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Distribution Studies of Actinides Using a Tetradentate Extractant, 4,4'-Nonanedioyl-Bis(2,4-Dihydro-5-Methyl-2-Phenyl-3H-Pyrazol-3-One)

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DISTRIBUTION STUDIES OF ACTINIDES USING A TETRADENTATE EXTRACTANT, 4,4'-NONANEDIOYL-BIS(2,4-DIHYDRO-5-METHYL-2-PHENYL-3H-PYRAZOL-3-ONE)

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ABSTRACT

The extraction of Th(IV), UO_2(II), Am(III), and Eu(III) from aqueous acid by a tetradentate extractant, 4,4'-nonanedioyl-bis(2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one), H_2NDBP, has been studied and compared with two bidentate model compounds, 4-hexanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one, HHMPP, and 4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one, HBMPP. The distribution coefficients of UO_2(II), Am(III), and Eu(III) were somewhat larger using H_2NDBP relative to the model compounds under the conditions studied. However, the Th(IV) extraction using H_2NDBP was greatly enhanced when compared to HBMPP or HHMPP. The distribution coefficient for Th(IV) from 0.5 M HNO_3 was 11.6 using 3.0×10^{-3} M H_2NDBP compared with values of $D < 0.01$ using 3.0×10^{-3} M HBMPP or HHMPP.

INTRODUCTION

The development of multidentate ligands to give improved separations of metal ions has many important applications from hydrometallurgy to treatment of toxic metal ions *in vivo* (1,2). This paper describes the extraction properties of a tetradentate ligand built by linking two bidentate units for some representative actinide and lanthanide ions. The broad goal of this effort is to develop ligand systems with improved properties for actinide separations and analyses. The potential applications of these compounds include use in liquid-liquid, chromatographic, and membrane extraction systems for actinide and lanthanide ions.

The 1,3-diketones have been extensively studied as extractants for actinide and lanthanide ions (3). The linking of multiple 1,3-diketone units to give compounds with increased binding constants for UO_2(II) and some lanthanide ions has been reported. Alberts and Cram (4,5) prepared a series of linear and macrocyclic ligands containing two or three 1,5-substituted acetylacetone units. The tetradentate compounds showed increased formation constants for divalent ions (including UO_2(II)) of two to four orders of magnitude when compared with the bidentate analogue. The compound containing three acetylacetone units showed a corresponding increase of five to six orders of magnitude in the formation constants with La(III), Ce(III), and Cr(III). Tabushi et al. reported on the preparation and extraction properties of a macrocycle containing three 1,3-diketone units (6). A solution of the potentially hexadentate ligand was shown to be over 260 times more effective than dicyclohexyl-18-crown-6 in the extraction of UO_2(II).

The tetradentate compound described in this report was prepared by linking two acyl pyrazolone units. The acyl pyrazolones belong to the general class of 1,3-diketone compounds. Their relatively high acidity has been exploited for extracting actinide and lanthanide ions from moderately acidic solutions primarily for analytical purposes (7). The tetradentate compound was expected to have substantially higher binding constants for An and Ln ions. The compounds studied in this work are diagrammed in Figure 1. HBMPP was chosen because it is commercially available and considerable extraction data is available in the literature. HHMPP was synthesized to give an acyl substituent that has electronic properties similar to H_2NDBP, thus eliminating any extraction differences from increased acidity of the extractants (7). The results of comparing the extraction characteristics of these two model compounds with H_2NDBP for representative actinide and lanthanide ions are reported.

