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SELECTIVE EXTRACTION OF TRIVALENT ACTINIDES FROM LANTHANIDES WITH DITHIOPHOSPHINIC ACIDS AND TRIBUTYLPHOSPHATE

Author(s):

Gordon Jarvinen, Richard Barrans, Norman Schroeder,
Karen Wade, Marianne Jones, Barbara Smith, Jerry Mills,
Greg Howard, Henry Freiser, S. Muralidnaran

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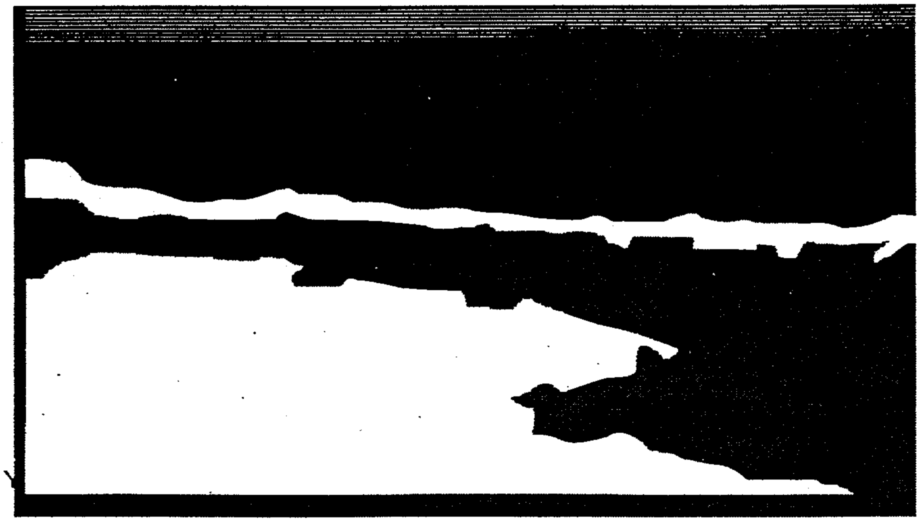

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Gordon Jarvinen, Richard Barrans, Norman Schroeder, Karen Wade,
Marianne Jones, Barbara F. Smith,

Los Alamos National Laboratory
Los Alamos, NM

Jerry Mills, Greg Howard
Texas Tech University
Lubbock, TX

Henry Freiser, S. Muralidharan
University of Arizona
Tucson, AZ

ABSTRACT

A variety of chemical systems have been developed to separate trivalent actinides from lanthanides based on the slightly stronger complexation of the trivalent actinides with ligands that contain soft donor atoms. The greater stability of the actinide complexes in these systems has often been attributed to a slightly greater covalent bonding component for the actinide ions relative to the lanthanide ions. We have investigated several synergistic extraction systems that use ligands with a combination of oxygen and sulfur donor atoms that achieve a good group separation of the trivalent actinides and lanthanides. For example, the combination of dicyclohexyldithiophosphinic acid and tributylphosphate has shown separation factors of up to 800 for americium over europium in a single extraction stage. Such systems could find application in advanced partitioning schemes for nuclear waste.

INTRODUCTION

The separation of the trivalent actinides from the lanthanides has provided a notable challenge to chemists during the past half century because of the many similarities in the chemistry of these metal ions. A variety of chemical systems have been developed to accomplish this separation based on the slightly stronger complexation of the trivalent actinides with ligands that contain "soft" donor atoms, such as sulfur and nitrogen. The greater stability of the actinide complexes in these systems has often been attributed, beginning with a paper by Diamond, Street, and Seaborg (1954), to a slightly greater covalent bonding component for the actinide ions relative to the lanthanide ions. There is a considerable amount of experimental data that is consistent with this hypothesis, but thus far, attempts to measure a difference in the enthalpy of binding of trivalent actinide and lanthanide ions to ligands containing soft donor atoms have not clearly shown a stronger actinide bond. These concepts are discussed in more detail in a recent review on developments in trivalent f-element separations by Nash (1993).

Musikas and coworkers (Fitoussi 1984) have evaluated some extraction systems containing sulfur donor ligands to determine their ability to discriminate between the trivalent actinides and lanthanides. The synergistic system di-2-ethylhexyldithiophosphoric acid /tributylphosphate (HDEHDTP/TBP) gave excellent separation factors of up to 100 at certain concentrations of aqueous acid, HDEHDTP, and tributylphosphate (TBP). Such selectivity is not observed for the oxygen-donor analogue di-2-ethylhexylphosphoric acid. The TBP synergist increased the extraction coefficient to useful values as HDEHDTP alone is a poor extractant relative to its oxygen analog. The synergistic system also showed increased selectivity for americium over europium relative to HDEHDTP or TBP alone. One disadvantage of these systems is the relatively low stability of the dithiophosphoric acid derivatives to hydrolysis. The hydrolysis products are stronger extractants of both americium and europium, but they show low selectivity.

Extraction studies reported in the literature indicated that dithiophosphinic acid derivatives have improved stability relative to the dithiophosphoric acid systems. Tjioe et al. (1989) reported on the extraction of Cd(II) from "black" phosphoric acid at 90° C with diphenyl- and dicyclohexyldithiophosphinic acids. These compounds showed considerable stability under these rather severe conditions, with the dicyclohexyl derivative exhibiting the greatest resistance to oxidation and hydrolysis. Rickelton (1992) also described the separation of Cd(II) from phosphoric acid solutions using Cyanex™ 301, a dithiophosphinic acid derivative. In this paper, we report on the initial results of testing three different dithiophosphinic acid/synergist systems for their ability to separate trivalent actinides from trivalent lanthanides.

EXPERIMENTAL

Instrumentation

Radioactivity measurements were carried out with NaI well-type counters (Packard Models 500C, 5000, or MINAXI γ Auto-Gamma® 5000). Other instrumentation included NMR (Varian Model Gemini 200), FT-IR (Mattson Model Galaxy 5020), UV-VIS diode array (Hewlett-Packard Model 8451A), GC-FID (Hewlett-Packard Model 5710A, DB-1 column, 12m, 0.2-µm bore, 0.33-µm coating) and pH meter (Fisher Model 610A). Elemental analyses were performed by Galbraith Laboratories.

Materials

Dicyclohexyldithiophosphinic acid (HDCHDTP) was prepared at Texas Tech University using the method of Rauhut et al.(1961). Bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex™ 301) was prepared by American Cyanamid and was purified at the University of Arizona. Diphenyldithiophosphinic acid (HDPhDTP) was purchased from Alfa/Aesar and was recrystallized from hexane. Other chemicals such as tributylphosphate (TBP), $NaNO_3$, HNO_3, toluene, and sulfanilic acid (4-aminobenzenesulfonic acid, $pK_a = 3.23$) were Baker Analyzed reagents and were used as received. The TBP was checked by thin layer chromatography (TLC) for acidic impurities. All water used in this work was deionized to a resistance of 18 MΩ by a Millipore MILLI-Q™ system.

Ligand Synthesis/Purification

Dicyclohexyldithiophosphinic Acid (HDCHDTP). HDCHDTP was synthesized according to the procedure of Rauhut and coworkers (1961).

Bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex™ 301). Commercial, crude Cyanex™ 301 (40 g, 0.12 mol), which had a green color, was dissolved in 200 mL of analytical-grade hexane. It was washed once with 200 mL of 6 M H_2SO_4. The green color in the hexane phase became light. The hexane solution was then equilibrated with 170 g (0.6 mol) of $ZnSO_4$ in 400 mL of 0.05 M H_2SO_4 for 15 min. This procedure was repeated with fresh $ZnSO_4$ solution. A yellow zinc complex was obtained in the hexane phase. This phase was then dried over 25 g of anhydrous Na_2SO_4 for 4 h. The resulting hexane solution was pale yellow in contrast to the darker fresh extract. The hexane was removed by rotary evaporation to obtain a pale yellow, viscous product. This product was washed three times with 150 mL of methanol; the methanol was decanted after phase separation. This step yielded a milky white product. The traces of methanol were removed by rotary evaporation in a 38°C water bath to yield a zinc-Cyanex™ 301 chelate as an almost clear viscous product. (CAUTION: higher temperatures lead to the decomposition of the zinc chelate as evidenced by the darkening of the color to deep yellow.) The material was stored as the zinc complex because it is more stable in this form. Stripping of zinc was effected by redissolving the zinc-Cyanex™ 301 chelate in 100 mL of hexane and equilibrating with 100 mL of 4 M HCl a total of three times. The resulting hexane solution was dried over anhydrous Na_2SO_4 after which it was rotary evaporated at room temperature to remove the hexane. The viscous liquid obtained after this procedure was placed in a refridgerator where it crystallized after a couple of days. This solid was removed from the remaining liquid by filtration and was air dried for 2 to 3 hrs. It had a melting point of 34°C.

Diphenyldithiophosphinic Acid (HDPhDTP). The material, as received from Alfa/Aesar, required purification before use. The procedure that follows was adapted from Higgins et al. (1955) The greenish solid (20.7 g) was dissolved in 225 mL of distilled water and 12.5 mL of 50% NaOH. The solution was separated from considerable undissolved solid by filtration through Whatman #2 filter paper. The solution was washed with 2 x 50 mL of toluene in a separatory funnel. To the slightly yellowish solution, 100 mL of 2.4 M HCl was added dropwise over 75 min. with cooling in an ice water bath and rapid stirring. A milky mixture and a white solid consisting of small crystals resulted. The crystals were collected on a glass frit, washed three times with 50 mL of cold water, and dried under vacuum. The yield was 11.2 g, and the melting point was 56.8 to 57.8°C.

