistic effect has been reported for the extraction of trivalent metals by different dipicolinamides in the presence of the voluminous and hydrophobic CCD anion (10). The objective of the present work was to expand results of that previous study and evaluate the extraction properties of several different diamides of DPA in the presence of HCCD. Modification to the DPA structure with respect to different hydrocarbon substituents attached at the amide nitrogen's (R_1 and R_2 in Fig.1) are anticipated to effect both the solubility of DPA in the organic diluent and basicity (extraction properties) of the dipicolinamide. The effect of substituting various simple hydrocarbon groups symmetrically attached at the diamide nitrogen's on the extraction properties of the molecule where examined in the presence of HCCD. The structures of the various functionalized DPA extractants investigated are indicated in Table 1, along with the abbreviations adopted and used in this work.

EXPERIMENTAL

The dichloroanhydride of picolinic acid was prepared in accordance with literature accounts (11). Chloroanhydride (5 mM in chloroform) prepared in this manner was added to a solution of chloroform containing 20 mM of the appropriate amine (diethylamine, di-*n*-butylamine, di-*i*-butylamine, benzylamine,

Table 1. Structures and nomenclature of aminated DPA studied in this work

Structure	Abbreviation	Structure	Abbreviation
	TEDPA tetraethyl DPA (R1 = R2 = Et)		PhMDPA N,N′-diphenyl-N,N′-dimethyl DPA (R1 = Me, R2 = Ph)
	TBDPA Tetra-*n*-butyl DPA (R1 = R2 = n-Bu)		DHpDPA N,N′-diheptyl DPA (R1 = H, R2 = C_7H_{15})
	DBzDPA N,N′-dibenzyl DPA (R1 = H, R2 = $-CH_2Ph$)		TiBDPA Tetra-*i*-butyl DPA (R1 = R2 = iBu)

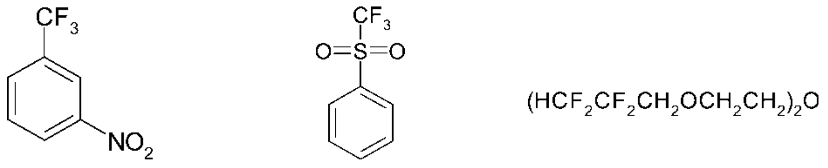
phenylmethylamine, or *n*-heptylamine), stirred and cooled to ≤40°C. After addition of the entire amount of dichloroanhydride, the mixture was kept overnight. This was followed by washes with 3 M HCl, water, 5% NaOH solution and again with water. Thereafter, the product was dried over anhydrous sodium carbonate and the chloroform was distilled. Tetraethyl DPA (TEDPA, Mp = 82°C, yield 74%) and N,N′-diheptyl DPA (DHpDPA, Mp = 97°C, 45% yield) were re-crystallized from a hexane-benzene mixture. The tetra-*n*-butyl DPA (TBDPA, 60% yield) was obtained as an oil and purified by column chromatography on silica gel. N,N′-dibenzyl DPA (DBzDPA, Mp = 193°C, 80% yield) and N,N′-diphenyl-N,N′-dimethyl DPA (PhMDPA, Mp = 169°C, 56% yield) were purified by dissolution in chloroform and re-precipitation from chloroform solution with hexane addition. Tetra-*i*-butyl DPA (TiBDPA, Mp = 90°C, 85% yield) was re-crystallized from ethanol.

NMR and mass-spectroscopy were used to confirm the structure and purity of the resulting compounds. The final purity of all DPA derivatives was not lower than 98%. NMR-spectra were taken on a Bruker, Avance DPX-300 spectrometer. Solutions in $CDCl_3$ and chemical shifts were calculated from residual solvent proton signals (7.28 ppm) for ^{1}H-spectra and from the average carbon-13 triplet signal of the solvent (77.4 ppm) for ^{13}C-spectra.

