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SYNERGISTIC EXTRACTION STUDIES USING n-OCTYL(PHENYL) N,N-DIISOBUTYLCARBAMOYL-METHYLPHOSPHINE OXIDE

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ABSTRACT

The effectiveness of n-octyl(phenyl)-N,N'-diisobutylcarbamoyl-methylphosphine oxide, CMPO, as a neutral extractant for the trivalent actinides and lanthanides from strong acid media has been well established. This investigation characterized the use of CMPO as a synergistic agent in the extraction of Am(III) and Eu(III) by thenoyltrifluoroacetone (HTTA). The distributions of the metal ions were measured using radiotracer techniques as functions of HTTA concentration, CMPO concentration and pH. The results show that the presence of CMPO enhances the extraction of Eu(III) and Am(III) by 10^8. The synergistic adduct was $M(TTA)_3 \cdot$ CMPO with no indication of higher complexes being formed. Unlike previous studies, the extraction of Eu(III) was more strongly enhanced than that of Am(III). The results showed little, if any, enhancement in the extraction efficiency due to the bidentate nature of the CMPO.

INTRODUCTION

The separation of trivalent lanthanide and actinide elements offers one of the most difficult challenges in the field of separation science. There are few differences in the chemical and physical properties of these elements, which makes it difficult to develop efficient processes for separating the metal ions. Synergistic solvent extraction systems have been applied to these elements numerous times with large increases in the efficiency being observed. However, little, if any, improvement in the separation characteristics have resulted (1).

Most synergistic studies have been done with monodentate compounds such as trioctylphosphine oxide (TOPO) or tributyl phosphate (1) and little attention has been given to bidentate compounds to see if the chelate effect will provide stronger enhancement in these systems. In order to investigate this possibility, the bidentate ligand n-octyl(phenyl)-N,N'-diisobutylcarbamoyl-methylphosphine oxide, CMPO, was chosen. This compound has been shown to be effective in the extraction of actinides from concentrated nitric acid (2). Its use as a synergistic agent for lanthanide elements in combination with 1-phenyl-3-methyl-4-(trifluoroacetyl)-5-pyrazolone has also been reported (3). This paper reports the use of CMPO as a synergistic agent in combination with thenoyltrifluoroacetone, HTTA, to extract Am(III) and Eu(III) from dilute acid solutions.

EXPERIMENTAL

Materials

HTTA (mp. 42-43°C) was obtained from the Sigma Chemical Company and used as received. CMPO (99+% purity) was obtained from Dr. E. P. Horwitz of the Separation Group at Argonne National Laboratory. All other chemicals used in this study were analytical reagent grade.

The trivalent metals, ^{152,154}Eu and ^{241}Am, were used in tracer-level experiments to study the distribution of the metal ions in the presence of the synergistic reagents. The organic phase contained weighed quantities of HTTA and CMPO dissolved in toluene. The aqueous phase contained 0.5 M $NaNO_3$ with a 0.02 M acetate buffer to control the pH. The experimental distribution, D_{exp}, of the metal tracer was measured by equilibrating equal volumes of the aqueous and organic phases at 25° ± 0.1°C and measuring the activity in both phases. This D_{exp} was then corrected for acetate complexation of the metal ion in the aqueous phase as described in reference 5.

Data Treatment

The extraction of trivalent metals by HTTA and a synergistic agent (S) can be represented by equations (1) and (2).

$$M^{+3}_{(aq)} + 3HTTA_{(org)} + S_{(org)} \overset{K_{syn}}{====} M(TTA)_3S_{(org)} + 3H^+_{(aq)} \, . \tag{1}$$

$$K_{syn} = \frac{[M(TTA)_3S]_{(org)}\ [H^+]^3_{(aq)}}{[M^{+3}]_{(aq)}\ [HTTA]^3_{(org)}\ [S]_{(org)}} \, . \tag{2}$$