Ligand Evaluation for Actinide/Lanthanide Separations

Distribution Determinations. Europium-152 (SRM #4370) was obtained from the National Institute of Standards and Technology (NIST). Americium-241 was obtained from Los Alamos in house supplies. We prepared separate aqueous radioisotope stock solutions of ^{241}Am(III) and ^{152}Eu(III) by fuming the individual isotopes to dryness several times in HNO_3 and redissolving the tracers in dilute HNO_3 (pH ~ 3.5). Aqueous solutions for extraction contacts were buffered with 0.01 M sulfanilic acid, adjusted to a pH between 3.00 and 3.60 with 50% NaOH, and set at an ionic strength of 0.10 with $NaNO_3$. These solutions were spiked with the isotope concentrates such that the tracer concentrations, determined directly from the gamma activity of the solution, were approximately 10^{-8} M. Carrier europium in the ^{152}Eu tracer was present at ~ 10^{-5} M in the aqueous phases.

Variable concentrations of dithiophosphinic acids and synergist ligand TBP were dissolved in toluene to give the concentration ranges needed for the extraction experiments. Extractions were performed by contacting equal volumes of aqueous and organic phase (1 to 2 mL) for 30 min. at room temperature (22 to 24°C) using a mechanical shaker, followed by centrifugation for phase separation. (All equilibrations discussed in this paper were performed in this manner unless otherwise noted). Known aliquots (0.25 to 1.00 mL) of each phase were counted on a gamma counter for 10 minutes. Accountability for all extractions was 100 ± 10%. The distribution ratio (D) was calculated as the net cpm/mL in the organic phase divided by the net cpm/mL in the aqueous phase. The estimated errors in the D values are 8% to 10 % for americium and 9% to 30% for europium. The pH of the aqueous phase was determined after extraction. The reversibility of the HDCHDTP extraction was measured by taking the organic phase after extraction and contacting it with an equal volume of fresh untraced aqueous solution. Back-extraction of americium and europium from HDCHDTP was done by contacting the organic phase after extraction with an equal volume of 0.01 M HNO_3 /1.00 M $NaNO_3$ solution.

Slope analysis was used to obtain information about the composition of the extracted species. The simplifying assumptions used in interpreting plots of log D versus pH at constant [ligand] and [synergist] and log D versus log [ligand] or log [synergist] at constant pH and [synergist] or [ligand] are discussed in detail by Cox and Flett (1983).

Ligand Distribution and Stability Studies

^{1}H NMR Studies of Ligand Distribution and Stability. For the ^{1}H NMR studies d_8-toluene was used to prepare the organic phase and D_2O containing 1% DSS (3-trimethylsilyl-1-propanesulfonic acid, sodium salt) as an internal standard was used for the aqueous phase. Solutions were prepared containing 0.50 M ligand. Equilibration with the aqueous phase was performed as described above. The ^{1}H NMR of each phase was taken periodically.

Also, studies were done with variable aqueous phase pH values. Three solutions of 0.50 M HDPhDTP in d_8-toluene were prepared and were equilibrated with equal volumes of the aqueous phase as before. A 2.27 M solution of NaOH in D_2O was slowly added to these solutions. After 15 minutes of shaking, the pH was determined, and the process was repeated until the desired pH was obtained. ^{1}H NMR spectra were taken of each phase.

Ligand Distribution and Stability Studies Using Gamma Counting. For several weeks, a 10-mL solution of 0.40 M HDCHDTP and 0.20 M TBP in toluene was shaken in a Teflon centrifuge tube in air while in contact with aqueous acid containing 1 mM HNO_3, 0.10 M $NaNO_3$, and 0.01 M sulfanilic acid buffer. Organic phase samples (1.00 mL) were removed periodically and gamma-counted to determine the activity of americium and europium. The organic material was returned to the reaction mixture. Also, the pH of the aqueous phase was measured periodically.

RESULTS AND DISCUSSION

Dicyclohexyldithiophosphinic Acid (HDCHDTP) Studies

Job's Plot. A variety of pH values and concentrations of HDCHDTP and TBP were initially tested to find a parametric space where large separation factors (SF) between americium and europium might occur. It was found that a significant SF could be obtained near pH 3.50 with 0.50 M HDCHDTP and 0.10 M TBP. A Job's plot study for the two metal (III) ions (Figure 1) was used to optimize the SF at this pH and total concentration of TBP and HDCHDTP (0.60 M). The SF was generally high (>100) across the plot, dropping to low values (<10) only when the individual ligands (TBP or HDCHDTP) were present. The highest SF (>300) occurred in the mole fraction range of 0.17 to 0.33 TBP. The plot for americium is broad but peaks at approximately 0.33 mole fraction of TBP, indicating that the extracted complex contains a 1: 2 ratio of TBP : HDCHDTP ligands. However, the broadness of the peak may also indicate that two or more complexes with varying stoichiometries are involved in the extraction. The europium D values are low across the plot and therefore give a less reliable indication of the composition of the extractant complexes. Even though the solutions were at an initial pH of 3.60, the final aqueous solution pH values varied from 2.80 to 3.60. The lower pH values occurred for the higher HDCHDTP concentrations indicating that the compound was partially distributing into the aqueous phase. The Job's plot data was corrected for the pH variation to a common pH of 3.00. The details of how this correction was applied are given below.

pH Dependency. The effect of the aqueous phase pH on the extraction of ^{241}Am and ^{152}Eu was studied at 0.28 M TBP and 0.25 M HDCHDTP. The initial aqueous phase pH values and the corresponding equilibrium pH values after the extraction contact are given in Table I. A qualitative estimate of the solubility of the HDCHDTP can be obtained from the pH changes. For instance, at pH 4.00 the sulfanilic acid buffer (0.01 M) is 83% in the base form. A pH change to 3.18 reduces the amount of base form to 43%, requiring ~0.004 M protons. If the source of protons is the solubilized HDCHDTP, then the approximate distribution coefficient for HDCHDTP at this pH is 62 (or 1.5% distributes to the aqueous phase). The HDCHDTP is less soluble in the aqueous phase at lower pH. A pH dependent solubility in the aqueous phase was also observed for HDPhDTP as discussed below. The plot of the log D versus the equilibrium pH is shown in Figure 2. Slopes were determined from a least squares fit of the data (R = 0.99 for americium and 0.80 for europium). The poorer fit of the europium data is due to the inherently greater inaccuracy in measuring the low count rates of ^{152}Eu in the organic phase. Slope analysis gives a pH dependency of 2.9 for americium indicating that 3 protons are released during the extraction process and, therefore, three HDCHDTP ligands may be involved in the americium extracted complex. The europium pH dependency of ~1 is not as reliable due to the very low D values. The pH dependency plot shows that the Am/Eu separation factor increases with pH. The factor ranges from 40 at pH 2.53 to 630 at pH 3.20.

Table I. Aqueous Phase pH Before and After Extraction

Initial pH	Equilibrium pH
2.50	2.53
2.98	2.80
3.57	3.00
4.00	3.18
4.53	3.20

Dependency of the ^{241}Am and ^{152}Eu Extractions on the HDCHDTP Concentration. Figure 3 shows a plot of log D versus log [HDCHDTP] at 0.50 M TBP and an initial pH of 3.66. The first four lines in Table II list the results for this experiment. The log of the distribution coefficients of both metals increase linearly with increasing log [HDCHDTP]. It should be noted that the HDCHDTP dependency for americium (1.5) is not consistent with the pH dependency (2.9) because of the increasing solubility of HDCHDTP in the aqueous phase as its concentration in the organic phase increases. The HDCHDTP solubility is manifested in different equilibrium pH values which have substantial effects on the data. Thus the data in Figure 3 needs to be corrected for pH variation. Equations 1 and 2 were applied to the americium and europium data, respectively, and the data was corrected to a common pH of 3.00. The pH dependencies were obtained from the pH study described above (Figure 2) with one additional significant figure used in the calculations.

(1) $\log D(\mathrm{Am})\mathrm{corr.} = \log D(\mathrm{Am}) + 2.85(\Delta \mathrm{pH})$

(2) $\log D(\mathrm{Eu})\mathrm{corr.} = \log D(\mathrm{Eu}) + 0.94(\Delta \mathrm{pH})$

The corrected data are plotted in Figure 4. The slope of the HDCHDTP dependency for americium (2.6) is now more consistent with the pH dependency, but the dependencies are less consistent for europium (1.4 compared to 1.0). Although the least squares fit of the data are excellent for both elements ($R = 0.99$ for Am and 0.99 for Eu) the correction is probably less meaningful for the europium data because the 0.94 pH coefficient has a larger uncertainty associated with it. The ligand dependency plot shows that the Am/Eu separation factor increases with the HDCHDTP concentration. The factor ranges from 16 to 228 across the ligand range studied.

Table II. Summary of the Corrected ^{241}Am and ^{152}Eu Extraction Data Using HDCHDTP and TBP

Equilibrium pH	**[HDCHDTP]**	**[TBP]**	**D (Am)**	**D (Eu)**	**SF (Am/Eu)**
3.35	0.05	0.50	0.0424	0.0026	16
3.23	0.10	0.50	0.2858	0.0087	33
2.98	0.37	0.50	8.264	0.0483	171
2.93	0.50	0.50	16.98	0.0747	228
3.0	0.50	0.11	4.980	0.0061	819
3.0	0.50	0.20	9.010	0.0128	704
3.0	0.50	0.30	13.00	0.0200	650
3.0	0.50	0.40	14.20	0.0367	387
3.0	0.50	0.50	16.72	0.0694	241

Reversibility of the Extraction. Americium's extraction reversibility was studied between 0.05 and 0.37 M HDCHDTP at 0.50 M TBP by contacting the organic phase from the forward extraction with an equal volume of fresh aqueous solution containing no tracers. The corresponding equilibrium pH values measured for the forward and reverse reactions were within 0.05 pH units of each other. The D values for the forward and reverse extractions, after the pH correction was applied, agreed within 10%. The data for europium was unreliable because of the difficulty in measuring the low counts for the reverse extraction.

Back-Extractions. Americium and europium, after being extracted by 0.05 to 0.37 M HDCHDTP /0.50 M TBP solutions, were efficiently back-extracted by a 0.01 M HNO_3/1.0 M $NaNO_3$ solution. Greater than 99% of the americium and europium were removed from the organic phases.