Chlorinated cobalt dicarbollide was obtained from Katchem Co. (Czech Republic) as the Cs salt (CsCCD) and used without additional purification. Stock, concentrated solutions of CsCCD (in the appropriate diluent) were converted to the acid form, HCCD, by repeated contacts with dilute $HClO_4$. The resulting HCCD stock solutions were subsequently washed with dilute HNO_3 to remove traces of $HClO_4$ from the organic phase prior to preparation of the test solution. Other reagents were of analytical grade and used as received from Vekton Co. (St. Petersburg, Russia). Uranyl nitrate, as well as ^{137}Cs, ^{241}Am and ^{239}Pu isotopes (as nitrates), were obtained from the Isotope Co. (St. Petersburg, Russia), and used as received. Two different types of polyethylene glycol (PEG) were used in this study as the synergistic Sr extractant in the organic phase. Polyethylene glycol with an average molecular weight of 400 (PEG-400, $HO(CH_2CH_2O)_{8-10}H$) from Merck and Slovafol-909 (the n-nonylphenyl ether of nonaethylene glycol, $C_9H_{19}C_6H_4(OCH_2CH_2)_9OH$) produced by Spolona (Slovakia) were used as received.

Metanitrobenzotrifluoride (F-3), phenyltrifluoromethylsulfone (FS-13) and the bis- tetrafluoropropyl ether of diethylene glycol (F-8) were used as diluents. The F-3 was obtained from Rhodia and used after washing twice with equal volumes of 5% sodium hydroxide solution, followed by a water wash and drying over anhydrous sodium carbonate and distillation. FS-13 and F-8 were synthesized in accordance with known procedures (5, 12). Chemical structures of the different diluents used in this work are indicated by the structures shown in Fig. 2.

Distribution ratio measurements were performed by adding 1 ml of the appropriate acidity aqueous phase containing 10^{-5} M stable Eu, Sr, and Cs



F-3 FS-13 F-8

Figure 2. Structural formulas of the diluents used in this work.

(as metal nitrates) and trace quantities of Eu, Sr, and Cs radioisotopes into a 5 ml test tube. Next, 1 ml of the organic extractant solution was added. Phase contact time was 3 minutes at room temperature (21 ± 1°C). Phases were separated by centrifuging at 2200 rpm for 5–10 min. Samples of the aqueous and organic phase, 0.4 ml each, were then taken for analysis. The equilibrium distribution ratios were determined radiometrically using a scintillation γ-spectrometer (DeskTop InSpector 1270). Americium was extracted in the same manner with addition of ^{241}Am tracer and 10^{-5} M stable Eu. The organic phase acid concentration was determined by titration with standard base in a mixture of acetone and water with using cresol green indicator. All distribution measurements were repeated a minimum of three times. Error in the radiometric measurements was typically ±10–15%. The error associated with higher distribution ratios of $D > \sim 100$ increased up to as much as ±30% due to very low activity and concomitant uncertainties associated with counting the aqueous phase.

RESULTS AND DISCUSSION

The solubility of the diamide extractants is an important consideration, especially when dealing with the substantial concentrations of target metals in the aqueous phases encountered in spent nuclear fuel separations schemes. Limited extractant solubility in the organic phase coupled with high metals concentrations in the aqueous phase can result in poor extraction efficiency and other problems associated with loading of the organic solvent. For the series of DPA derivatives in Table 1 that were synthesized and tested in this work, the solubility in the different diluents was considered. The aryl derivatives DBzDPA and PhMDPA were less soluble than the alkyl derivatives in the polar F-3 diluent. The DBzDPA indicated the lowest solubility limit in F-3 at no more than 0.05 M DBzDPA. Due to the limited solubility, only very limited testing was performed with this diamide derivative. The solubility of the PhMDPA was marginally higher at ≤ 0.1 M in F-3. The solubility of the tetraalkyldiamides in F-3 is much higher (up to 0.3 M diamide), making them more attractive extractants for nuclear fuel related separations than the aryl derivatives.