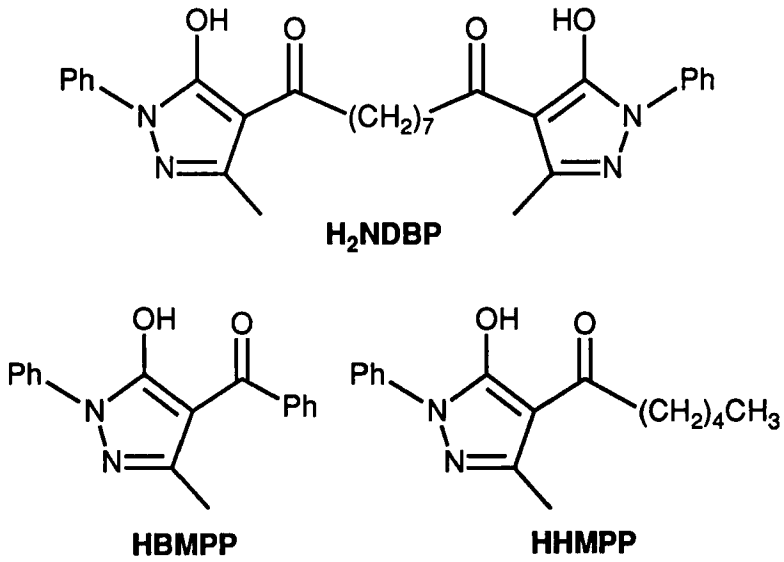

Fig. 1. Structures of multidentate extractants.

EXPERIMENTAL

Materials. The 4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one, HBMPP, was obtained from Aldrich and recrystallized from cyclohexane before use. The 4,4'-nonanedioyl-bis(2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one), H_2NDBP, and 4-hexanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one, HHMPP, were prepared and characterized by the following procedures.

Synthesis of H_2NDBP. The H_2NDBP was synthesized according to the procedure of Jensen (8) and later by Chang (9) with some modification. 2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (H_2MPP; Aldrich; 17.6 g) was dissolved in anhydrous dioxane (Eastman, distilled over lithium aluminum hydride; 300 mL) under a nitrogen atmosphere. Anhydrous $Ca(OH)_2$ (Baker; 15 g) was added all at once with rapid stirring. Nonanedioylchloride (Aldrich; 11.4 g) was added dropwise at a rate that gave controlled refluxing. The reaction was refluxed for 30 min more and then rapidly filtered while hot to remove excess $Ca(OH)_2$. The filter cake was washed several times with hot dioxane (20 mL), and the filtrates were combined and after cooling yielded a crystalline solid. The solid was filtered, washed with cold dioxane (20 mL), and put into 250 mL of 2 M HCl with stirring to break up the lumps. The product was filtered, washed with water, and further washed with methanol to remove a yellow impurity to yield 16.8 g (67% yield) of crude white product with mp 122-122.5°C. The solid was recrystallized in a minimum of hot chloroform with methanol added to induce crystallization. ^{1}H-NMR ($CDCl_3$/TMS): 1.00-1.85 (m, CH_2 chain, 10H), 2.23 (s, CH_3, 6H), 2.42-2.85 (t, CH_2, 4H), 6.85-7.80 (m, Ph, 10H), 12.0 (s, acidic proton, 2H); IR (KBr): 2946(m), 2920 (m), 2851(m), 1635(s), 1564(s), 1499(s), 1461(s), 1458(s), 1389 (m), 1079(s), 982(s), 782(m), 760(s), 691(s) cm^{-1}; Elemental analysis: calcd C 69.58, H 6.44, N 11.19, O 12.78; obsd C 69.01, H 6.54, N 11.30, O 13.17 (by diff).

Synthesis of HHMPP. HHMPP was synthesized in a manner similar to above using 87.2 g H_2MPP, 66.8 g $Ca(OH)_2$, and 67.3 g hexanoyl chloride (Aldrich) in 750 mL dioxane. The reaction mixture was refluxed 0.5 h and filtered while hot to remove excess $Ca(OH)_2$. The filter cake was washed with hot dioxane and the combined filtrates put into 1 L of 2 M HCl while stirring. The resulting solid was filtered, washed with water and air dried. The solid was recrystallized from methanol to give a product yield of 93 g (68%) with a mp 59-60°C and greater than 99% purity by GC. (Temperature program: 200° to 290°C at 80°/min). NMR ($CDCl_3$/TMS): 0.82 (t, CH_3, 3H), 1.13-1.42 (m, CH_2, 4H), 1.48-1.86 (m, CH_2, 2H), 2.31 (s, CH_3, 3H), 2.58 (t, CH_2, 2H), 6.89-7.71 (m, Ph, 5H), 12.96 (s, acidic proton, 1H); IR (KBr): 2954(m), 2932(m), 2868(m), 1635(s), 1595(s), 1558(s), 1501(s), 1458(2), 1441(s), 1012(s), 983(s), 755(s), 693(s), 685(s) cm^{-1}; Elemental analysis: calcd C 70.56, H 7.40, N 10.29, O 11.75; obsd C 70.52, H 7.39, N 10.23, O 11.85 (by diff).

