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Solvent Extraction Separations of Trivalent Lanthanide and Actinide Ions using an
Aqueous Aminomethanediposphonic Acid

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ABSTRACT

The possibility of separating the trivalent lanthanides, represented by Eu^{3+} , and actinides, represented by Cf^{3+} , using HDEHP in toluene and an aqueous phase containing N-piperidinomethane-1,1-diphosphonic acid, PMDPA, has been investigated. This modified aqueous phase offers potential advantages over the diethylenetriaminepentaacetic acid based TALSPEAK process because of the improved complexation properties of PMDPA in acidic solutions, and the ability to decompose PMDPA before disposal. Extraction experiments were conducted at 25 °C in 2 M NaClO_4 between $-\log [\text{H}^+]$ 1 and 2. The studies enabled us to derive the aqueous phase speciation, the stability constants of the aqueous complexes, and the Cf/Eu separation factors. Despite the presence of an amino group in PMDPA that should favor the retention of the actinides in the aqueous phase, the Cf/Eu separation factors are near unity under the conditions studied.

INTRODUCTION

Given the similar ionic radii of the trivalent lanthanide (Ln^{3+}) and actinide (An^{3+}) cations, practical intergroup separation of these elements remains a challenge for separations science. One key to achieving this separation is to exploit the small differences in the chemical hardness of the two groups. Experimentally the An^{3+} cations appear to be slightly softer Lewis acids, interacting more strongly with softer donors than the Ln^{3+} cations. Recently, the objective of incorporating nitrogen and sulfur donors into extractant molecules has made progress toward useful extractants capable of effecting this separation (Smith *et al.*, 1987 and Musikas, 1985). Historically, however, most Ln/An group separation schemes have incorporated modified aqueous phases (Nash, 1993). The most thoroughly studied of these schemes, the TALSPEAK process, involves the preferential extraction of Ln^{3+} cations by bis-(2-ethylhexyl)phosphoric acid (HDEHP) from pH 2-3 aqueous phases containing 1 M lactic acid and 0.05 M diethylenetriaminepentaacetic acid (DTPA) (Weaver and Kappelmann, 1968). The separation is based on the extraction of the 1:1 metal:lactate complexes and the stronger interaction of the An^{3+} with the nitrogen donors of DTPA.

While the TALSPEAK process has been shown effective for separating Ln^{3+} from An^{3+} , the concentrations of lactic acid and the moderate pH require substantial adjustment to

the nitric acid feed solutions usually encountered in nuclear processing. An alternative to the original TALSPEAK aqueous phase that could function in more acidic solutions, such as 1 M HNO₃, would be desirable. Methanediphosphonic acid ligands are powerful Ln/An complexants, even in 1 M acid, (Nash and Horwitz, 1990; Nash, 1991; Nash 1993b; Jensen *et al.*, 1997) that have been studied as stripping agents for the TRUEX process (Lumetta and Swanson, 1993). They are members of a class of ligands known as thermally unstable complexants or TUCs, so called because they can be degraded by gentle heating in the presence of mild oxidizing agents. A ligand that combines the powerful complexing properties of the methanediphosphonate group with the softer nitrogen donor might favor An³⁺ complexation in the aqueous phase and allow selective extraction of Ln³⁺ ions. N-piperidinomethane-1,1-diphosphonic acid (PMDPA), Figure 1, is one such ligand whose Eu³⁺ extraction has been studied previously (Jensen *et al.*, 1997). To explore the possibility of a PMDPA based Ln/An separation, we have studied

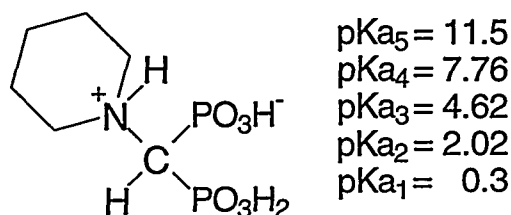


Figure 1. N-piperidinomethane-1,1-diphosphonic acid, H₄(PMDPA)

the HDEHP/toluene extraction of an An³⁺ cation, Cf³⁺, from aqueous solutions of 2 M H/NaClO₄ between -log [H⁺] 1 and 2. This actinide was chosen because it has a similar crystal radius to Eu³⁺ (109 pm vs. 108.7 pm CN=6) (Shannon, 1976). An observation of stronger Cf³⁺ complexation by PMDPA could thus be attributed to a greater covalent character in the Cf-ligand bonds since the electrostatic component of M-L bonding for Eu³⁺ and Cf³⁺ are the same.

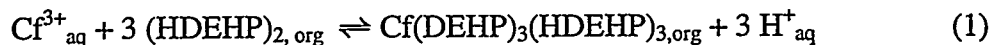
EXPERIMENTAL

The ²⁴⁹Cf tracer (t_{1/2} = 351 yr.) was obtained as the daughter of ²⁴⁹Bk supplied by Oak Ridge National Laboratory. A 0.13 M HNO₃ solution of ²⁴⁹Cf was evaporated to dryness and taken up in 0.01 M HNO₃. A high resolution γ-ray spectrum showed only ²⁴⁹Cf emissions. The initial aqueous phase concentration of ²⁴⁹Cf was ca. 3 x 10⁻⁸ M (3 x 10⁴ cpm).