Dependency of the ^{241}Am and ^{152}Eu Extractions on the Synergist Ligand (TBP) Concentration. The effect of the synergist ligand, TBP, on the extraction of ^{241}Am and ^{152}Eu was studied at 0.50 M HDCHDTP. A plot of the log D versus log [TBP] is shown in Figure 5. The results are also tabulated in the last five lines of Table II. The distribution coefficients are uncorrected because the equilibrium pH, although not measured, was expected to be ~ 3.0. The consistency in the americium D value at 0.50 M HDCHDTP and 0.50 M TBP in this experiment and at the corresponding concentrations in the log D versus HDCHDTP experiment (line 4 in Table II) supports this assumption. The slopes in Figure 5 give a TBP dependency of 0.8 (R = 0.99) for the americium extraction and 1.5 (R = 0.98) for the europium extraction. The nonintegral slopes indicate that more than one extraction complex is formed. What is striking about this graph is the large separation factors across the TBP range studied, especially at low TBP concentrations. Table II lists the separation factors (SF) obtained. An SF of up to 819 is possible when 0.50 M HDCHDTP and 0.11 M TBP is used at a pH of 3.0.

Ligand Distribution and Stability Studies. HDCHDTP distributes, to some degree, into the aqueous phase as observed by the decrease in pH with increasing HDCHDTP concentration in the organic phase. An attempt was made to use ^{1}H NMR to determine the distribution coefficient of the ligand between the organic and aqueous phase. Also, ^{1}H NMR was used to observe any decomposition of the ligand over time under the conditions in which it was used. The limit of detection for ^{1}H NMR under the conditions employed (~ 400 ppm) was too high to observe the presence of HDCHDTP in the aqueous phase even at the higher organic concentrations. No decomposition products were observed over a one-month period.

Another long term stability study of the extractant solution at room temperature in contact with the aqueous solution (pH = 3.00) containing tracers was performed to determine if the ligand was degrading under these conditions. If hydrolysis of HDCHDTP was occurring, one would expect decreased separation factors and increased total extraction of both americium and europium. After 3 weeks, no decrease in the separation factor or increase in the total extraction was observed under the conditions of the experiment.

Cyanex™ 301 Studies

Purification of Cyanex™ 301. Cyanex™ 301, bis(2,4,4-trimethypentyl)dithiophosphinic acid is commercially available from American Cyanamid Corporation, but contains about 10% of an alkylphosphine oxide impurity. Because the impurity could act as a synergist and cause erroneous extraction results, the crude Cyanex™ 301 was purified. A zinc complex has been reported to be readily formed from the dithiophosphinic acid, as demonstrated by Rickelton (1990), but not by the alkylphosphine oxide impurity. Thus, the zinc complex of the dithiophosphinic acid can be readily separated from the impurity. The free ligand can then be obtained through release of the zinc ion by treatment with sulfuric acid. The purified Cyanex™ 301 showed evidence of some decomposition that was indicated by development of a dark yellow color upon contact with 6 M HCl or when warmed to temperatures above 38°C. The colored species have not yet been identified. Under the conditions of the extraction experiments, decomposition of the Cyanex™ 301 does not appear to be a problem.

Extraction Studies with Unpurified Cyanex™ 301. Preliminary americium and europium extraction studies were performed at pH 1 and 2 at an ionic strength of 1.0 ($NaNO_3$) with unpurified Cyanex™ 301 alone (0.75 M) and with addition of TBP or trioctylphosphine oxide (TOPO) at 0.20 M. The D values ranged from 0.25 to 158. Separation of americium from europium was minimal in all cases and, for five of the six extractions studied, the europium extraction was slightly favored over americium. The TBP and TOPO enhanced the europium extraction at both pHs, but decreased the americium extraction, especially at a pH of 2.

Extraction Studies with Purified Cyanex™ 301. A Job's plot experiment, with purified Cyanex™ 301 and the synergist ligand TBP, was performed at pH 3.00 to determine the optimal ligand ratios. These conditions were chosen because they gave good separation factors for americium over europium in the HDCHDTP study. The Job's plot is shown in Figure 6. Separation factors were >10 for TBP mole fractions ranging between 0.17 and 0.70, with the highest factors (25) occurring between 0.30 and 0.50 mole fraction. Essentially no separation occurred when only the individual ligands (TBP or Cyanex™ 301) were present. The difference between the initial and equilibrium pH values was ≤ 0.08 pH units, thus, there did not appear to be a problem with the ligand distributing into the aqueous phase at this concentration range and initial pH.

pH Dependency. The effect of the aqueous phase pH on the extraction of ^{241}Am and ^{152}Eu was studied at 0.50 M TBP and 0.50 M Cyanex™ 301. The initial aqueous phase pH values and the corresponding equilibrium pH values were the same. The plot of the log D versus the equilibrium pH is shown in Figure 7. Slopes were determined from a least squares fit of the data (R = 0.99 for both americium and europium). Slope analysis gives a pH dependency of 2.8 for americium indicating that 3 protons are released during the extraction process and, therefore, three Cyanex™ 301 ligands may be involved in the major extracted americium complex. For europium, the dependency is 1.4. It should be noted that the americium pH dependency is very similar for HDCHDTP and Cyanex™ 301. The pH dependency plot shows that the Am/Eu separation factor increases with pH. The factor ranges from 20 at pH 2.72 to 250 at pH 3.50.

Dependency of the ^{241}Am and ^{152}Eu Extractions on the Cyanex™ 301 Concentration. Figure 8 shows a plot of log D versus log [Cyanex™ 301] with 0.10 M TBP at pH 3.10. The log of the distribution coefficients of both metals increase linearly with increasing Cyanex™ 301 concentration. The nonintegral slopes indicate that complexes with different stoichiometries are extracted. For europium, the slope is 2.4 (R = 0.99). The Am slope is 1.7 (R = 0.98), which is inconsistent with the pH dependency (2.8). This discrepancy may be caused by the narrow concentration range (0.4 - 0.6 M) studied for the Cyanex™ 301 dependency. The ligand dependency plot shows that the Am/Eu separation factor decreases slightly with the

Cyanex™ 301 concentration; at 0.40 M the factor is 46, and the factor is 34 at a Cyanex™ 301 concentration of 0.60 M. The data is tabulated in the first five lines of Table III.

Table III. Summary of Separation Studies of ^{241}Am and ^{152}Eu Using Cyanex™ 301 and TBP

Equilibrium pH	**[Cyanex™ 301]**	**[TBP]**	**D_{Am}**	**D_{Eu}**	**$SF_{Am/Eu}$**
3.08	0.40	0.10	6.1	0.134	46
3.09	0.45	0.10	8.2	0.177	46
3.09	0.50	0.10	9.1	0.232	39
3.07	0.55	0.10	10.3	0.268	38
3.10	0.60	0.10	12.8	0.380	34
3.09	0.50	0.05	4.8	0.208	23
3.09	0.50	0.075	6.8	0.214	32
3.09	0.50	0.10	9.3	0.226	41
3.10	0.50	0.125	13.3	0.238	56
3.09	0.50	0.15	14.1	0.242	58

Dependency of the ^{241}Am and ^{152}Eu Extractions on the Synergist Ligand (TBP) Concentration. The effect of the synergist ligand, TBP, on the extraction of ^{241}Am and ^{152}Eu was studied at 0.50 M Cyanex™ 301 and a pH of 3.10. (The data is listed in the last five lines of Table III.) A plot of the log D versus log [TBP] is shown in Figure 9. The slopes show a TBP dependency of 1.0 (R = 0.99) for the americium extraction and 0.2 (R = 0.98) for the europium extraction. What is striking about this experiment is the almost constant D value for the Eu extraction. This is in contrast with the HDCHDTP which had a dependency of 1.5. The separation factors in this system are not as large as the separation factors obtained with HDCHDTP. The factors range from 23 at 0.05 M TBP to 58 at 0.15 M TBP. A difference between these two systems is that the relative slopes are diverging with increasing TBP concentration in the Cyanex™ 301 system while in the HDCHDTP system they are converging.

Diphenyldithiophosphinic Acid Studies

Studies of the Effect of Ligand Concentration on ^{241}Am(III) and ^{152}Eu(III) Extraction. The stability of HDPhDTP was somewhat lower than that of the other two dithiophosphinic acids. The odor of H_2S was detectable and a greenish color was visible within a day or two after purification. After dissolution in toluene, the solution had a greenish tint. In addition, an interfacial scum formed in some of the extraction samples, even so, the accountability of the americium and europium tracers was >98%. Figure 10 shows a plot of log D versus log [HDPhDTP] at 0.50 M TBP and an initial pH of 3.57. Nonintegral slopes were obtained but could not be corrected using the pH dependencies. Control of the pH with this ligand was quite difficult because of its high distribution into the aqueous phase (discussed further below). The data from this study, listed in the first four lines of Table IV, indicates that a separation factor of up to 52 was possible using 0.50 M HDPhDTP and 0.50 M TBP.

Table IV. Summary of Separation Studies of ^{241}Am and ^{152}Eu Using HDPhDTP and TBP

Equilibrium pH	**[HDPhDTP]**	**[TBP]**	$\mathbf{D_{Am}}$	$\mathbf{D_{Eu}}$	$\mathbf{SF_{Am/Eu}}$
1.94	0.10	0.50	10.89	0.21	52
-----	0.30	0.50	28.18	0.63	45
1.58	0.50	0.50	28.26	1.01	28
1.47	0.78	0.50	63.14	1.36	46
-----	0.50	0.10	3.32	0.01	332
-----	0.50	0.30	20.59	0.16	129
-----	0.50	0.50	28.26	1.01	28
-----	0.50	0.77	61.53	5.16	12

Studies of the Effect of Synergist Concentration on ^{241}Am(III) and ^{152}Eu(III) Extraction. Figure 11 shows a plot of log D versus log [TBP] at 0.50 M HDPhDTP and an initial pH of 3.57. Although the equilibrium pH values were not measured, the data in the third line of Table IV indicates that 0.50 M HDPhDTP systems have a final pH of ~1.6. The TBP dependencies for the extraction of americium and europium are nonintegral. This plot shows that the separation factor can be increased up to 332 by decreasing the [TBP] to 0.10 M and keeping the [HDPhDTP] at 0.50 M. Table IV lists the data from this study in the last four lines.