Compounds containing four, five, and six carbon chains linking two acyl pyrazolone units were also synthesized by similar procedures. The six carbon compound was insoluble in the organic solvents tested and thus unsuitable for further studies. The four and five carbon compounds were soluble, but their extraction studies were hampered by third-phase formation.

Distribution Measurements. The solutions of the extractants, HBMPP, HHMPP, and H_2NDBP, were prepared by dissolving a weighed sample in analytical

reagent grade toluene. The aqueous phase was prepared using either $NaNO_3$ or $LiClO_4$ to control the ionic strength and HNO_3 or $HClO_4$ to adjust the acidity. The pH was defined as the -log[H^+]. All chemicals used were reagent grade or better.

The distribution coefficients, D, of the metal ions were defined as the $[M]_{org}/[M]_{aq}$. A batch equilibrium method was used to obtain the distribution data. Duplicate extractions were performed with equal volumes of pre-equilibrated aqueous and organic phases that were contacted at room temperature (22-24°C) by using a mechanical shaker for 30 min or a vortex mixer for 15 min. Measurement of D at various contact times indicated 15 min was more than sufficient for attaining equilibrium with either method. The samples were then centrifuged and aliquots were taken of each phase. The pH of the aqueous phase was determined after extraction. For the Am and Eu extractions at pH 2-3, 0.01 M sulfanilic acid was used as a buffer. The use of sulfanilic acid under these conditions does not require correction for metal binding in the aqueous phase.

The concentrations of the metal ions were determined by either a spectrophotometric method or by the use of radiotracers. The thorium concentration was determined by a spectrophotometric technique using Arsenazo III (10). The UO_2(II) was measured by both spectrophotometric and radiotracer techniques using ^{233}U. The ^{233}U was assayed using a liquid scintillation counting technique. The concentration of the metal ions was kept at least 100 times smaller than the concentration of the extractants studied. The distribution studies of Eu(III) and Am(III) were performed using carrier-free radioisotopes (~10^{-8} M) ^{152}Eu and ^{241}Am (New England Nuclear). The gamma activity was measured separately for equal aliquots (1 mL) of both phases. Accountability for all tracer extractions was 100 ± 10%. The D measurements for thorium and some for uranium were done at relatively high metal ion concentrations (~10^{-4} M) where trace impurities in the organic phase should not effect the D values. Several of the D values for the tracer studies were verified by comparing the D value for forward and back extraction and for two successive extractions with the same organic phase. The excellent agreement observed is an indication that strongly extracting trace impurities were not a problem with these compounds.

The least squares fits of the ligand and pH dependencies all gave R^2 values of 0.96 or higher and the slopes are reported to the nearest 0.1 (range of standard deviations of the slope 0.04-0.14). The K_{ex} values were calculated using these experimental dependencies and the uncertainties reported are the standard deviations of the average values.

RESULTS AND DISCUSSION

The extraction of UO_2(II) and Th(IV) from 0.1 M $NaNO_3$ was measured using HBMPP in toluene. The results of these studies are contained in Table I. The slope analysis showed the expected concentration dependence of two for UO_2(II) and four for Th(IV). Comparison with previously published results showed good agreement for the UO_2(II) data and the Th(IV) data considering the differences in solvent and ionic strength. The slope analysis indicates the following extraction equilibria:

$$UO_2^{+2}{}_{(aq)} + 2\ HBMPP_{(org)} \text{<====>} UO_2(BMPP)_{2(org)} + 2H^+_{(aq)} \quad (1)$$

$$Th^{+4}{}_{(aq)} + 4\ HBMPP_{(org)} \text{<====>} Th(BMPP)_{4(org)} + 4H^+_{(aq)} \quad (2)$$