Other reagents, procedures, equipment, and data analysis have been previously described (Jensen *et al.*, 1997), except that the distribution ratio of Cf³⁺, *D*, was determined radiometrically by γ-counting between 300 and 450 keV with a NaI detector. Each combination of aqueous and organic phase was run in duplicate. All uncertainties are expressed at the ±2σ level.

RESULTS AND DISCUSSION

Characterization of Cf^{3+} extraction by HDEHP/toluene in the absence of PMDPA was the first step. Slope analysis of the extractant and acid dependencies gave 2.98 ± 0.05 and 3.16 ± 0.08 respectively, confirming the expected extraction equilibrium,



in agreement with the Eu^{3+} results. The extraction constant for Cf^{3+} , K_{ex} , was determined to be 0.493 ± 0.048 .

Table 1. Solution Compositions for Extraction Studies

$-\log [\text{H}^+]_{\text{aq}}$	$[(\text{HDEHP})_2]_{\text{org}}, \text{M}$	$[\text{PMDPA}]_{\text{aq}}, \text{M}$	Number of Concentrations
0.981	0.0250 - 0.250	0	8
0.981 - 1.998	0.0250	0	8
0.981	0.250	0 - 0.020	10
1.266	0.125	0 - 0.016	10
1.656	0.050	0 - 0.012	10
1.998	0.025	0 - 0.008	10

The effect of PMDPA on the Cf^{3+} extraction equilibrium was measured by varying the concentration of PMDPA at four different sets of $-\log [\text{H}^+]$ and HDEHP concentrations, as summarized in Table 1. The normalized extraction data are shown in Figure 2. Slope analysis of the extraction data indicate that Cf complexes containing 1, 2, and 3 molecules of PMDPA form in the aqueous phase under these experimental conditions. If we assume that only mononuclear complexes are formed and that Cf-PMDPA complexes are not extracted, the stability constant, β_n^* , of the hypothetical equilibrium,



can be calculated at each $-\log [\text{H}^+]$ for $n = 1, 2,$ and 3 according to the standard solvent extraction equation

$$\frac{D_o}{D} = 1 + \sum_{n=1}^3 \beta_n^* [\text{PMDPA}^{4-}]^n \quad (3)$$

where D_o is the distribution coefficient of Cf^{3+} in the absence of PMDPA. D_o is calculated from K_{ex} , $[(\text{HDEHP})_2]$, $[\text{H}^+]$, and the slopes of the extractant and acid dependencies. Slope analysis of the dependence of $\log \beta_1^*$, $\log \beta_2^*$, and $\log \beta_3^*$ on $\log [\text{H}^+]$ gives three lines representing the average H^+ stoichiometry of the 1:1, 1:2, and 1:3 Cf:PMDPA complexes respectively (Nash and Horwitz, 1990). Next, the full set of distribution ratios were systematically fit to the expression

$$\frac{D_o}{D} - 1 = \sum_{n=1}^3 \sum_{h=0}^{2n} \beta_{hn} [H^+]^h [H_2PMDPA^{2-}]^n \quad (4)$$

by weighted non-linear least squares regression to obtain the stoichiometries and stability constants, β_{hn} , of the $CfH_h(H_2PMDPA)_n^{3+h-2n}$ complexes. The parameters giving the best fit and the uncertainties are summarized in Table 2.