Studies of the Effect of Variable pH of the Aqueous Phase on ^{241}Am and ^{152}Eu Extraction. It was not possible to obtain the pH dependencies of the extractions as had been done for HDCHDTP because most of the equilibrium pH values were at the same value, 1.56. Table V lists the initial pHs of the aqueous phases and the equilibrium pHs after extraction. A plot of log D versus equilibrium pH gives a cluster of points for which a linear fit is meaningless. For this reason, no attempt was made to correct for the aqueous solubility using the pH changes.

Table V. Initial and Equilibrium pH values of the Aqueous Phase for the Extraction of ^{241}Am and ^{152}Eu from 0.50 M HDPhDTP and 0.50 M TBP

Initial pH	Equilibrium pH
2.50	1.48
2.98	1.55
3.57	1.57
4.00	1.56
4.53	1.56

Ligand Distribution Studies. A ^{1}H NMR was taken of the organic (without TBP) and aqueous phases (initial pH 3.66) after a 30-minute contact period to determine the distribution of HDPhDTP between the organic and aqueous phases (final pH ~1). The integrations of the peaks were normalized to the peaks of the internal standard, DSS, and the concentration of HDPhDTP in the aqueous phase was calculated relative to the standard. This amount was subtracted from the original concentration to determine the equilibrium concentration in the organic phase. Then D was calculated to be $[\text{HDPhDTP}]_{\text{org}}/[\text{HDPhDTP}]_{\text{aq}} = 30$. When TBP was added at ~ 1 M concentration, D decreased to 26. No decomposition products were observed in either case.

The equilibrium pH of the aqueous phase was adjusted using NaOH in D_2O to a pH of 2.40, 3.90, and 12.3, and the distribution tests were repeated. The aqueous phase solubility of the ligand increases greatly as the pH is increased; by a pH of 4, the ligand is essentially completely soluble ($D \leq 0.01$). At a pH of 12.3, a thick scum formed that was not isolated or analyzed. However, no soluble decomposition products were observed in the ^{1}H NMR spectra of the solutions.

Changes in the distribution of a 0.34 M HDPhDTP solution were observed over time through ^{1}H NMR. The aqueous solubility increases with contact time from a D of 30 after 30 minutes to D = 23 after 2 weeks to D = 22 after 1 month. An interfacial scum was noted to have grown over time, however, no impurities were observable in the ^{1}H NMR spectra of the d_8-toluene solutions.

Because of its instability and relatively high solubility in the aqueous phase, HDPhDTP will not be used in further studies unless it can be derivatized to increase its stability and decrease its aqueous solubility.

Comparison of the Ligands. From the studies described in this paper, it appears that the HDCHDTP - TBP and Cyanex™ 301 - TBP extraction systems have promise for separating trivalent actinides from lanthanides. The greater instability and substantial aqueous solubility of HDPhDTP made this ligand appear less useful for this potential application. Both Cyanex™ 301 and HDCHDTP appear to be stable under the testing conditions. While Cyanex™ 301 showed less solubility in the aqueous phase, HDCHDTP yielded the greatest separation factors for americium over europium. Table VI lists the relative Am/Eu extraction separation factors for the three compounds studied under similar concentrations of dithiophosphinic acid and TBP, however, the pH value of the HDPhDTP system was different than the other two systems. The complex $AmL_3(TBP)$ appears to be a major complex in the organic phase as indicated by the slope analysis of the extraction data for the HDCHDTP - TBP and Cyanex™ 301 - TBP extraction systems. This agrees with the data from the French work on the di-2-ethylhexylphosphoric acid - TBP extraction system (Fitoussi 1984, Pattee 1986). However, the slope values for the conditions studied in this paper are generally further from integral values suggesting that complexes with other compositions are contributing substantially to the observed distribution ratios. The composition of the europium extraction complexes is much less certain since the D values under the conditions studied were quite low.

Table VI. Separation Factors (SF) for 0.50 M Dithiophosphinic Acids and 0.125 M TBP

Compound	**Equilibrium pH**	**SF**
HDCHDTP	3.0	1000
HDPhDTP	1.6	250
Cyanex™ 301	3.1	58

CONCLUSIONS

The americium and europium distribution ratios of three dithiophosphinic acid/tributylphosphate extraction systems were measured. Very large separation factors for americium over europium were observed for these compounds, again demonstrating the usefulness of the soft donor concept for obtaining systems that selectively extract trivalent actinides. The stability studies indicated that these compounds, except perhaps for diphenyldithiophosphinic acid, have considerably greater stability than the dialkyldithiophosphoric acid compounds studied by Musikas and coworkers. Further testing will be needed to determine if these compounds have potential for analytical or process applications. Future studies will include extraction measurements with a wider range of lanthanides, actinides, and other metal ions, use of other synergists and solvents, and more extensive evaluation of the chemical and radiation stability of these compounds.

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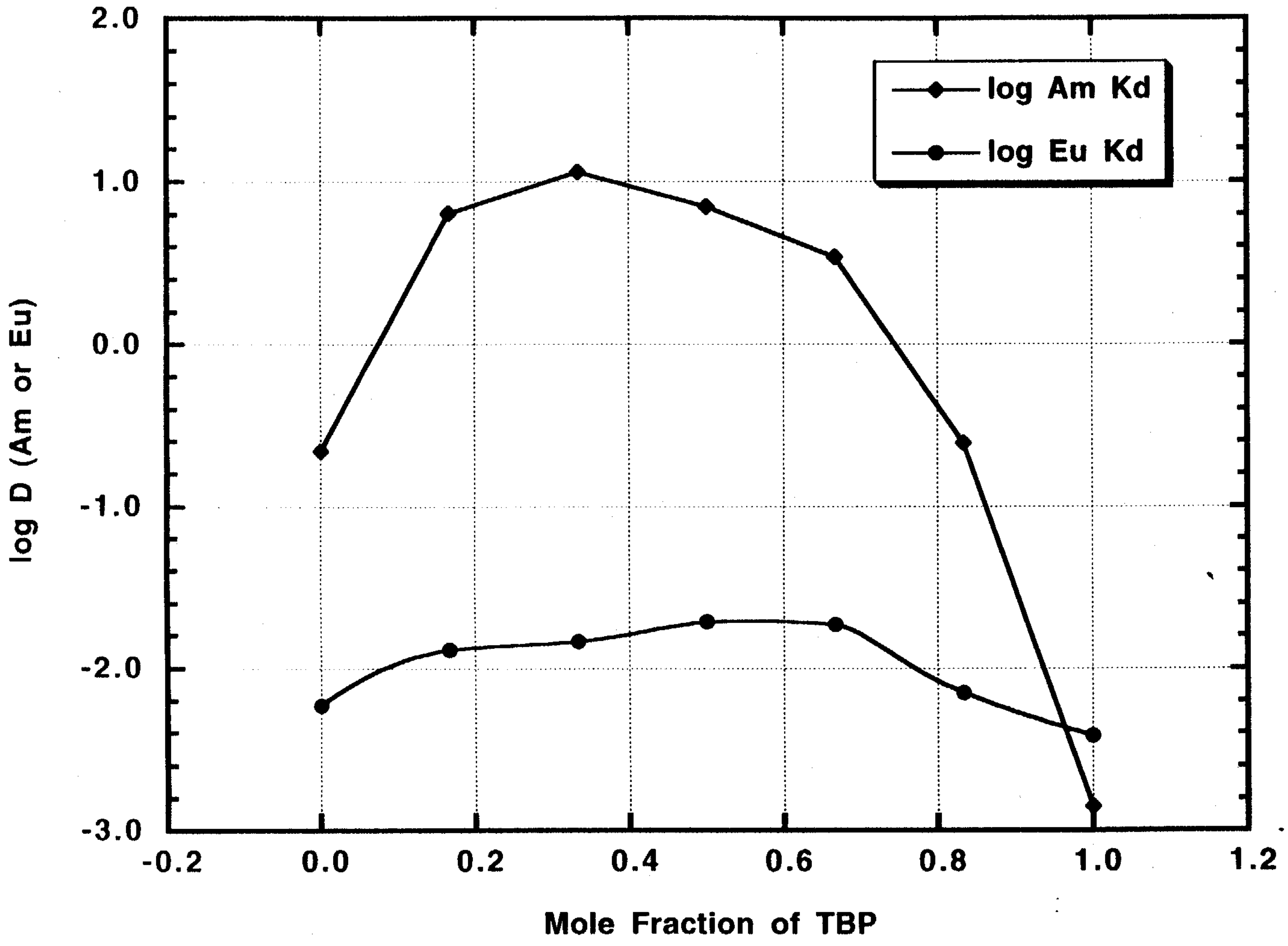

Figure 1. Job's Plot for ^{241}Am and ^{152}Eu extraction for the System [HDCHDTP] + [TBP] = 0.60 M. Data corrected to pH = 3.00