The strength of the synergistic species formed in the organic phase is represented by the organic phase stability constant described by the following equations:

$$M(TTA)_{3(org)} + S_{(org)} \overset{\beta_{(org)}}{====} M(TTA)_3S_{(org)} \,. \tag{3}$$

$$\beta_{(org)} = \frac{[M(TTA)_3S]_{(org)}}{[M(TTA)_3]_{(org)}\,[S]_{(org)}} \,. \tag{4}$$

The distributions of the metal ions were obtained as a function of one of the variables, ($[H^+]$, [HTTA], or [S]), while keeping the other two constant. The data were analyzed by the slope analysis method (4), and the composition of the synergistic species was established by a plot of log D_{syn} vs log [variable].

The equilibrium constants measured in this work are not true equilibrium constants, but concentration quotients. These values are dependent on the experimental conditions and the assumption that the activity coefficients of the various species in solution did not change during the reaction. A detailed description of the experimental procedure and data treatment have been previously published (5).

RESULTS

No measurable extraction (D <0.001) of Am(III) or Eu(III) by CMPO was observed at the experimental conditions used in this investigation. This agrees with the previous data which showed that CMPO only extracts these elements at high concentrations of acid and nitrate. When combined with HTTA, the CMPO showed a significant ability to enhance the distribution of these metal ions into the organic phase when compared to using HTTA alone.

The slope analysis method indicates that the extracted complex has the formula $M(TTA)_3 \cdot$ CMPO for both Eu(III) and Am(III). No indication of higher order complexes was observed. Figures 1 and 2 show the variation of the distribution as a function of either pH or [HTTA]. The equilibrium data and slope dependencies are summarized in Table 1.

Table 1. Equilibrium data for CMPO at 25°C

Metal (III)	Log K_{TTA}(9)	Log K_{syn}	Slopes pH	 [CMPO]	 [HTTA]
Am	-8.40	-0.25	3.08	1.04	2.86
Eu	-8.02	+0.30	3.04	0.94	2.91

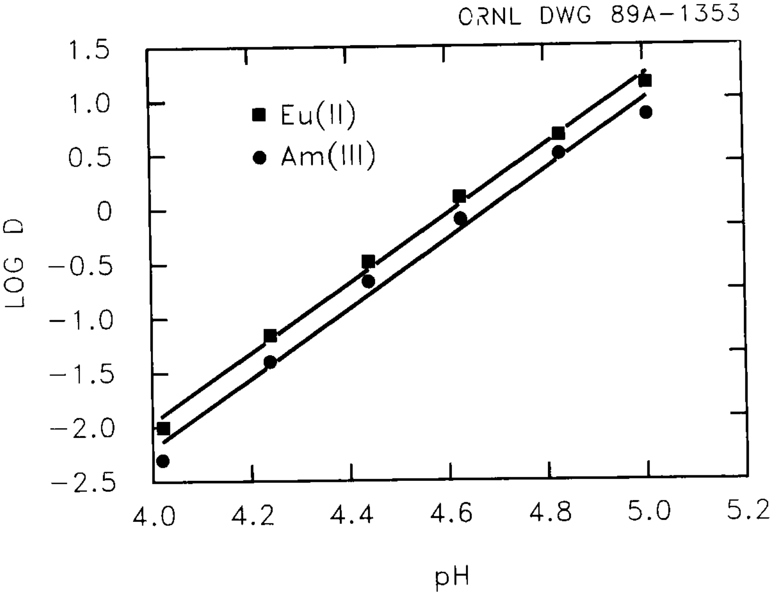

Fig. 1. Effect of varying the [HTTA] at a constant [CMPO] on the distribution coefficient of Am(III) and Eu(III). [CMPO] = 1.5 x 10^{-4} M - pH = 4.5.

