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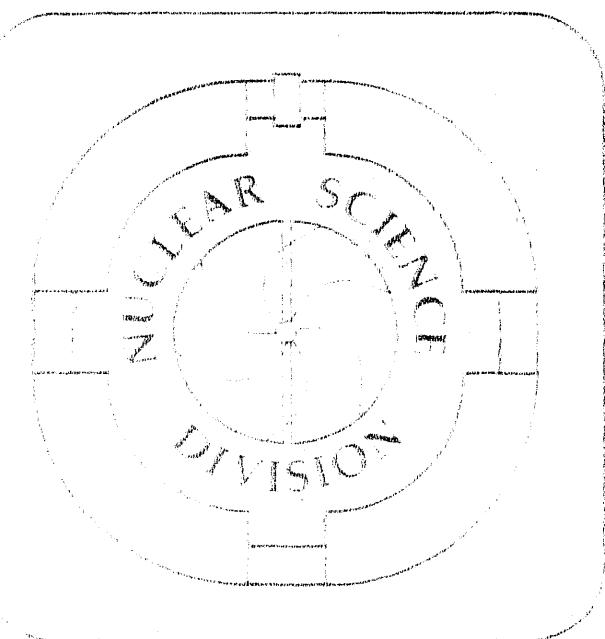
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## Extraction Studies of Selected Actinide Ions from Aqueous Solutions with 4-Benzoyl-2,4-Dihydro-5-Methyl-2-Phenyl-3H-Pyrazol-3-Thione and Tri-n-Octylphosphine Oxide

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4-BENZOYL-2,4-DIHYDRO-5-METHYL-2-PHENYL-3H-PYRAZOL-3-THIONE  
AND TRI-n-OCTYLPHOSPHINE OXIDE**

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## ABSTRACT

The first measurements of distribution coefficients ( $K_d$ ) for Cm(III), Bk(III), Cf(III), Es(III), and Fm(III) between aqueous perchlorate solutions and solutions of 4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-thione (BMPPT) and the synergist tri-n-octylphosphine oxide (TOPO) in toluene are reported. Curium-243, berkelium-250, californium-249, einsteinium-254, and fermium-253 were used in these studies. The  $K_d$  for  $^{241}\text{Am}$  was also measured and is in agreement with previously published results. Our new results show that the  $K_d$ 's decrease gradually with increasing atomic number for the actinides with a dip at Cf. In general, the  $K_d$ 's for these actinides are about a factor of 5 to 10 greater than the  $K_d$ 's for the homologous lanthanides at a pH of 2.9, a BMPPT concentration of 0.2 M, and a TOPO concentration of 0.04 M. The larger  $K_d$ 's for the actinides are consistent with greater covalent bonding between the actinide metal ion and the sulfur bonding site in the ligand.

## INTRODUCTION

Separations involving the trivalent actinides and lanthanides are difficult to achieve because the general chemistry of these elements is very similar. A simple method for a group separation of actinides from lanthanides would be highly desirable for a number of practical applications and in fundamental research. Even though such separations are intrinsically difficult, both ion-exchange and solvent extraction techniques have been developed(1,2) to achieve group separations between the lanthanides and trivalent actinides; however, quicker, more efficient separations would be desirable.

Ligands for use in ion-exchange or solvent-extraction techniques ordinarily do not have sulfur atoms at binding sites since the trivalent actinide and trivalent lanthanide cations exhibit "hard acid" properties; therefore, they will interact with "hard" ligand bonding sites such as oxygen to a greater degree than with "soft" ligand bonding sites such as sulfur(3).

Recently, several papers have been published on a synergistic solvent extraction system using BMPPT and TOPO(4-7). The unusual aspect of BMPPT is that it has one oxygen and one sulfur bonding site, so it has both "hard" and "soft" ligand sites. The previous studies(4-7) have focused on the stoichiometry of the extracted complex and a systematic study of the lanthanides. In the current work, we have studied six actinides, Am, Cm, Bk, Cf, Es, and Fm, to compare the results with the work previously done with the lanthanides(7).