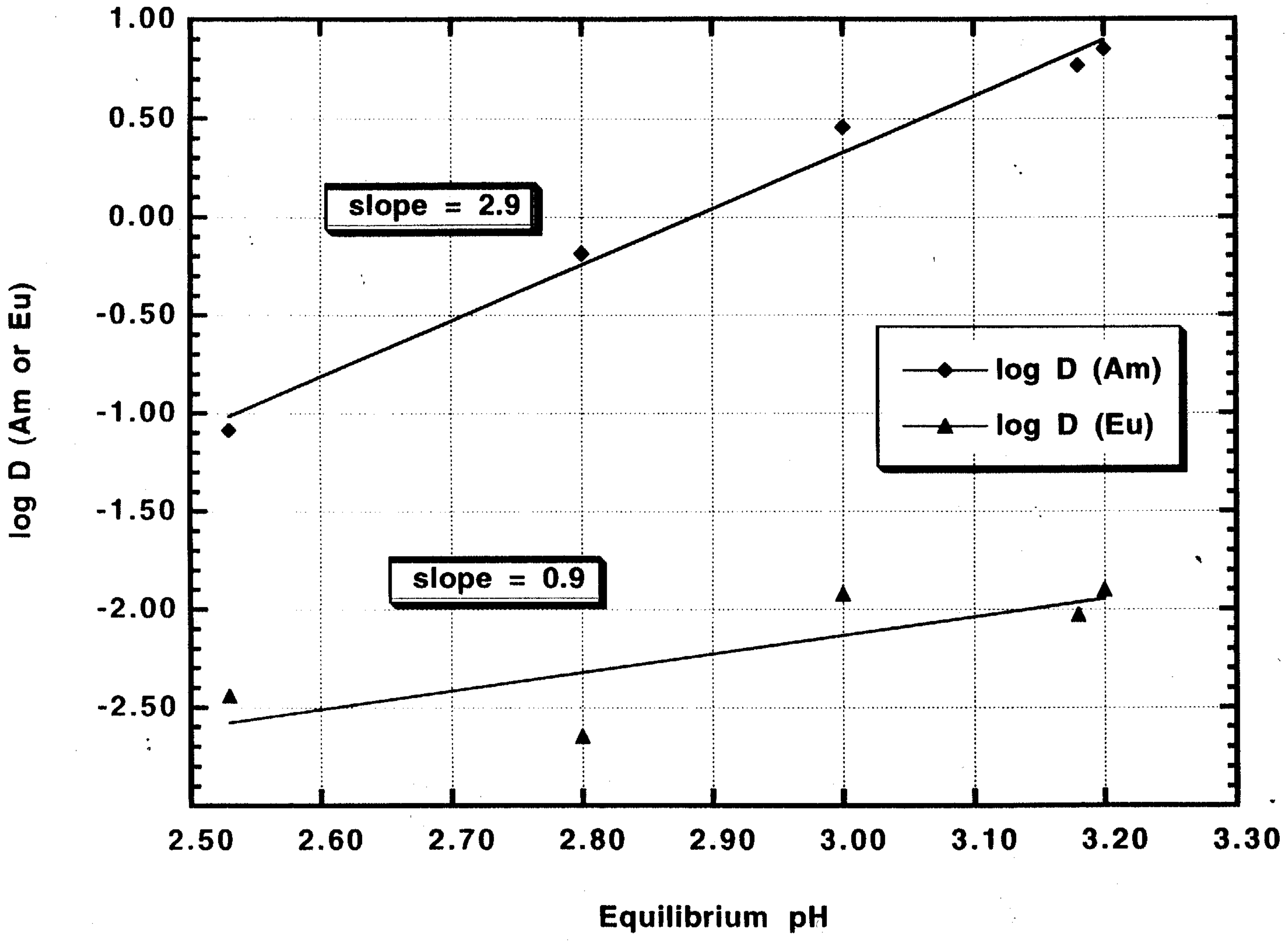

Figure 2. pH Dependency for ^{241}Am and ^{152}Eu Extractions at 0.25 M HDCHDTP and 0.28 M TBP