Table I. Extraction Studies Using HBMPP

Metal	Log K_{ex}	Slope	Reference
UO_2(II)	-1.26 ± 0.10	2.0[a]	present work,[b] radiotracer
	-0.97 ± 0.05	1.7[a]	spectroscopic[b]
		2.1[c]	
	-1.15	2	(11)[d]
Th(IV)	2.8 ± 0.1	3.7[a]	present work[b]
		3.7[c]	
	3.63 ± 0.27	4.0[a]	(12)[e]

[a]Variation of extractant concentration.
[b]Aqueous phase = 0.1 M $NaNO_3$, pH = 2.0.
[c]Variation of pH.
[d]Aqueous phase = 0.1 M $NaClO_4$, pH = 2.0, organic phase = chloroform.
[e]Aqueous phase = 1.0 M $NaClO_4$, pH = 2.0, organic phase = chloroform.

The extraction of UO_2(II) by H_2NDBP showed an increase in efficiency over both model compounds in the ranges studied. The log K_{ex} values for H_2NDBP and HHMPP are found in Table II. A direct comparison of the extraction efficiency for UO_2(II) can be made at an extractant concentration of 1 x 10^{-2} M and pH of 2.0 and shows that for HBMPP, D = 0.58 and for H_2NDBP, D = 3.29. This ratio of D values will change as a function of ligand concentration or pH because of the different extraction dependencies. The K_{ex} values indicate that HHMPP is about four times better for U(VI) extraction than HBMPP. The concentration dependence for the tetradentate H_2NDBP was near one, compared to two for HBMPP and HHMPP, showing that both acyl pyrazolone units are participating in the extraction process for H_2NDBP. The slopes of the concentration studies of H_2NDBP and HBMPP can be compared in Figure 2. Based on the slope analysis the overall reaction was

$$UO_2^{+2}{}_{(aq)} + 2H_2NDBP_{(org)} \text{ <====> } UO_2(NDBP)_{2(org)} + 2H^+{}_{(aq)}. \quad (3)$$

The H_2NDBP extraction data can be compared to data obtained using chloroform as a solvent for the compound with eight methylene groups between the acyl pyrazolone units (13). The slope analysis for this compound showed a ligand dependence of 1.2 and a pH dependence of 2.1 with K_{ex} of -1.27 compared to 0.22 for H_2NDBP in toluene.

The Th(IV) data for all three extractants studied shows that the tetradentate extractant is much more effective for Th(IV) than either the HBMPP or HHMPP. A direct comparison of the data for H_2NDBP and HBMPP shown in Figure 3 is not possible since the HBMPP data was obtained at [HNO_3] = 1.0 x 10^{-2} M and the H_2NDBP data was obtained at [HNO_3] = 0.87 M. However, at an extractant concentration of 1.0 x 10^{-3} M the H_2NDBP yields a similar distribution value to HBMPP even though it is extracting from much stronger acid media. The ligand dependence for H_2NDBP was near 2 indicating that both acyl pyrazolone groups of each ligand were complexing the Th(IV). The pH dependence for H_2NDBP was 3.8, which indicates that the overall reaction for the extraction of Th(IV) with H_2NDBP is

$$Th^{+4}{}_{(aq)} + 2(H_2NDBP)_{(org)} \text{ <=====> } Th(NDBP)_{2(org)} + 4H^+{}_{(aq)}. \quad (4)$$

Table II. Extraction Studies[a] of UO_2(II) and Th(IV) Using H_2NDBP and HHMPP

Metal	Log K_{ex}	Slope	Reference
		HHMPP	
UO_2(II)	-0.68 ± 0.20	2.0[b]	present work
		1.9[c]	
Th(IV)	3.4 ± 0.4	3.0[b]	present work
		2.9	
		H_2NDBP	
UO_2(II)	0.22 ± 0.16	0.8[b]	present work
		2.2[c]	
Th(IV)	4.69 ± 0.05	1.9[b]	present work
		3.8[c]	

[a]Aqueous phase = 1.0 M $NaNO_3/HNO_3$.
[b]Variation of extractant concentration.
[c]Variation of pH.

