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Synergistic Extraction of Trivalent Actinides and Lanthanides Using Htta and an Aza-Crown Ether

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SYNERGISTIC EXTRACTION OF TRIVALENT ACTINIDES AND LANTHANIDES USING HTTA AND AN AZA-CROWN ETHER

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ABSTRACT

An aza-crown ether, 4,13-didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (K22DD) has been shown to have a synergistic effect on the extraction of trivalent lanthanides and actinides by thenoyltrifluoroacetone (HTTA). The extraction of Am(III), Cm(III), Am(III), Eu(III), Ce(III), and Pm(III) from an aqueous acetate buffer system (pH = 4.8) into HTTA/K22DD/chloroform phase was studied at 25°C. Distribution coefficients were measured as a function of HTTA concentration, K22DD concentration, and pH user radiotracer techniques. The synergistic species was determined from these studies to be M(TTA)3•K22DD. The results show that the presence of K22DD synergizes the extraction of each of the metals studied by factors of approximately 10^4-10^5. Slightly larger organic phase stability constants were measured for the trivalent actinides relative to the trivalent lanthanides.

INTRODUCTION

The separation of the trivalent actinide and lanthanide elements from each other remains one of the most difficult challenges in radiochemistry and nuclear waste management. These elements are very similar in their chemical and physical properties, and so are not easily separated by methods that rely on such differences. Most solvent extraction reagents, for example, extract the elements of one group about as well as the elements of the other. Thenoyltrifluoroacetone (HTTA) is an acidic extractant that works well for both groups, but is selective for neither. Efforts to increase the selectivity of HTTA and other acidic extractants by the addition of neutral oxygen donors (which act as synergistic reagents) to the organic phase (1,2) have been largely unsuccessful, as the synergists increased the distribution coefficients of all the elements by about the same amount.

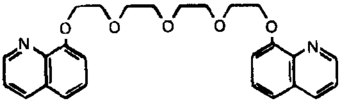
A recent review (3) summarizes much of the thermodynamic and kinetic data for cation-macrocycle interactions in aqueous and nonaqueous systems. Figure 1 shows the structures of the ligands used in the present study. The size-selective coordinating properties of macrocyclic compounds have been used to separate a variety of metals (4,5). Crown ethers and cryptands have also been used as synergistic agents in the extraction of actinides and lanthanides (6,7). The results from these studies, though interesting, are inconclusive since the partitioning of the crown ethers and cryptands between the aqueous and organic phases was apparently not accounted for. The use of a linear polyether, (1,13-bis-quinoly)-1,4,7,10,13-pentaoxatridecane (K-5) in combination with HTTA showed enhanced selectivity for the trivalent actinide ions (8). This selectivity was attributed to the slightly greater affinity of the actinide ions for nitrogen donors. This paper reports the use of an aza-crown ether, 4,13-didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (K22DD), as a synergistic agent. The experiments were undertaken to determine what effect the steric differences between the linear compound (K5), which is flexible, and the crown (K22DD), which has a fixed cavity size, would have on the selectivity of the synergistic system.

EXPERIMENTAL

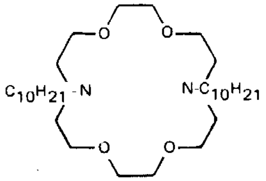
Materials

K22DD (Kryptofix K22DD) was obtained from PCR Research Chemicals, Inc. and used without further purification. HTTA (Sigma Chemical Co.) was recrystallized from cyclohexane (mp 42-43°C) and stored away from light under vacuum until used. All other chemicals used in this study were analytical reagent grade.

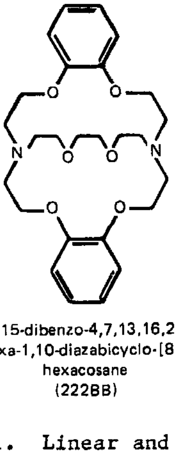
All organic phase solutions were prepared by dissolving weighed amounts of HTTA and the desired synergist in chloroform and diluting to the required volume. The aqueous phase for all experiments contained 0.5 M $NaNO_3$ to fix the ionic strength and 0.01 M acetic acid/acetate buffer to maintain the pH of this phase at 4.8. The pH was defined as the $-\log[H^+]$ using a 1.00×10^{-3} M HCl + 0.50 M $NaNO_3$ solution as a standard. All organic phase solutions were pre-equilibrated with fresh aqueous phase to saturate the chloroform with water and minimize the mass transport of HTTA during the extraction process.