## EXPERIMENTAL

### Reagents

The BMPPT was obtained from the Analytical Chemistry Group at Los Alamos National Laboratory (The preparation of BMPPT is described in Ref. 8). The reagents  $\text{NaClO}_4$  (Fisher Scientific), sulfanilic acid (Baker), and TOPO (Kodak) were all used as received.

All aqueous solutions, which contained 0.1 M  $\text{NaClO}_4$  and 0.01 M sulfanilic acid were made with distilled water. The pH of the aqueous solutions was adjusted with 1 M NaOH. The aqueous solutions were pre-equilibrated with toluene.

The organic phase was toluene (Aldrich, spectrophotometric grade) with BMPPT and TOPO dissolved in it. In the studies of the dependence of  $K_d$  on BMPPT concentration, the TOPO concentration was kept at 0.01 M while the BMPPT concentration was varied from 0.04 M to 0.30 M. In actinide extraction studies as a function of pH, the TOPO concentration was kept at 0.04 M and the BMPPT concentration was kept at 0.2 M. The organic solutions were pre-equilibrated with the aqueous phase.

#### Instrumentation

A GCA/Precision Scientific Model Fifty shaker bath was used with the water at room temperature and shaker speed at 200 oscillations per minute. The pH was measured using a Corning digital 109 pH meter and a Beckman comb. electrode #39835. The activity of the samples was measured with a high-purity-Ge gamma-ray spectrometer system (Canberra model 4610).

#### Procedure

For  $^{152}\text{Eu}$ ,  $^{241}\text{Am}$ ,  $^{243}\text{Cm}$ ,  $^{249}\text{Cf}$ , and  $^{254}\text{Es}$ , 2 mL of the aqueous phase and 2 mL of the organic phase were placed in Teflon vials along with the desired activity (approximately 2500 dpm of the activity in 0.1 M  $\text{NaClO}_4$ ). The vials were capped and placed in the shaker bath at room temperature (approximately 20°C) and shaken for 30 min. to 1 h. To determine the distribution coefficients, we assayed 1 mL of each phase separately to measure the amount of radionuclide in each phase. For the  $^{254}\text{Es}$ , the phases were assayed more than 30 h. after separation of the phases to allow the daughter,  $^{250}\text{Bk}$  ( $t_{1/2} = 3.22$  h.), to grow into secular equilibrium; gamma rays from  $^{250}\text{Bk}$  were then measured.

The  $^{253}\text{Fm}$  and  $^{250}\text{Bk}$  were obtained from the actinide fraction from OLGA II (On-Line Gas Chemistry Apparatus)(9) separated from an  $^{18}\text{O}$  bombardment of  $^{249}\text{Bk}$  at the 88-in. cyclotron at Lawrence Berkeley Laboratory. The actinide fraction was collected in dilute HCl, evaporated, fumed with concentrated nitric acid, and dissolved in 1 mL of 0.1 M  $\text{NaClO}_4$ . The extractions were then performed in the same manner as described for the other actinides.

The measurements of the radioactivity were based on gamma radiation as all of the nuclides used have a reasonably intense gamma ray associated with their decay. Table 1 shows the decay data and gamma-ray information for each isotope.

TABLE 1. Isotope Data

Isotope	Half Life	Decay Mode <sup>a</sup>	Energy(keV)	Branching Ratio	Gamma Ray
<sup>152</sup> Eu	13.4 yrs.	EC-73% $\beta^-$ -27% $\beta^+$ -0.019%	121.79	0.3068	
<sup>241</sup> Am	432 yrs.	$\alpha$	59.5	0.357	
<sup>243</sup> Cm	28.5 yrs.	$\alpha$ -99.74% EC-0.26%	277	0.140	
<sup>250</sup> Bk	3.22 hr.	$\beta^-$	989	0.452	
<sup>249</sup> Cf	350.6 yrs.	$\alpha$	388.2	0.66	
<sup>254</sup> Es <sup>b, c</sup>	275.7 days	$\alpha$	----	----	
<sup>253</sup> Fm	3.00 days	EC-88% $\alpha$ -12.1%	271.6	0.026	

<sup>a</sup> EC-electron capture;  $\beta^-$ -beta;  $\beta^+$ -positron.