Nitric acid extraction into the organic phase is often prevalent in actinide solvent extraction systems and this effect is often an important consideration in accounting for the behavior of such systems; the most common example being nitric acid extraction by TBP in the PUREX process. The extraction of nitric acid by the pure F-3 diluent and solutions of PhMDA and TBDPA in F-3 is presented in Fig. 3. These data indicate that both diamides extract more acid than the pure diluent, and TBDPA extracts slightly more nitric acid than PhMDPA, but the differences decrease with increasing nitric acid concentration. In these systems, even at the higher aqueous HNO_3 concentrations, the distribution ratio of nitric acid, $D_{HNO3} \equiv [HNO_3]_{org}/[HNO_3]_{aq}$ is <0.05, indicating only minor quantities of HNO_3 are soluble or extracted into the organic phase.

Diamides of DPA by themselves do not effectively extract metals from acidic solutions as indicated in the available literature (9, 10). These accounts indicate that the diamides evaluated did not measurably extract Am or Eu from 3 M HNO_3 solutions ($D_M < 0.01$) at diamide concentrations of 0.1 M (9). However, distributions were measurable at higher diamide concentrations (where possible) with increasing concentrations of salt or acid in the aqueous phase. In order to verify and expand on these observations, the extraction of Am by several of the different diamides in F-3 was examined from aqueous solutions containing higher concentrations of HNO_3 or $NaNO_3$; these data are presented in Table 2. Americium distribution ratios,

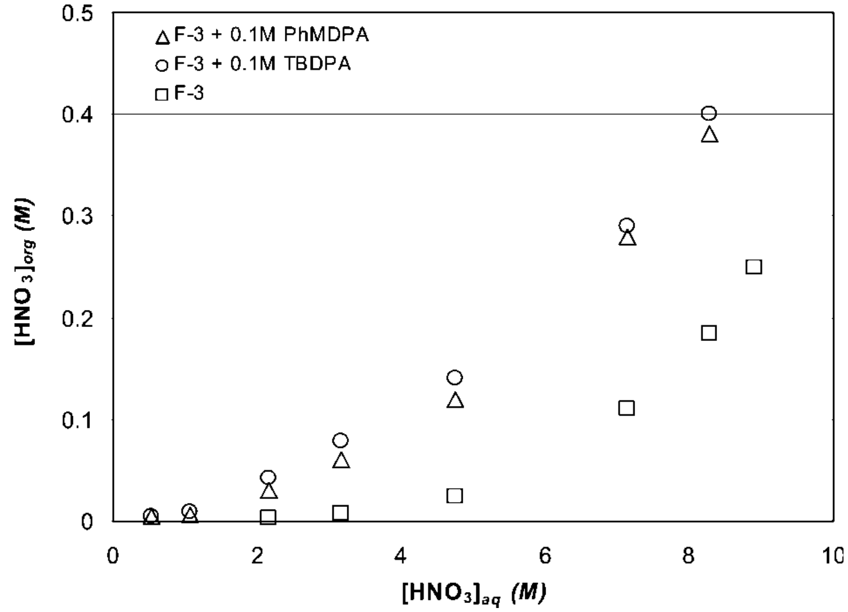


Figure 3. Extraction of nitric acid by F-3 and diamide solutions in F-3.

Table 2. Distribution ratios of Am by DPA solutions in F-3 diluent

Diamide	Concentration (M)	D_{Am}	
		3 M $HNO_3 + 3$ M $NaNO_3$	6 M HNO_3
PhMDPA	0.1	1.13	1.72
TEDPA	0.2	0.06	—
	0.3	0.13	—
TBDPA	0.2	0.02	—
	0.3	0.06	0.15
T*i*BDPA	0.2	0.02	—
	0.3	0.03	0.08