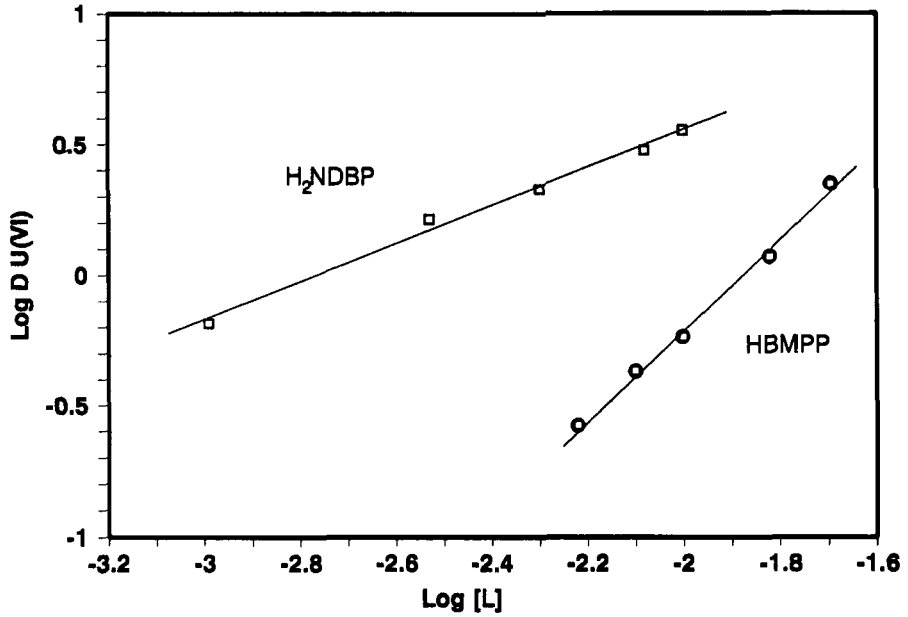

Fig. 2. Concentration dependence of UO_2(II) extraction using H_2NDBP and HBMPP (pH = 2.0, μ = 0.1, $NaNO_3$).

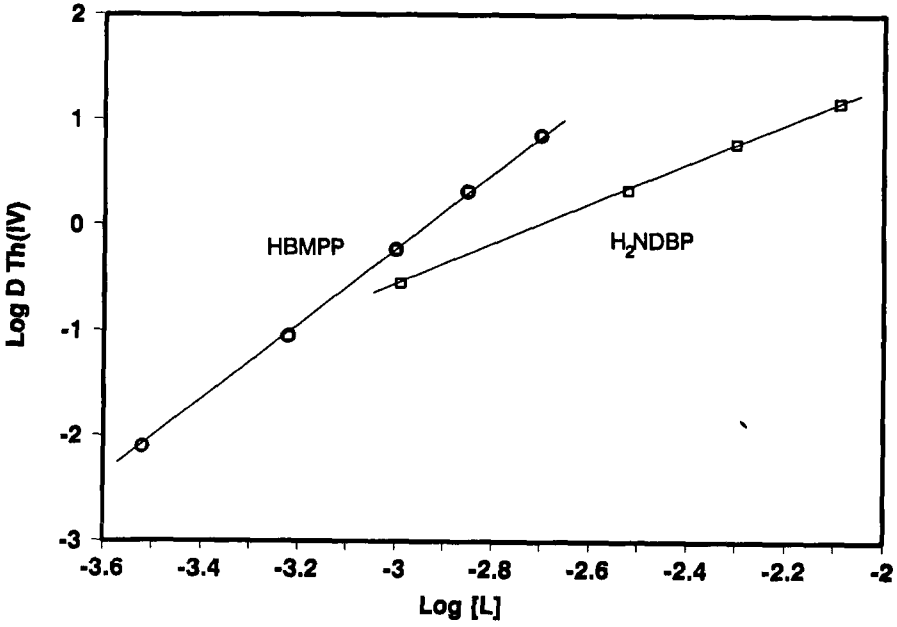

Fig. 3. Concentration dependence of Th(IV) extraction using H_2NDBP (pH = 0.060) and HBMPP (pH = 2.0), μ = 1.0, $NaNO_3$.

The extraction dependencies for Th(IV) with HHMPP were different from those of HBMPP. The concentration dependence and the pH dependence were both near 3 suggesting the following equilibrium:

$$Th^{+4}_{(aq)} + 3HHMPP_{(org)} + NO_3^-{}_{(aq)} <=> Th(HHMPP)_3NO_{3(aq)} + 3H^+_{(aq)} \quad (5)$$

The high concentration of nitrate in the aqueous media presumably promotes the formation of this mixed complex.