<sup>b</sup> Decays to <sup>250</sup>Bk.

<sup>c</sup> Analysis done by allowing <sup>250</sup>Bk daughter to grow into secular equilibrium (about 10 half-lives) and analyzing for the daughter activity.

### RESULTS AND DISCUSSION

We studied the dependence of  $K_d$  on BMPPT concentration using Am tracer to repeat the Am results obtained by Smith, et al.(5), so that they could be used as a reference in all future studies to ensure that the results were consistent, and with Es tracer to determine if there is a difference in the dependence of the  $K_d$ 's for Am and Es on BMPPT concentration. The results obtained in our study indicate that the Am  $K_d$ 's as a function of BMPPT concentration are the same as those obtained by Smith et al.(5). The Es  $K_d$ 's also show a linear dependence on the BMPPT concentration and are about a factor of 2.5 lower than the Am  $K_d$ 's at the higher concentration of BMPPT(Fig. 1). The slopes of the  $K_d$  as a function of BMPPT concentration were obtained by using a weighted least-squares fit to the data. The slope for Es is  $1.96 \pm 0.11$ , which is 0.32 units lower than the slope for Am(slope is  $2.28 \pm 0.04$ ). The results of Nekimken, et al.(7) indicate that there is a change in the composition of the extracted complex from  $\text{Ln}(\text{BMPPT})_2(\text{HBMPPT})(\text{TOPO})_2\text{ClO}_4$  to  $\text{Ln}(\text{BMPPT})_2(\text{TOPO})_3\text{ClO}_4$  in going from Eu to Gd. The different slopes for Am and Es seem to indicate a similar transition for the actinides.

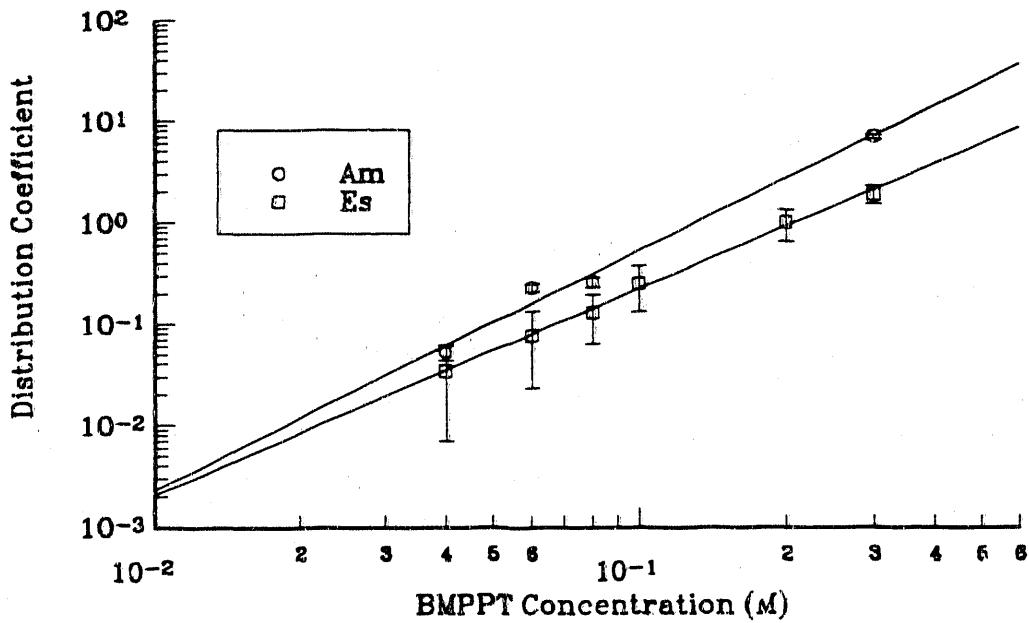


FIGURE 1. Dependence of  $K_d$  on BMPPT concentration for Am and Es with  $[TOPO]=0.01M$  and  $pH=3.0$ .