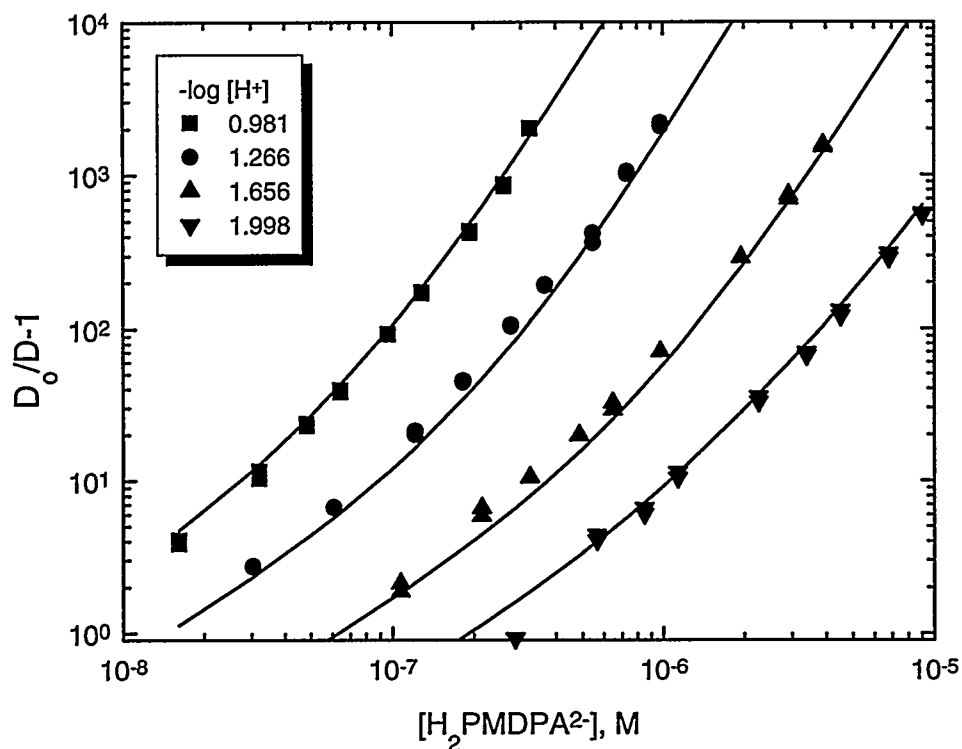


Figure 2. HDEHP/toluene extraction of Cf^{3+} from 2 M H/NaClO₄ at 25 °C fit to Equation 4. Lines are the fit of the data to the model of Table 2.

Table 2. Measured Cf^{3+} - H^+ - H_2PMDPA^{2-} stability constants compared with Eu^{3+} stability constants from Jensen *et al.*, 1997.

Species	Stoichiometry, $h n$	Cf^{3+} Log β_{hn}	Eu^{3+} Log β_{hn}
$Cf(H_3PMDPA)_2^{2+}$	1 1	8.42 ± 0.16	8.56
$Cf(H_4PMDPA)_2^{3+}$	2 1	10.22 ± 0.11	9.92
$Cf(H_3PMDPA)_2^{2+}$	2 2	16.62 ± 0.06	16.21
$Cf(H_4PMDPA)_2^{3+}$	4 2	19.56 ± 0.12	19.47
$CfH_2(H_3PMDPA)_3^{2+}$	5 3	27.47 ± 0.06	27.13

The stoichiometries of the Cf-PMDPA complexes derived from the extraction experiments (Table 2) are the same as those previously observed for the Eu-PMDPA complexes in the same range of acidity and ligand concentration. The stability constants of the Cf-PMDPA complexes are comparable to those of Eu^{3+} , and are the same within experimental error for the 11, 21, and 42 complexes. The stability constants are slightly higher for Cf^{3+} in the case of $\text{Cf}(\text{H}_3\text{PMDPA})_2^+$ and $\text{CfH}_2(\text{H}_3\text{PMDPA})_3^{2+}$, which may also be written as $\text{Cf}(\text{H}_3\text{PMDPA})(\text{H}_4\text{PMDPA})_2^{2+}$.

These differences in the stability of the aqueous phase complexes are not sufficient, however, to separate Eu^{3+} from Cf^{3+} by HDEHP extraction. Using the constants measured for Eu^{3+} and Cf^{3+} , the distribution of these metal ions into HDEHP/toluene may be calculated for comparison. Between $-\log [\text{H}^+] 0$ and 3 and in the presence of 0.01 M PMDPA, the separation factor $\text{Eu}/\text{Cf} = 1.0 \pm 0.1$ for HDEHP/toluene extraction. This is comparable to the value 0.9 reported by Stry in the absence of PMDPA (Stry, 1966). There is no significant separation between the trivalent lanthanides and actinides, unlike the original TALSPEAK process, which gives a Eu/Cf separation factor of 16 (Weaver and Kappelmann, 1968).

The lack of Ln/An separation by PMDPA indicates that the piperidino nitrogen does not bind the metal center under the conditions studied. The affinity of the piperidino nitrogen for H^+ is substantial, as indicated by $\text{pK}_a=11.5$. However, the basicity of this amino group can be compared to the amino groups of 1,2-dimethylethylenedinitrilotetraacetic acid ($\text{pK}_a = 11.53$, $I=0.1$ M), nitrilotriacetic acid ($\text{pK}_a=9.34$, $I=1.0$ M), and iminodiacetic acid ($\text{pK}_a=9.26$, $I=1.0$ M) (Martell *et al.*, 1997). In each of these ligand systems the amino nitrogen is coordinated to Ln or An cations in the respective 1:1 complexes. Therefore, the H^+ affinity of PMDPA's nitrogen probably is not an intrinsic limitation on metal binding and does not account for the absence of an interaction with Eu^{3+} or Cf^{3+} . With this in mind, it is likely that the ligand geometry is responsible for the absence of direct complexation of the metal cations by the PMDPA nitrogen. These results suggest that a ligand incorporating aliphatic amines and phosphonate groups not bound to the same methylene group might be a more promising reagent for Ln/An separations.

CONCLUSIONS

Despite the simplifications in aqueous phase feed adjustment and waste disposal that would be realized if an aminomethanediphosphonic acid could be substituted for lactic acid and DTPA in a TALSPEAK flowsheet, PMDPA shows no significant preference for trivalent actinides over trivalent lanthanides in 2 M H/NaClO_4 between $-\log [\text{H}^+] 1$ and 2. The lack of differentiation between the Eu and Cf cations, implies that the piperidino nitrogen of PMDPA, which would bind Cf^{3+} more strongly, does not bind either metal ion under the conditions studied due to the geometric constraints of the ligand.

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