D_{Am}, were measured for several diamides from aqueous solutions containing 3 M $HNO_3 + 3$ M $NaNO_3$ or 6 M HNO_3. The PhMDPA was not soluble in F-3 at concentrations greater than 0.1 M; interestingly, even at this relatively low concentration, this was the only diamide tested which indicated a marginal affinity for americium ($D_{Am} > 1$) from the high nitrate media. The reason for the higher exaction ability of PhMDPA, relative to the other diamides tested, cannot presently be explained. By way of comparison, it is of interest to note that the Eu distribution ratio for 0.5 M PhMDPA in $CHCl_3$ was reported to be $D_{Eu} = 1.6$ from aqueous solution containing 5 M HNO_3 (9) (note that this diamide is referred to as DMDPhDPA in reference (9)). In any case, data in Table 2 verify that the diamides tested, in and of themselves, are poor actinide extractants and their extraction ability at moderate (3–6 M) HNO_3 concentrations must be enhanced if such dipicolinamides are to be useful AN/LN extractants.

The synergistic effects on AN/LN extraction resulting from the combination of the DPA derivatives with the cesium extractant, HCCD, with and without the addition of the Sr extractant Slovafol 909 were investigated. Distribution data are compared in Table 3 for the diamides as a function of concentration in the organic phase where the diamide concentration was incrementally increased from 0.01 M to 0.06 M. For comparison, data for the actinide extractant used in the current UNEX process, Ph_2Bu_2CMPO, are also included in Table 3.

Data in Table 3 indicate that the extraction of cesium by the HCCD - diamide (or CMPO) systems is quite consistent as indicated by the very similar magnitude of D_{Cs} for each of the extractants. Cesium distributions consistently decrease with increasing diamide (CMPO) concentration. This observation is consistent with other HCCD-based extraction systems and is attributed to the unique properties of the CCD^- anion. Metal extraction by the CCD^- anion in polar diluents occurs by an ion pairing or liquid-liquid cation-exchange mechanism with complete dissociation of the solvated species in the organic phase, i.e., a neutral species is not extracted into the

Table 3. Radionuclide extraction from 3 M HNO_3 as a function of diamide or CMPO concentration in the organic phase

		Distribution coefficient				
		0.06 M HCCD + extractant in F-3		0.06 M HCCD + extractant + 1 vol.% Slovafol-909 in F-3		
Extractant	Extractant concentration, (M)	Cs	Am	Cs	Sr	Am
Ph_2Bu_2CMPO	0.01	–	–	6.1	12	25
	0.02[a]	2.0[a]	590[a]	4.0	12	[b]
	0.03	–	–	2.3	9.4	[b]
	0.04	–	–	0.95	6.0	[b]
	0.06	–	–	0.26	3.7	[b]
TEDPA	0.01	11	90	7.4	14	250
	0.02	9.5	[b]	5.2	15	[b].
	0.03	7.1	[b]	2.6	7.6	[b]
	0.06	0.43	[b]	0.2	0.7	[b]
TBDPA	0.01	14	3.7	6.6	15	30
	0.02	9.9	15	4.7	11	100
	0.03	7.7	20	2.4	8.0	30
	0.06	1.4	20	0.23	0.9	20
PhMDPA	0.01	14	3.6	8.3	15	8.9
	0.02	11	25	5.4	12	65
	0.03	8	[b]	3.4	9.7	230
	0.06	1.1	[b]	0.16	0.34	[b]
DHpDPA	0.01	12	5	7.9	14	100
	0.02	10	60	5.5	12	[b]
	0.03	7.7	100	2.8	10	[b]
	0.06	2.9	[b]	1.3	5.9	[b]
TiBDPA	0.01	14	1.5	9.2	18	89
	0.02	11	3.1	6.3	15	200
	0.03	9.3	4.7	3.7	11	110
	0.06	1.7	6.4	0.32	1.9	8.7

[a] Organic diluent was FS-13, which suppresses D relative to the F-3 diluent.

[b] All measured activity in the organic phase, D >100.

organic phase. Thus, the CCD^- anion does not directly participate in the extraction process, but rather serves as the counter ion to stabilize the charge of the metal cation in the organic phase. The decrease in the Cs distribution ratio with increasing diamide (or CMPO) concentration is a direct result of metal competition for the CCD^- anion in the extraction system (13). Data in Table 3 indicate that addition of substituted PEG (Slovafol-909) to the systems (for simultaneous Sr recovery) typically resulted in slight decreases in Cs distributions, for the same reasons afore mentioned, and a trend which is consistent with previous studies of the UNEX solvent.