We also studied the dependence of  $K_d$  on pH at a BMPPT concentration of 0.2 M using Eu (lanthanide comparison), Am, Cm, Bk, Cf, Es, and Fm at up to three different pH's. The Eu results agree with the results of Nekimken, et al.(7)(top graph of fig. 2). The actinide results are shown in the bottom graph of fig. 2. The  $K_d$ 's for the actinides are up to a factor of 10 greater than the  $K_d$ 's for their lanthanide homologs; this is consistent with greater covalent bonding between the actinide metal ion and the sulfur in the ligand than for the homologous lanthanide. The dip at Cf can be explained by a change in the composition of the complex extracted. Such a change in complex composition is seen for the lanthanides(5) at Gd along with a decrease in  $K_d$ . This observation appears to indicate that the change in the composition of the complex results partly from the change in ionic radius; note that Cf and Gd have about the same ionic radius.

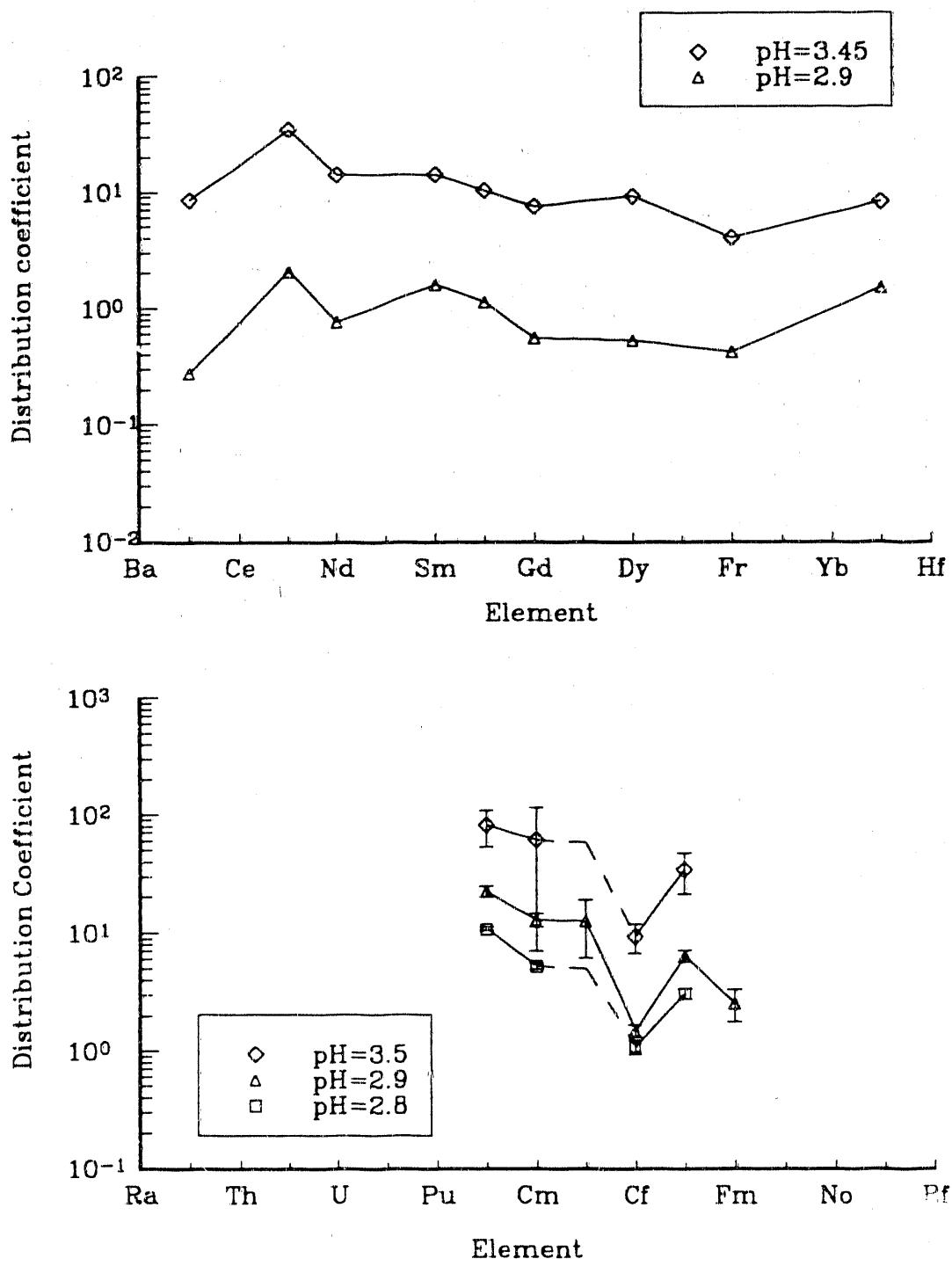


FIGURE 2. Dependence of  $K_d$  on element at various pH's with  $[TOPO]=0.04M$  and  $[BMPPT]=0.2M$ ; top graph is for some lanthanides (from Ref. 7), bottom graph for some heavy actinides.

## SUMMARY

In this study we have measured for the first time the  $K_d$ 's for Cm(III), Bk(III), Cf(III), Es(III), and Fm(III) between perchlorate solutions and solutions of BMPPT and TOPO in toluene. The  $K_d$ 's for the actinides decrease with increasing atomic number between Am and Fm (nearly a factor of 4 at pH 2.9) with an even larger dip at Cf. We have shown that, in general, actinides extract better than their lanthanide