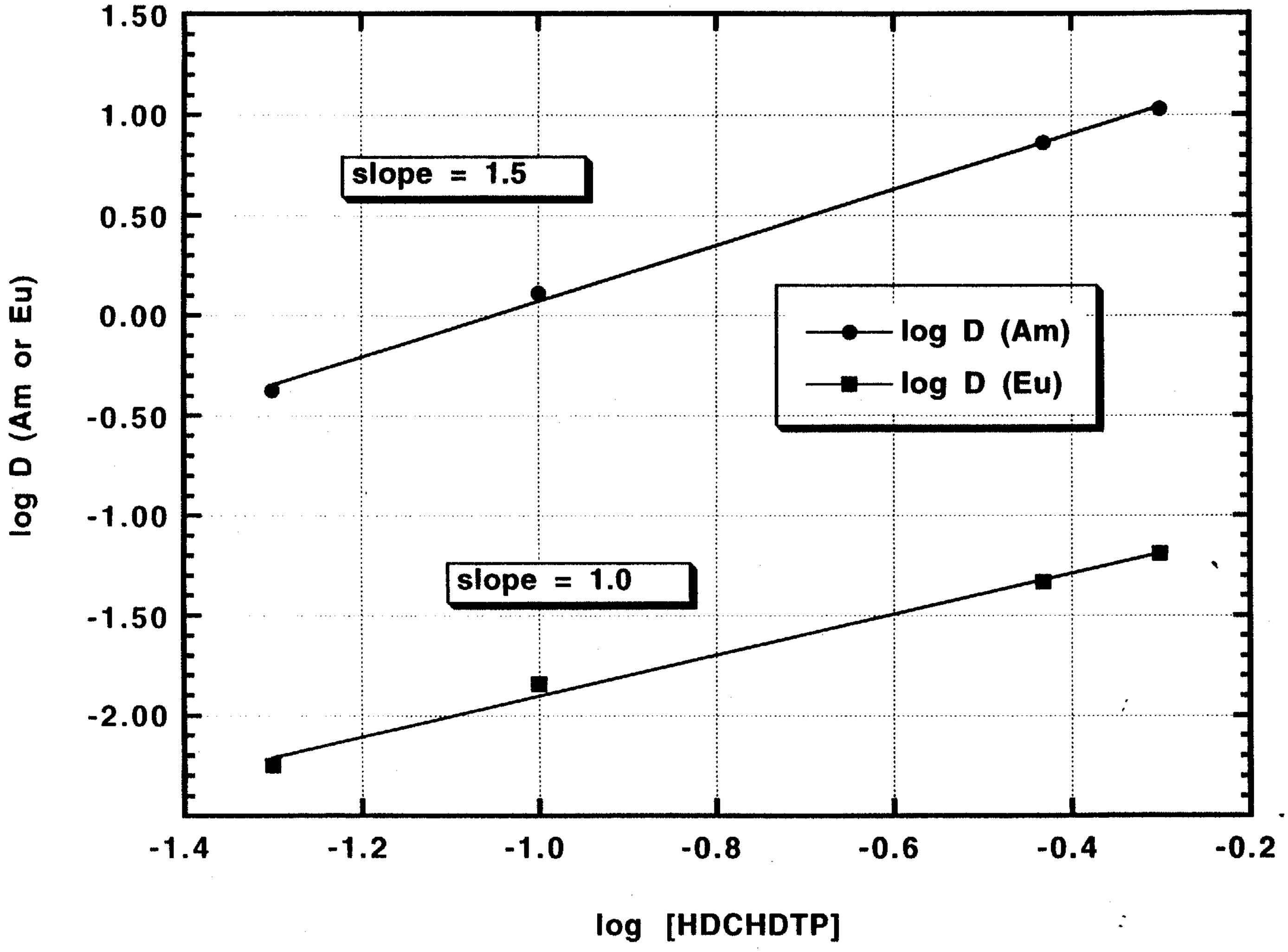

Figure 3. HDCHDTP Dependency for ^{241}Am and ^{152}Eu Extractions at 0.50 M TBP

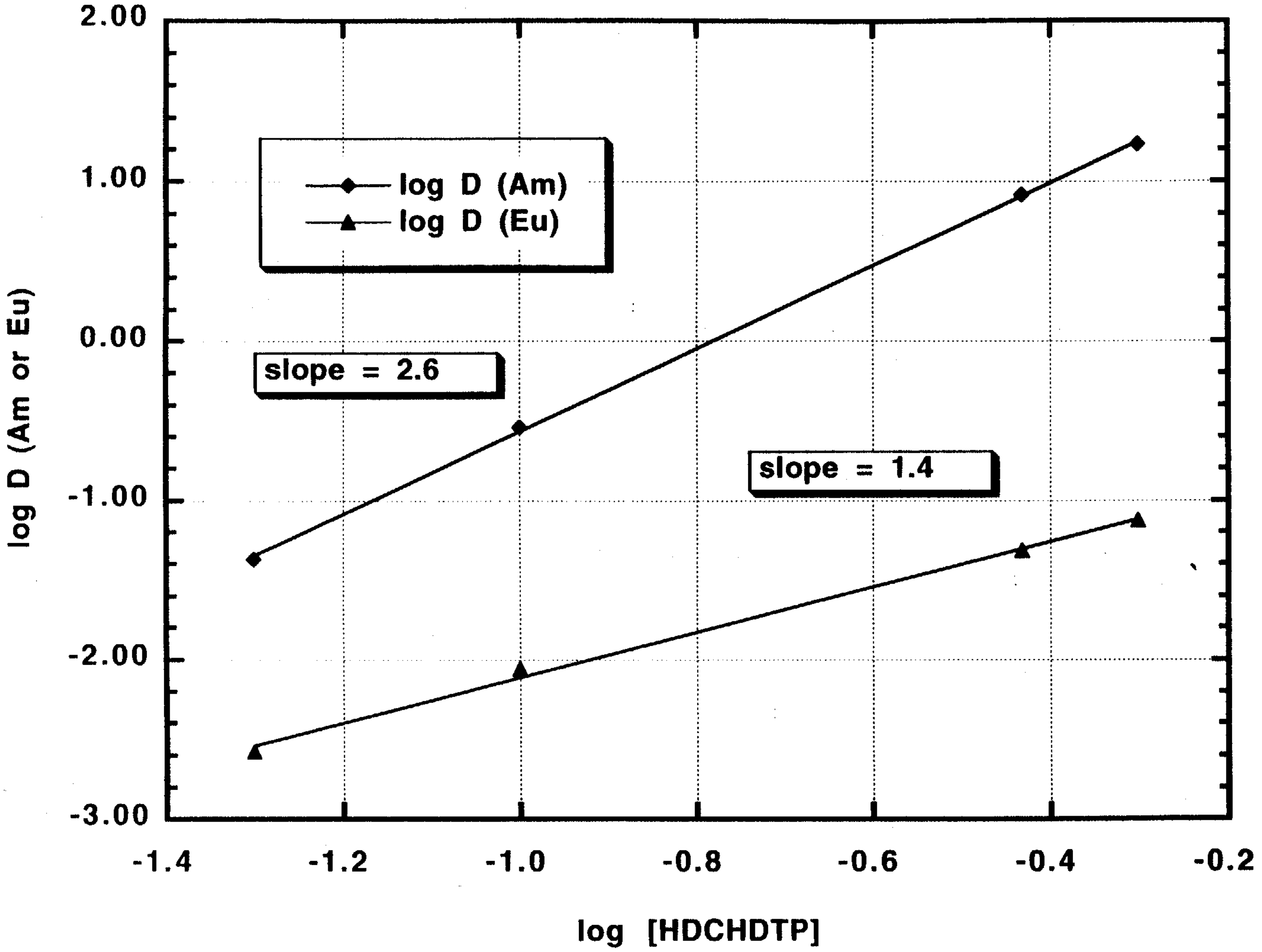

Figure 4. HDCHDTP Dependency for ^{241}Am and ^{152}Eu Extractions at 0.50 M TBP (corrected for aqueous distribution at pH = 3.00)

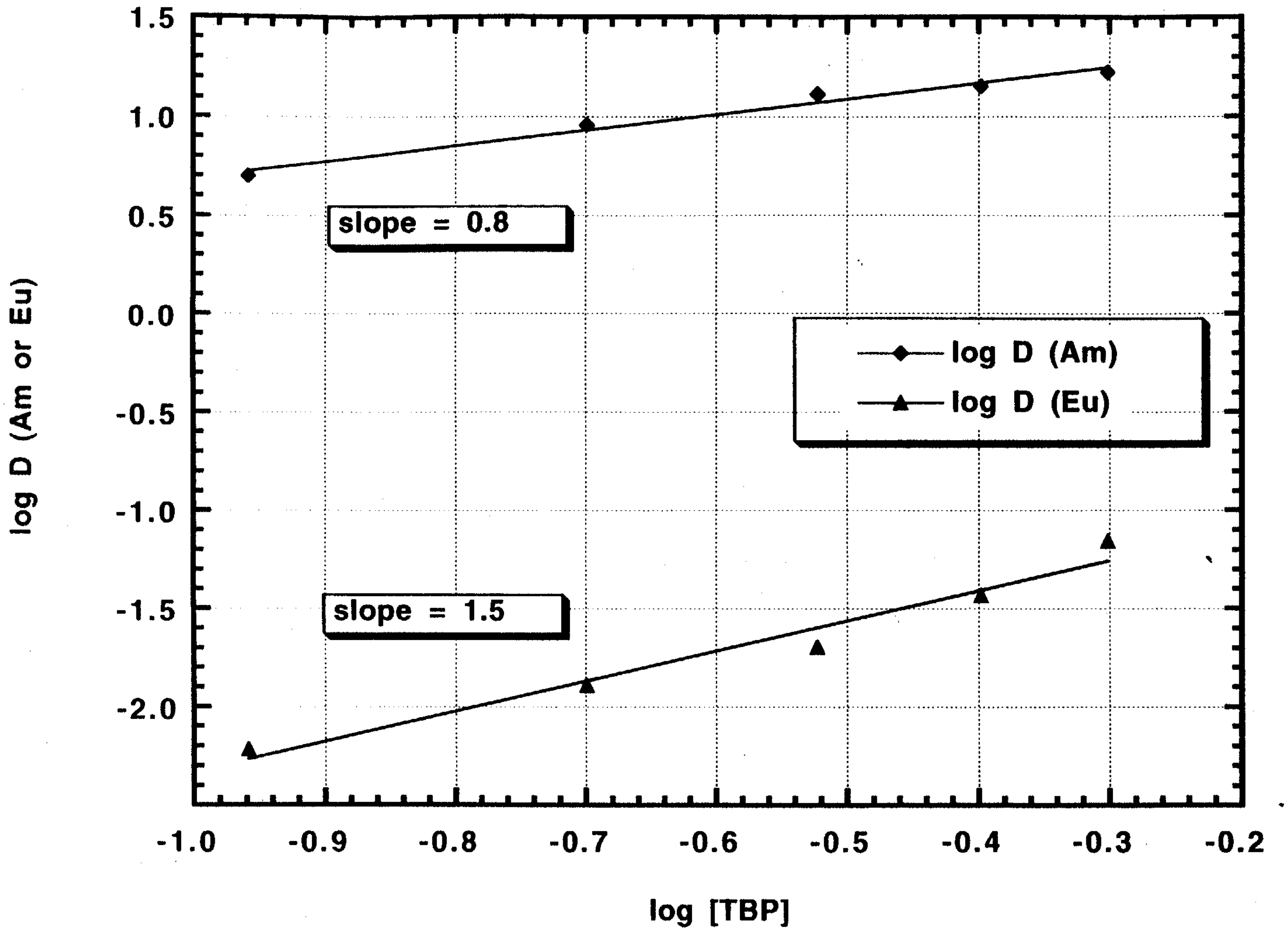

Figure 5. TBP Dependency for ^{241}Am and ^{152}Eu Extractions at 0.50 M HDCHDTP and pH = 3.00

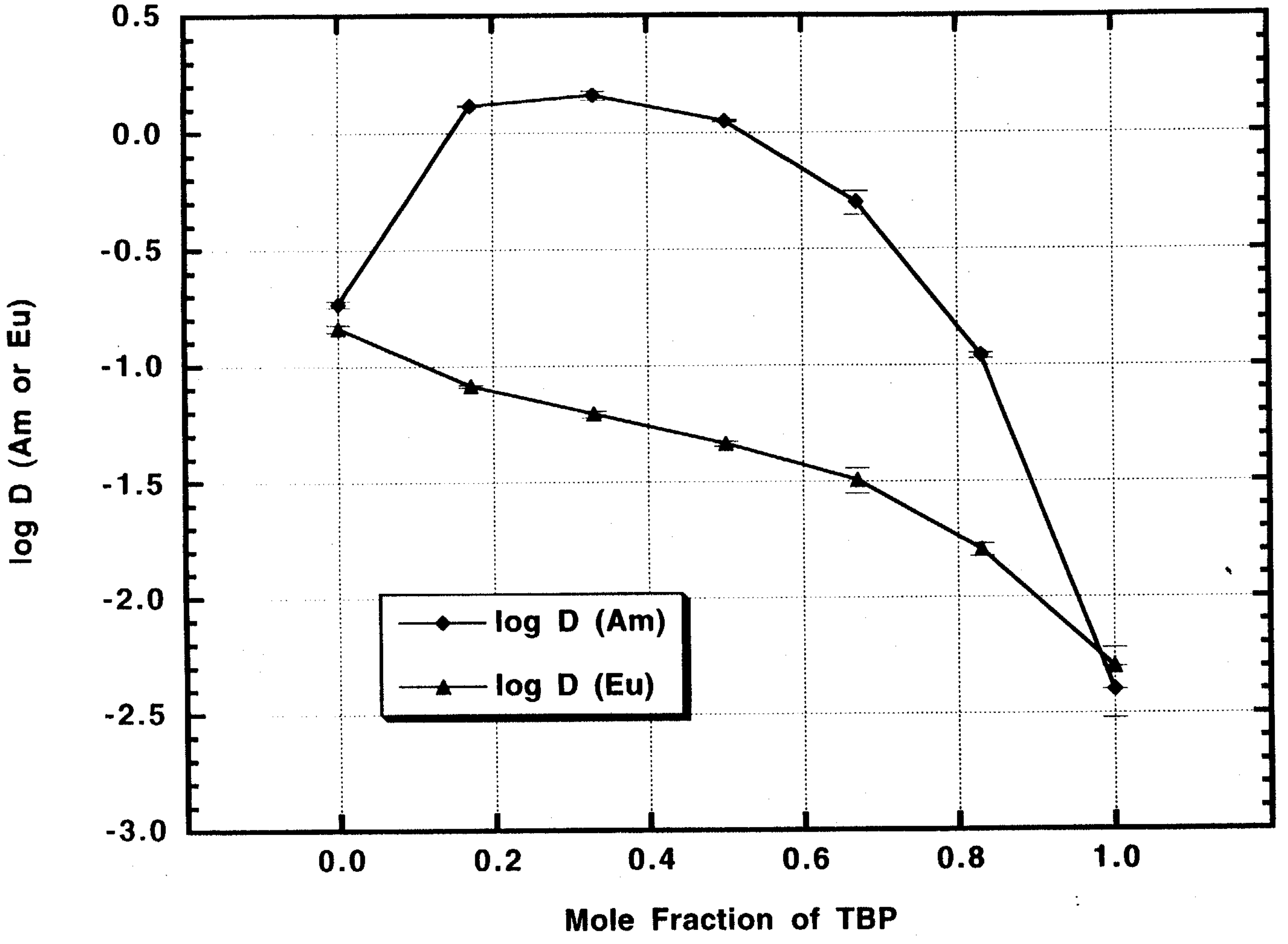

Figure 6. Job's Plot for ^{241}Am and ^{152}Eu for the System [Cyanex™ 301] + [TBP] = 0.60 M