The measured Sr distributions were $D_{Sr} \leq 0.01$ in the extractant systems void of PEG and are consequently not reported in Table 3. With the addition of Slovafol-909, Sr distributions increase to values typical of those encountered for the UNEX extractant. Note that D_{Sr} consistently decreases with increasing DPA (CMPO) concentration in the organic phase. As with Cs, this is attributed to metal competition with the CCD^- anion.

The synergistic effects of HCCD addition on Am extraction are particularly noteworthy compared with the data in Table 2 for the diamide/F-3 systems (without HCCD). The Am distribution ratios in Table 3 vary significantly for the different diamides; however, distribution ratios typically remain well above 1.0 in all cases. D_{Am} were typically quite high ($> \sim 10$) at all extractant concentrations for many of the diamides studied as well as CMPO. The most notable exception was TiBDPA. The Am distributions for TiBDPA were substantially suppressed in the absence of PEG, yet D_{Am} increased dramatically when Slovafol-909 was added to the system. The cause of this anomaly is uncertain at present; additional investigation is warranted if these data are correct.

Finally, and perhaps most importantly, the data in Table 3 indicate that the substitution of various diamides for the CMPO used in the current UNEX solvent is a potential alternative for the extraction of actinides. Based on the data, many of the diamides studied have slightly less affinity for the extraction of Am (measured D_{Am} are typically lower compared with Ph_2Bu_2CMPO), but remain sufficiently large to efficiently extract Am.

Combination of the DPA derivatives with HCCD and PEG-400 was investigated as a function of aqueous phase HNO_3 concentration. In Table 4, data are provided on the extraction of Cs, Sr, and Eu by a constant composition of HCCD-PEG-diamide in F-3 for the different DPA derivatives. The most noteworthy observation from these data is that the europium distribution ratios (D_{Eu}) are typically >100 at 1 M HNO_3 for the systems studied. The high extraction efficiency of Eu in these systems is attributed to the unique properties of the HCCD and the synergistic effects propagated from including HCCD in the organic phase. The measured D_{Eu} for PhMDPA were substantially lower than for the other systems. It is postulated that this phenomenon is attributed to the electronegativity of the aromatic rings and their proximity to the oxygen centers, the net result is an increase in the basicity of the carbonyl oxygens. Counter intuitively, the europium distribution ratio decreases as the basicity of the extractant increases; however, since the more basic extractants exhibit stronger interactions with acidic protons in the organic phase, there is competition between the hydrated proton in the organic phase and the metal for the extractant in the organic phase. This H^+/metal competition for the extractant is responsible for the observed reversal in the order of extraction efficiencies and extractant basicity.

The data in Table 4 also indicate that for each substituted DPA studied, in all cases the measured distribution ratios decrease with increasing acid concentration for the reasons described previously (*vide supra*); the decrease in

Table 4. Cs, Sr and Eu distributions for HCCD/PEG mixtures with different diamides of DPA (Extractant composition: 0.02 M HCCD + 0.01 M diamide + 0.002 M PEG-400 in F-3)

Diamide	Aqueous phase $[HNO_3]$	Distribution ratios Cs-137	Sr-85	Eu-152
TEDPA	1 M	12	60	>100
	3 M	2.4	5.9	>100
	6 M	0.6	1.5	12
TBDPA	1 M	13	64	>100
	3 M	2.8	6	60
	6 M	0.6	1.3	1.1
DHpDPA	1 M	16	50	>100
	3 M	2.5	6	61
	6 M	0.54	1.3	9.2
TiBDPA	1 M	11	70	>100
	3 M	3.3	7.5	0.74
	6 M	0.6	1.6	0.46
PhMDPA	1 M	14	84	54
	3 M	1.7	2.5	1.3
	6 M	0.5	1.1	0.15

distribution coefficient with increasing HNO_3 concentration is a direct result of H^+/metal competition for the CCD^- anion in the extraction system. The Cs and Sr distribution ratios are very consistent for a given aqueous acid concentration, regardless of which functionalized DPA is added to the system. This observation is again consistent with the ion pair extraction mechanism in the presence of neutral ligands where properties of the polar diluent, and not the nature of the ligand, are the predominate factors in extraction behavior (13).