Figure 4 shows the acid dependency of the extraction of Th(IV) by H_2NDBP at different concentrations of extractant. The fact that all three curves plateau at the same D value at low acid concentration indicates that polymeric complexes and self-adducts are not major contributors to the extraction of Th(IV) with H_2NDBP (14).

Figure 5 shows the results of the extraction of Th(IV) and UO_2(II) at acid concentrations from 0.5 to 6 M. The results show that UO_2(II) is not extracted significantly (D < 0.01) by either HHMPP or H_2NDBP over this entire range. The D values are also less than 0.01 for Th(IV) extraction with HHMPP. The H_2NDBP showed an entirely different behavior. The percentage of extraction initially decreases from >90% at 0.5 M HNO_3 to a minimum of <5% at about 2.5 M HNO_3 and then increases to > 90% at 6 M acid. This change indicates a new extraction mechnism is operating at the higher acid concentrations. An ion pairing mechanism involving anionic Th(IV) nitrate complexes and H_3NDBP^+ seems likely, but further work will be needed to define this high acid extraction mechanism.

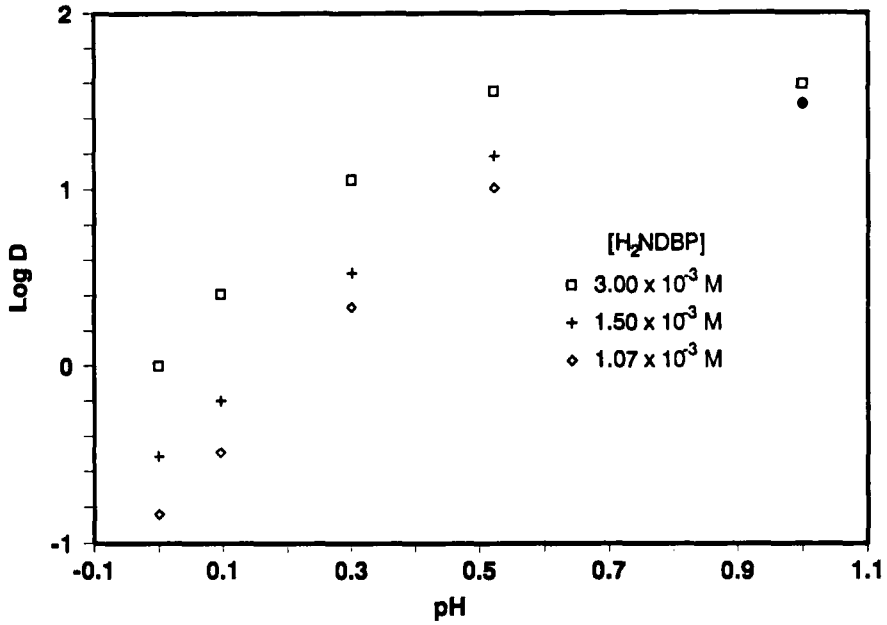

Fig. 4. Acid dependence of Th(IV) extraction using H_2NDBP.