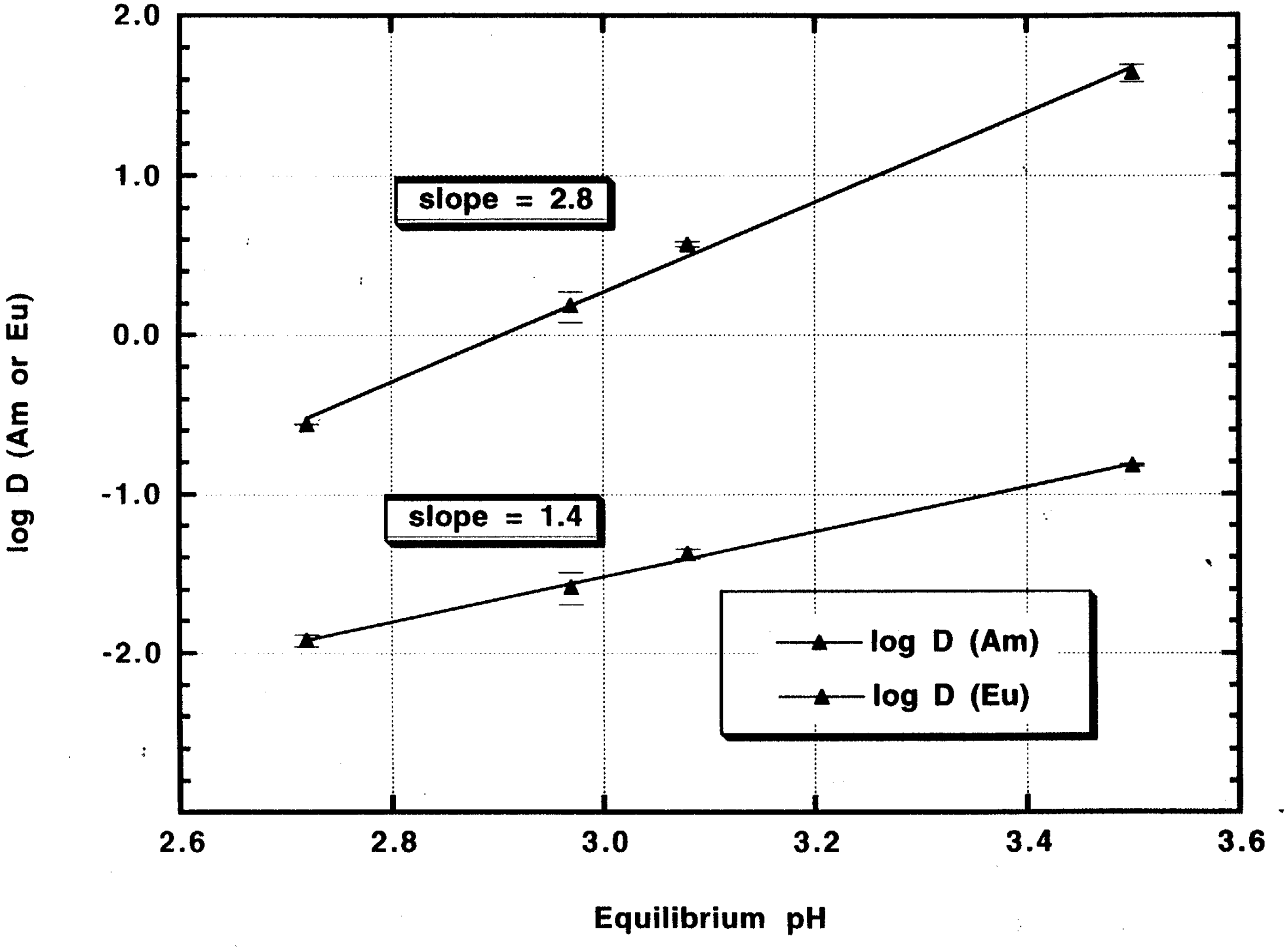

Figure 7. pH Dependency for ^{241}Am and ^{152}Eu Extractions at 0.50 M Cyanex™ 301 and 0.50 M TBP

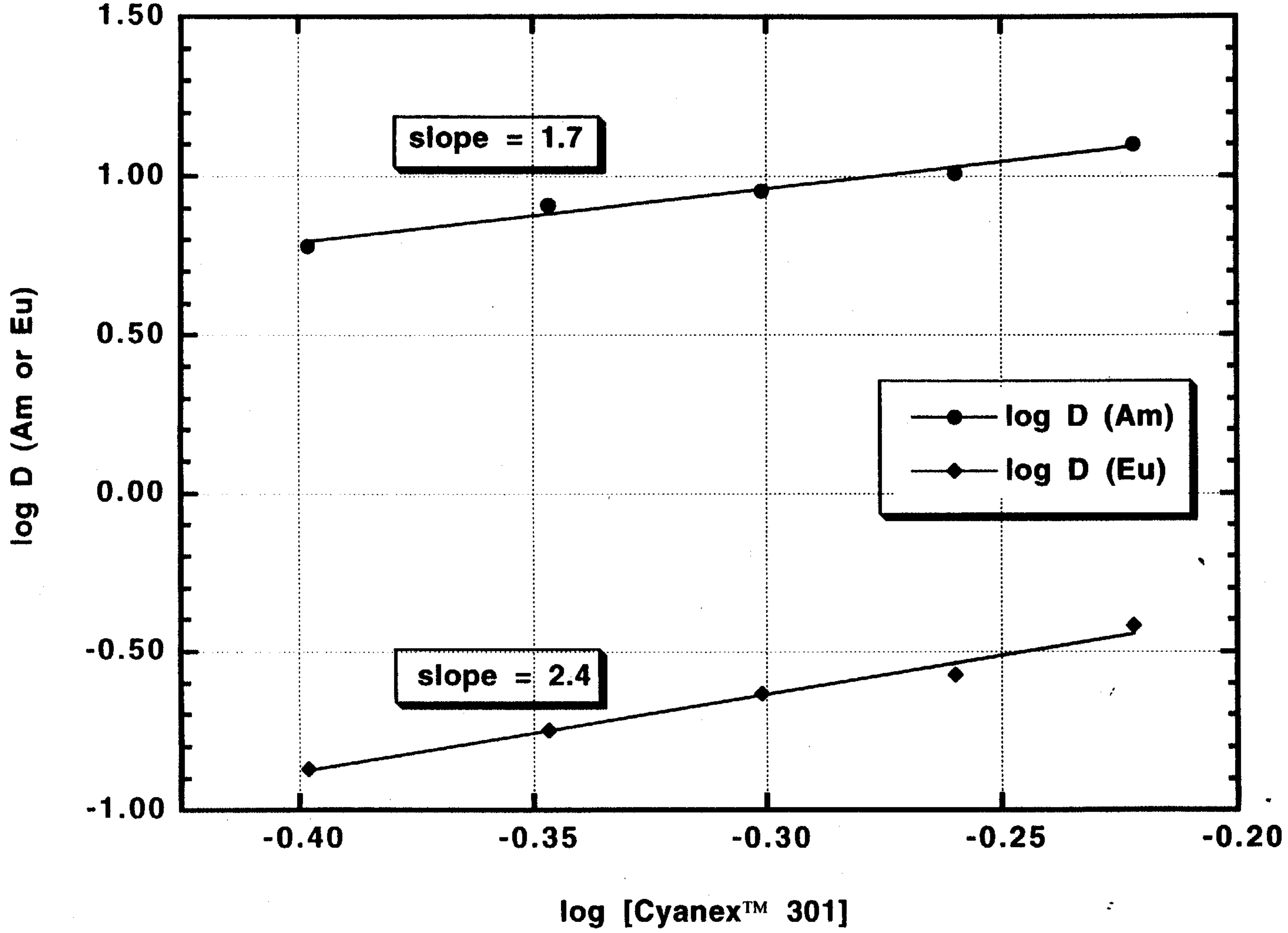

Figure 8. Cyanex™ 301 Dependency for ^{241}Am and ^{152}Eu Extractions at 0.10 M TBP and pH 3.10