It is also of interest to note that the Eu distributions tend to decrease in the following order for the different diamide derivatives in the presence of HCCD:

$$\text{TEDPA} > \text{TBDPA} \geq \text{DHpDPA} > \text{TiBDPA} > \text{PhMDPA}$$

indicating that the nature of the alkyl substituted derivatives has little effect on the extraction properties of Eu, particularly at lower nitric acid concentrations. The TiBDPA is the notable exception, particularly at the higher HNO_3 concentrations, where the Eu distribution ratio is comparable to the phenyl derivative. The use of aryl substituents in PhMDPA decreases the extraction ability of the system for all HNO_3 concentrations studied. Thus, these preliminary data indicate that the tetra-alkylated derivatives of DPA have more potential interest for application to nuclear fuel reprocessing.

The dependence of the various radionuclide distribution ratios was investigated as a function of diamide concentration at constant HCCD concentration. These data obtained for TBDPA are given in Table 5. Note that depleted uranium was added to the aqueous phase ([U]aq = 495 mg/L) to increase the heavy metal concentration to more realistic levels. It is observed that with increasing diamide concentration, the distribution ratios of uranium in the HCCD-amide system increase, while D_{Cs} decrease. This observation is again consistent with the extraction mechanism where the CCD^- anion is the counter ion, stabilizing the metal charge in the organic phase: As the diamide concentration is increased, U concentration increases in the organic phase and there is less free CCD^- available to stabilize (and extract) Cs. Europium extraction attains its maximum at a ratio of HCCD/TBDPA = 2 ([TBDPA] = 0.05 M). The Am distribution ratios reached a maximum value ($D_{Am} > 1000$) at a concentration of [TBDPA] = 0.03 M. The Am/Eu separation factors in the TBDPA system was consistently $D_{Am}/D_{Eu} \geq 2.6$, indicating the diamide system may have some possible potential for Am/Eu partitioning. Note that Sr distribution ratios were also measured for these systems, but were always $D_{Sr} \leq 0.01$, verifying that in the absence of PEG, Sr is not extracted by HCCD-diamide mixture.

As in the UNEX process, PEG concentration in the DPA + HCCD systems has a large impact on strontium extraction. Additional data were collected using TBDPA to further elucidate the effect of PEG concentration on radionuclide distribution ratios. In Table 6, data are presented for the distribution ratios of several radionuclides as a function of Slovafol-909 concentration. Note that the concentrations of HCCD and TBDPA were held constant. These data indicate that D_{Cs} consistently decreases, while D_{Sr} increases with increasing PEG concentration for a constant HCCD and TBDPA concentration. The distribution ratios of Am, Eu, and U are largely unaffected with changing PEG concentration, indicating that there are minimal, if any, interactions between the PEG and DPA.

Table 5. Metal extraction from 3 M HNO_3 as a function of TBDPA concentration (Extractant composition: 0.1 M HCCD + TBDPA in F-3. Aqueous phase: 10^{-4} M (Cs, Sr, Eu); 0.002 M U, Initial [U] = 495 mg/L)

TBDPA concentration (M)	Distribution ratio				
	Cs-137	U	Eu-152	Am-241	D_{Am}/D_{Eu}
0.01	23	2.3	6.6	19	2.9
0.02	19	10	29	230	7.9
0.03	14	25	100	$>10^3$	>10
0.04	12	48	170	$>10^3$	>5.9
0.05	9.5	49	390	$>10^3$	>2.6
0.075	3.7	—	—	—	—
0.1	0.6	81	250	$>10^3$	>4.0