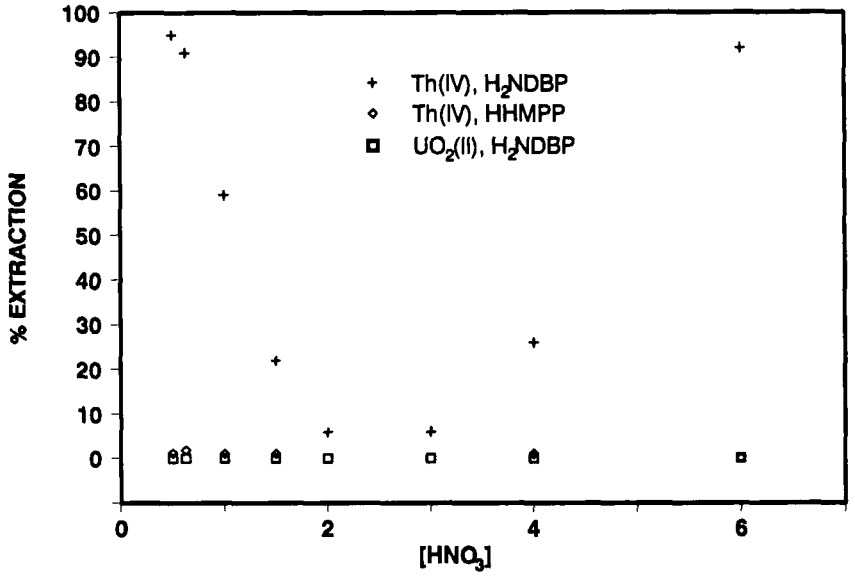

Fig. 5. Extraction of Th(IV) and UO_2(II) at high acid concentration.

The results of the extraction studies using Eu(III) and Am(III) are found in Table III. The slope analysis revealed the extraction equilibrium for these metals using HHMPP was

$$M^{+3}_{(aq)} + 3HHMPP_{(org)} \text{ <=====> } M(HMPP)_{3(org)} + 3H^{+}_{(aq)}. \quad (6)$$

The extraction constant of HHMPP was slightly higher for Eu(III) than Am(III) as would be expected with the slightly greater charge-to-radius ratio of Eu(III). For H_2NDBP the pH dependency was also near 3 but the concentration dependency was 2. This leads to the following extraction equilibrium:

$$M^{+3}_{(aq)} + 2H_2NDBP_{(org)} \text{ <===> } M(NDBP)(HNDBP)_{(org)} + 3H^{+}_{(aq)} \quad (7)$$

Three of the four acyl pyrazolone groups are deprotonated. The fourth protonated acyl pyrazolone group may be coordinated to the metal ion, but this must be examined in further studies. A previous study of the extraction of lanthanides and actinides by HBMPP reported self-adduct formation to give $M(BMPP)_3(HBMPP)$ as the major extractant species under the conditions studied (15) However, this self-adduct formation was not observed with HHMPP as noted above.

The use of a seven carbon chain to connect two acyl pyrazolone groups forms a very effective tetradentate extractant for Th(IV). The improvement of the extraction of UO_2(II), Am(III), and Eu(III) was significant, but the enhancement observed for Th(IV) was much greater. The increase in the Th(IV) extraction resembles that observed for a "classical" chelate effect produced primarily by favorable entropic factors (16) assuming that the increase in the extraction is primarily driven by an increase in the formation constant of the ligand with the metal ion. The enhancements of extraction of UO_2(II), Am(III), and Eu(III) seem rather small compared with the results of Alberts and Cram (4,5) for related multiple 1,3-diketone compounds with

Table III. Extraction Studies[a] of Eu(III) and Am(III) Using H_2NDBP and HHMPP

Metal	Log K_{ex}	Slope	Reference
		HHMPP	
Eu(III)	-5.24 ± 0.16	3.0[b]	present work
		3.3[c]	
Am(III)	-5.67 ± 0.14	3.2[b]	present work
		3.3[c]	
		H_2NDBP	
Eu(III)	-3.70 ± 0.18	2.0[b]	present work
		2.8[c]	
Am(III)	-4.18 ± 0.22	2.0[b]	present work
		2.8[c]	

[a]Aqueous phase = 0.1 M $LiClO_4/HClO_4$.
[b]Variation of extractant concentration, pH = 2.42 (HHMPP), 2.84 (H_2NDBP).
[c]Variation of pH, [HHMPP] = 0.10 M, [H_2NDBP] = 0.020 M.

divalent and trivalent metal ions. Presumably steric interactions or other factors influencing the overall extraction are decreasing the distribution coefficients for these metal ions. For example, the "wrapping" of the NDBP dianion around the linear uranyl ion may yield an unfavorable conformation of the ligand or steric interactions with the oxo groups.

CONCLUSION

The increased selectivity of the H_2NDBP system for tetravalent ions is a potentially useful property, regardless of the source of the discrimination between metal ions. Further studies are in progress to better understand the factors influencing the selectivity. These studies include an examination of compounds with other bridging groups linking the acyl pyrazolone units and an investigation of the structures and dynamics of complexes of these ligands in solution. A better understanding of the coordination chemistry will allow the design of even more selective separation systems for the actinides and lanthanides.

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