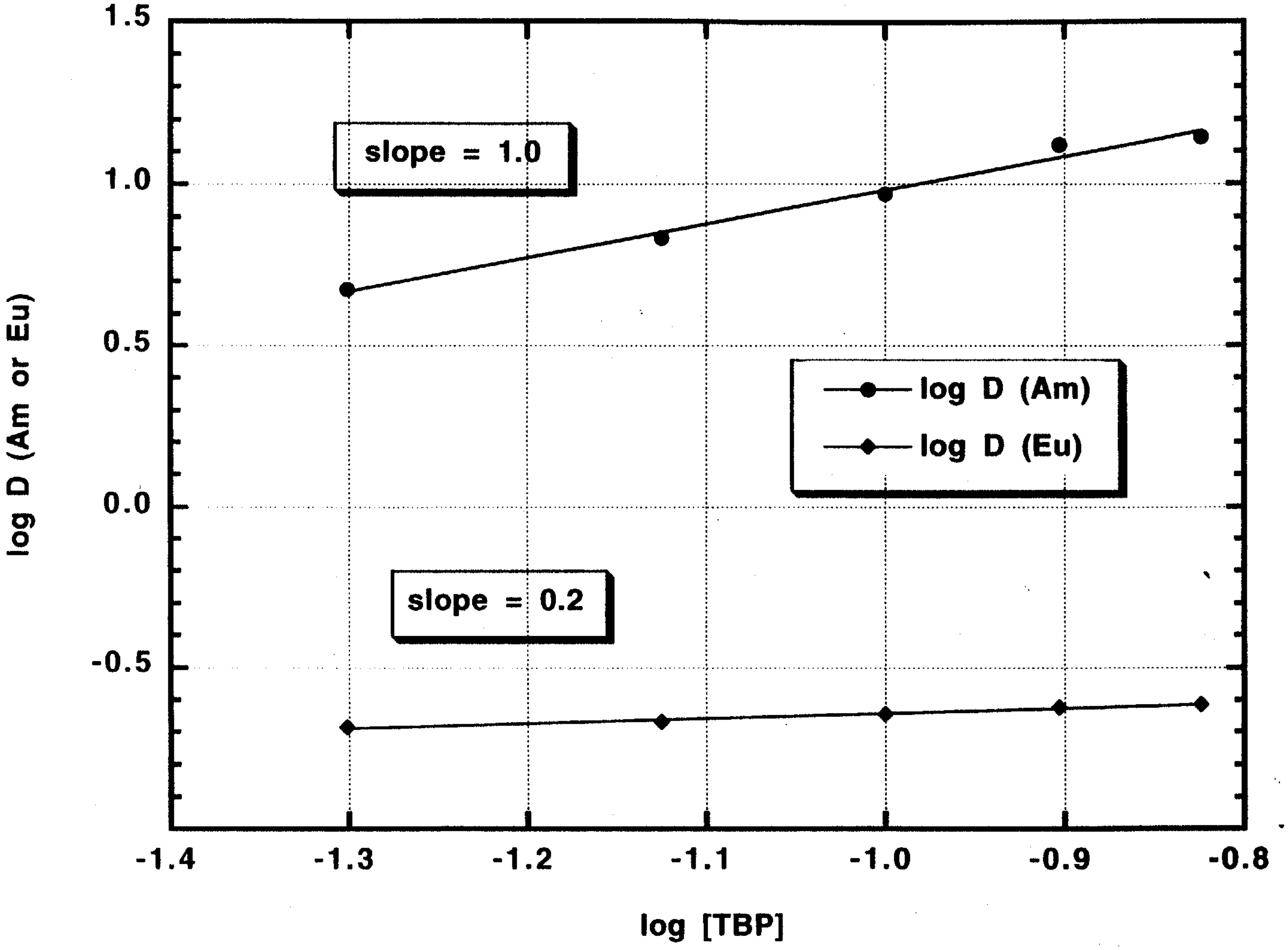

Figure 9. TBP Dependency for ^{241}Am and ^{152}Eu Extractions at 0.50 M Cyanex™ 301 and pH = 3.10

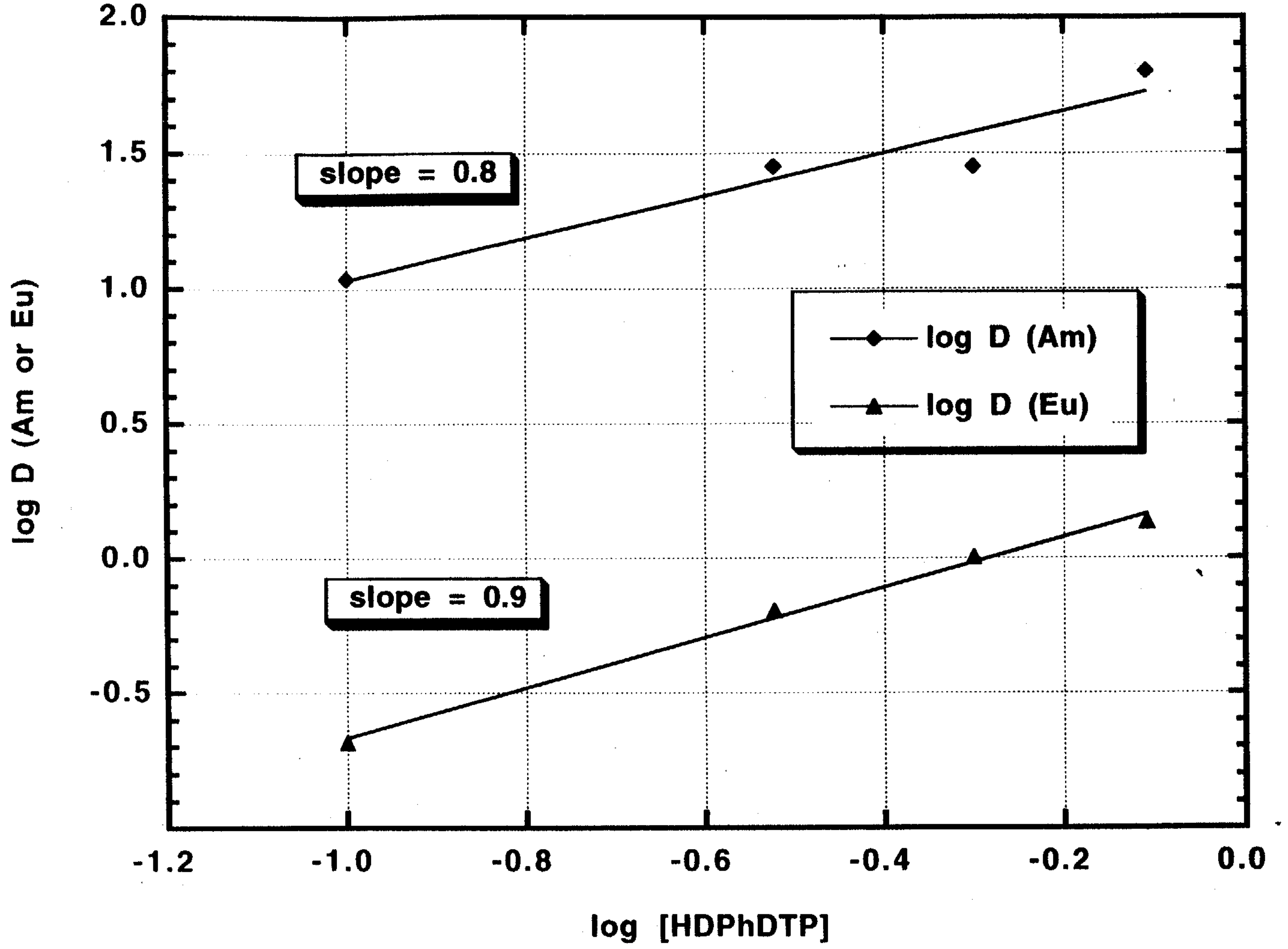

Figure 10. HDPhDTP Dependency for ^{241}Am and ^{152}Eu Extractions at 0.50 M TBP

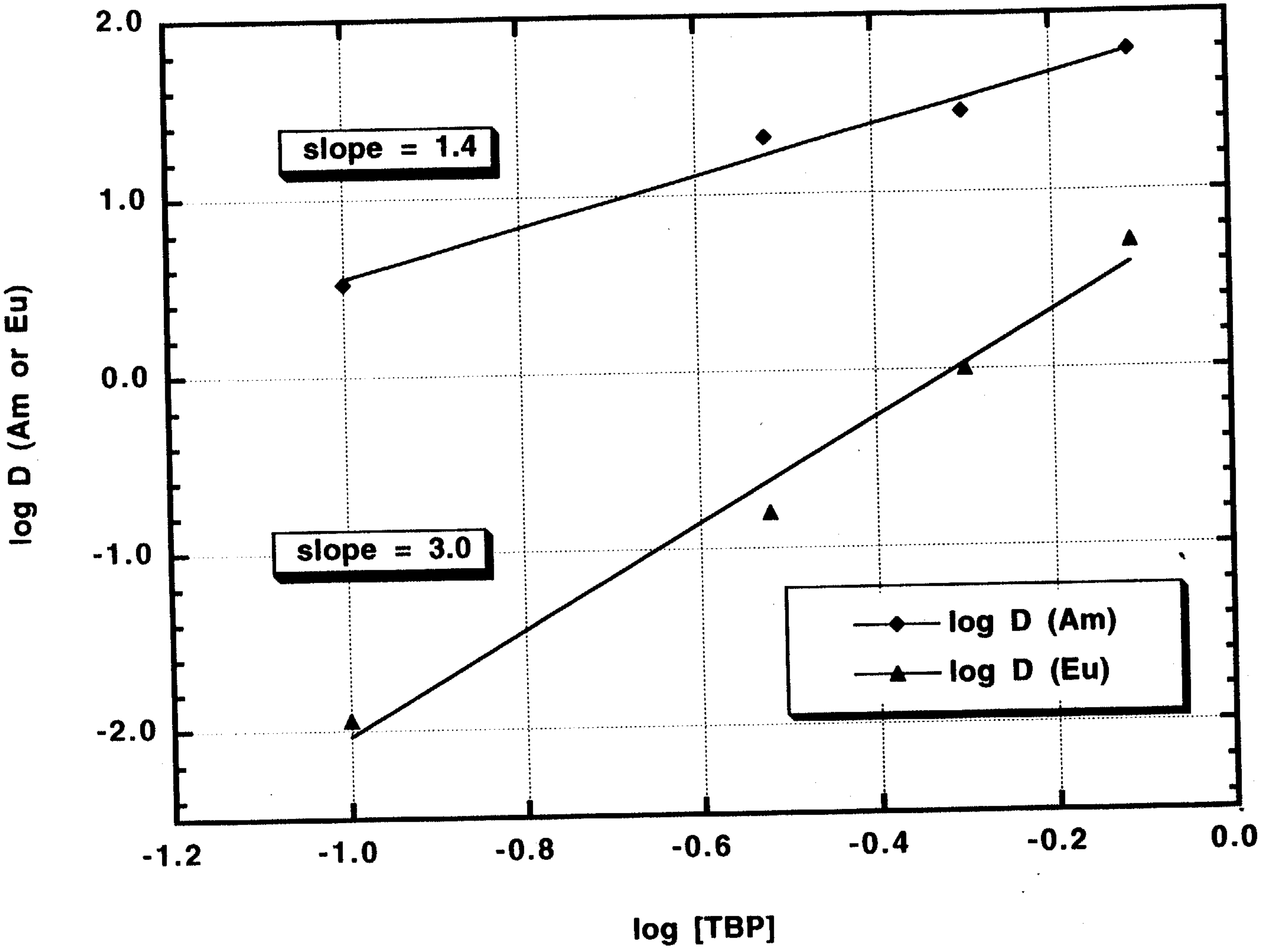

Figure 11. TBP Dependency for ^{241}Am and ^{152}Eu Extractions at 0.50 M HDPhDTP