Table 6. Extraction of Cs, Sr, Eu, Am, and U as a function of Slovafol-909 concentration (extractant composition: 0.1 M HCCD + 0.05 M TBDPA + Slovafol-909 in F-3. Aqueous phase: 10^{-4} M metal nitrate in 3 M HNO_3, 0.002 M U, Initial [U] = 495 mg/l)

Concentration of Slovafol-909, M	Distribution ratios				
	Cs-137	Sr-85	Eu-152	Am-241	U
0.005	7.3	3.7	$>10^3$	$>10^3$	40
0.010	5.7	7.5	$>10^3$	$>10^3$	48
0.015	4.4	9.9	740	$>10^3$	48
0.020	3.2	11	530	$>10^3$	32
0.025	4.3	25	>100	$>10^2$	—

The influence of diamide type and HCCD/diamide ratio on the Am/Eu selectivity was evaluated. These data are presented in Table 7, and indicate that for the different DPA and HCCD/diamide ratios, Am is consistently extracted slightly better than Eu. In the case of the DPA compounds, the pyridine nitrogen can theoretically form a tridentate coordination complex and perhaps increase Am/Eu selectivity. The data in Table 7 indicate only slightly higher separation factors than for similar CMPO systems. Typically, for example for in the system containing carbamoylphosphonate, Am is extracted slightly better than LN with separation factors of $D_{Am}/D_{Gd} \approx 2-2.5$ (14). The separation factors indicated in Table 7 are not large enough to permit the practical separation of Am and lanthanides in a direct extraction procedure. On the other hand, the slightly enhanced Am extraction, relative to Eu, may provide a basis to attempt to separate Am and LN using complexants. Such investigations will be an interesting topic of future studies.

During the course of this work, an interesting effect of solvent aging on measured distribution ratios was observed for several of the DPA extractants. A series of experiments were performed where the HCCD-DPA solutions

Table 7. Extraction of Am and Eu from 3 M nitric acid by different DPA with HCCD

Extractant composition in F-3	D_{Am}	D_{Eu}	D_{Am}/D_{Eu}
0.1 M PhMDPA + 0.01 M HCCD	0.86	0.22	3.9
0.1 M PhMDPA + 0.02 M HCCD	2.99	0.85	3.5
0.01 M PhMDPA + 0.06 M HCCD	3.6	0.66	5.4
0.1 M TBDPA + 0.01 M HCCD	0.02	0.01	2
0.1 M TBDPA + 0.02 M HCCD	0.38	0.13	2.9
0.01 M TBDPA + 0.06 M HCCD	3.5	0.7	5

were prepared and the Eu and Am distribution coefficients measured after different solvent aging methods:

1. immediately (less than 1 hour) after preparing the organic phase;
2. after standing at room temperature for 1–2 days, and
3. after heating at 70°C for 3 hours.

The measured distribution coefficients for these different aging procedures are summarized in Table 8. In the case of DBzDPA and TBDPA, the measured D_{Am} and D_{Eu} were 2 to 3 times higher after the solution was allowed to stand for several days or heated for several hours. It was also noted that the organic phases were often cloudy or hazy immediately after preparation, but cleared after standing or heating and standing for several days. Solids were not prevalent and extended centrifugation would not remove the haze; consequently, the cloudy appearance of the organic phase was attributed to water (likely from the concentrated HCCD solution used in the makeup procedure) in a non-equilibrium state in the initial organic phase. After standing, a film of aqueous phase was noted on the organic or adhering to the walls of the tube, indicating entrained non-equilibrium water is in part responsible for differences in the measured distributions as a function of organic phase aging. Ongoing efforts are planned to further evaluate this phenomenon experimentally; in the meantime, it is imperative that the organic phase be properly aged to insure consistent measurements of distribution ratios.