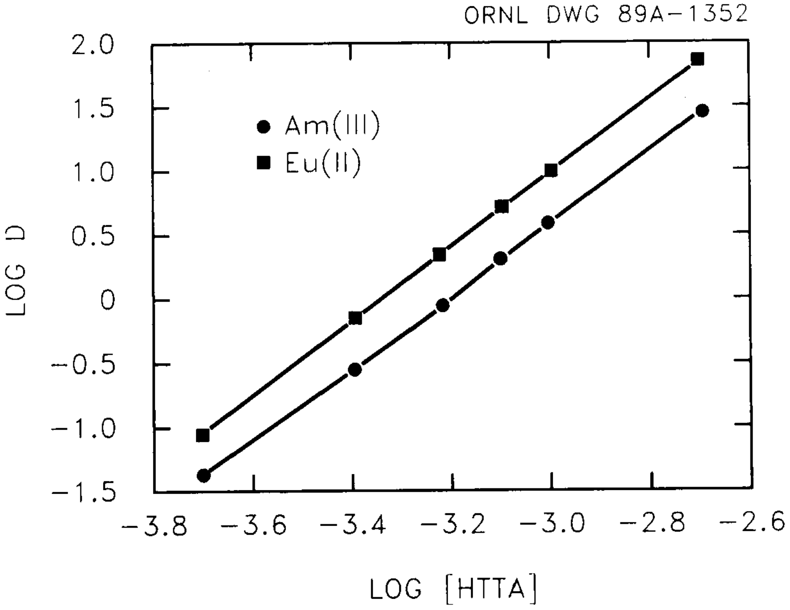

Fig. 2. Effect of varying pH at a constant [CMPO] and [HTTA] on the distribution coefficient of Am(III) and Eu(III). [CMPO] = 1.5 x 10^{-4} M; [HTTA] = 8.00 10^{-4} M.

The CMPO shows a slight preference for the $Eu(TTA)_3$ complex. This is consistent with the basic character of the phosphoryl group reacting more strongly with the Eu(III) which is a slightly stronger acid than Am(III). A slight improvement in the separation factor for Eu(III) over Am(III) (Table 2) in the synergistic system illustrates this behavior. A similar tendency was observed when the monodentate synergist trioctylphosphine oxide (TOPO) was combined with HTTA.

Table 2. Separation factors

[HTTA] (m$\underline{M}$)	[CMPO] (m$\underline{M}$)	Separation factor (D_{Eu}/D_{Am})
2.50	0.00	1.5
0.00	2.50	No detectable extraction
1.75	0.75	2.5

The organic phase stability constants for CMPO are reported in Table 3. β_1 for CMPO was larger than β_1 for trioctylphosphine oxide, TOPO, but less than β_2. This agreed with the previous work (3) which showed a β_1 for CMPO with 1-phenyl-3-methyl-4-(trifluoroacetyl)-5-pyrazolone fell between the values of β_1 and β_2 for TOPO. Since the basicity of the carbonyl oxygen on CMPO is much less than the phosphoryl group, a comparison of the sum of the log β_1's for TOPO and methylisobutylketone, MIBK, would be a more useful comparison. Taking into consideration the slightly different experimental conditions, Table 3 shows that the combination of log β_1 for TOPO and MIBK yields reasonable agreement with the log β_1 value for CMPO, considering the differences in experimental conditions. This is consistent with the CMPO acting as a bidentate synergist. Unfortunately, the enhanced stability of the synergistic adduct that might be expected as a result of the chelate effect was not observed.

Table 3. Comparison of CMPO with other synergists

	Log β_{org}			
Reference		Am(III)	Eu(III)	
CMPO	β_1	8.15	8.32	Present work
TOPO	β_1	6.4	7.2	(6,7)
	β_2	11.1	11.8	
MIBK	β_1	1.8	1.8	(8)
	β_2	2.5	2.5	

The results of this study show that CMPO is an effective synergistic agent, when combined with HTTA, for Am(III) and Eu(III). The magnitude of the organic phase stability constants measured in this work is indicative of CMPO forming a bidentate synergistic complex. The "hard" base nature of the CMPO shows a preference for $Eu(TTA)_3$ which leads to improved separation factors when compared to HTTA alone.

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