homologs by a factor of 5 to 10, apparently because of the greater covalent bonding of the actinide metal ions with the ligands. The composition of the complex that is extracted may be at least partly a result of changes in ionic radius; it appears that there is a change in complex composition for the actinides at Cf similar to the change at Gd, whose radius is nearly the same as that of Cf, for the lanthanides(7), which is reflected in relatively lower  $K_d$ 's. Data for the heavier trivalent actinides Md and Lr would be very valuable.

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### REFERENCES

1. G. R. Choppin and A. Chatham-Strode, *J. Inorg. Nucl. Chem.* **15**, 377(1960).
2. G. B. Kasting, E. K. Hulet, J. A. Heppert, and J. F. Wild, *J. Inorg. Nucl. Chem.* **41**, 745(1979).
3. G. R. Choppin, *Radiochim. Acta* **32**, 43(1983).
4. D. D. Ensor, G. D. Jarvinen, and B. F. Smith, *Solvent Extr. Ion Exch.* **6**, 439(1988).
5. B. F. Smith, G. D. Jarvinen, G. G. Miller, R. R. Ryan and E. J. Peterson, *Solvent Extr. Ion Exch.* **5**, 895(1987).
6. B. F. Smith, G. S. Jarvinen, M. M. Jones, and P. J. Hay, *Solvent Extr. Ion Exch.* **7**(5), 749(1989).
7. H. L. Nekimken, B. F. Smith, G. D. Jarvinen, and C. S. Bartholdi, Los Alamos National Laboratory, Los Alamos, New Mexico to be published in *Solvent Extr. Ion Exch.*
8. G. D. Jarvinen, R. R. Ryan, B. F. Smith, and J. M. Ritchey, *Inorg. Chim. Acta* **129**, 139(1987).
9. D. C. Hoffman, *Chemistry of the Transactinide Elements*, LBL-29815, Lawrence Berkeley Laboratory, Berkeley, California(October, 1990).

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