The diluent used in the DPA – HCCD system influences the extraction properties of the DPA-HCCD-PEG extraction systems. The results for metal extraction by 0.1 M HCCD + 0.05 M TBDPA + 0.025 M Slovafol-909 in

Table 8. Extraction of Am and Eu after different solvent aging techniques. (Extractant composition: 0.06 M HCCD + 0.01 M DPA in F-3. Aqueous phase: 10^{-5} M $Eu(NO_3)_3$, spiked with Eu-152 or Am-241 in 3 M HNO_3)

		Organic phase aging conditions		
Extractant	D	<1 hr @ Room temp.	1–2 days @ Room temp.	<1 day, after 3 hrs heating @ 70°C
DBzDPA	D_{Am}	5.7	19	13
	D_{Eu}	2.1	3.9	3.6
PhMDPA	D_{Am}	3.1	3.2	3.6
	D_{Eu}	0.65	0.67	0.66
TBDPA	D_{Am}	1.0	3.4	3.5
	D_{Eu}	0.38	0.71	0.70
T*i*BDPA	D_{Am}	0.30	0.63	0.57
	D_{Eu}	0.18	0.31	0.31

several different diluent systems from 3M HNO_3 are presented in Table 9. The influence of the diluent has also been noted in the UNEX process, in the extraction of Cs by HCCD, as well as for Cs and Sr in the HCCD-PEG system. These data indicate the effect of various diluents on the extraction of Cs, Sr, and Am and indicate that the distribution ratios consistently decrease for the different diluents in the following order: F-3 > FS-13 > FS-13/F-8 > F-8. This is the same trend that has been previously observed in both the HCCD and the HCCD + PEG systems, as well as in systems containing HCCD + diphosphine dioxides (15). We maintain that diluent polarity and the associated ability of polar diluents to contain minor quantities of dissolved water is a primary consideration in all HCCD containing extraction systems (15).

CONCLUSIONS

The data presented indicate diamides of DPA are of considerable interest as synergistic additions to chlorinated cobalt dicarbollide from the extraction

Table 9. Extraction of metals by 0.1 M HCCD + 0.05 M DPA + 0.025 M Slovafol-909 in different diluent systems

		Distribution ratio		
Diamide	Diluent system	Cs	Sr	Am
TEDPA	F-3	4.3	24.8	>100
	FS-13	1	6.5	>100
	FS-13 + 10 vol.% F-8	1.3	4.3	>100
	FS-13 + 20 vol.% F-8	1	2.6	>100
	F-8	0.44	0.46	26
TBDPA	F-3	4.3	25	>100
	FS-13	1.2	8.8	9.9
	FS-13 + 10 vol.% F-8	1.1	4.1	2.9
	FS-13 + 20 vol.% F-8	1	2.5	2.4
	F-8	0.38	1.2	1
PhMDPA	F-3	11.4	2.1	>100
	FS-13	1.2	9	>100
	FS-13 + 10 vol.% F-8	1.3	4.9	>100
	FS-13 + 20 vol.% F-8	1.1	2.9	>100
	F-8	insol.	insol.	insol.

of AN and LN species. The moderate extraction ability of the diamides of DPA is attributed to their low basicity. At the same time, the mixture of HCCD and diamides of DPA efficiently extracts trivalent metals from HNO_3 solution. Diamides are easier to synthesize and are much less expensive than carbamoylphosphine oxides, yet the extraction properties of the systems HCCD/diamides and HCCD/carbamoylphosphine oxides are practically the same. Different alkyl substituents in the diamides of DPA only slightly affect the extraction ability and selectivity in the case of Eu and Am. Introduction of aryl substituents further decrease basicity of the diamide and the extraction ability of HCCD/diamide system. Based on the preliminary data obtained in this study, additional investigations of the DPA/HCCD/PEG system are warranted to further elucidate the behavior of the system. Based predominately on the solubility and distribution data obtained to date, the tetra-alkyl substituted DPA's indicate the greatest potential for application to spent nuclear fuel reprocessing. Of those examined, the TBDPA appears to be the most interesting of the DPA's examined and additional work with the TBDPA/HCCD/PEG system is ongoing.

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