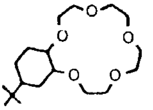
(1,13-bis-quinolyl)-1,4,7,10,13
pentaoxatridecane
(K-5)



4,13,-didecyl-1,7,10,16-tetraoxa-
4,13-diazacyclooctadecane
(K22DD)



5,6,14,15-dibenzo-4,7,13,16,21,24-
hexaoxa-1,10-diazabicyclo-[8,8,8]
hexacosane
(222BB)



4-tertbutylcyclohexo-15-crown-5
(15-C-5)

Fig. 1. Linear and cyclic polyethers tested as synergists.

The distribution of the metal ions was measured using a tracer technique. A spike of ^{144}Ce, ^{147}Pm, $^{152-154}$Eu, ^{241}Am, or ^{244}Cm was added to equal volumes of the aqueous and organic phases. Equilibrium was established by intimately mixing the two phases for 2 to 4 hours in a thermostated vessel at 25 ± 0.10°C. Experimental results showed that this time period was sufficient to establish equilibrium. After centrifuging, the phases were separated and the pH of the aqueous phase measured. Duplicate aliquots of each phase were assayed using gamma spectroscopy or liquid scintillation counting as appropriate for the tracer being studied. In order to avoid quenching by chloroform, the organic phase was back extracted into 0.01 M HCl before counting. The experiment distribution ratio, D_{exp}, was defined as the activity of the organic phase divided by the activity of the aqueous phase. This experimental method produced values of D_{exp} that were reproducible to <2%.

Data Treatment

The extraction of trivalent metal ions by HTTA can be represented by equation (1).

$$M^{3+}(aq) + 3HTTA(org) \rightleftarrows M(TTA)_3(org) + 3H^+(aq) \qquad (1)$$

The equilibrium constant for this reaction is:

$$K_{TTA} = \frac{[M(TTA)_3]_o[H^+]_a^{\,3}}{[M^{3+}]_a[HTTA]_o^{\,3}} \qquad (2)$$

The addition of a synergistic agent, S, yields the following overall reaction and equilibrium constant.

$$M^{+3}(aq) + 3HTTA(org) + S(org) \rightleftarrows M(TTA)_3S(org) + 3H^+(aq) \qquad (3)$$

$$K_{syn} = \frac{[M(TTA)_3S]_o[H^+]^3}{[M^{3+}]_a[HTTA]_o^{\,3}[S]_o} \qquad (4)$$

The formation of the synergistic complex can be described as an organic phase reaction represented by the organic phase stability constant, β_{org}.

$$M(TTA)_3(org) + S(org) \rightleftarrows M(TTA)_3S(org) \qquad (5)$$

$$\beta_{org} = \frac{[M(TTA)_3S]_o}{[M(TTA)_3]_o[S]_o} \qquad (6)$$

The experimental distribution coefficient, D^{exp}, of the metal ion was corrected for the presence of acetate ion in the aqueous phase using equation (7). The values for the stability constants, $\beta_{acetate}$, for the reaction of the metal ions and acetate were taken from reference (9).

$$D = D_{exp}\,(1 + \beta_{acetate}[CH_3COO^-]) \qquad (7)$$

The organic phase stability constants were calculated using the slope analysis method. The combination of equations (4) and (6) can be rearranged to yield:

$$D_{syn} = D_{TTA} + D_{TTA}\beta_{org}[S] \qquad (8)$$

The D_{syn} was measured as a function of the concentration of S with all other parameters held constant. The value of D_{TTA} obtained from this treatment was used to calculate K_{TTA} and compared to the experimentally measured value. The dependance of the extraction on pH and [HTTA] were evaluated by varying the parameter of interest and holding all others constant. The equilibrium constants calculated in this manner are conditional constants and are based on the assumption that the activity coefficients of all the species involved in the reaction do not change significantly under the experimental conditions. This treatment is consistent with the treatment of synergistic equilibrium described by Sekine and Hasegawa (10).

RESULTS AND DISCUSSION

K22DD alone showed no ability to extract any of the trivalent metal ions examined under the experimental conditions that were used in this study. The combination of HTTA and K22DD showed a significant increase in the distribution of these metal ions to the organic phase relative to that obtained using HTTA alone.

Figure 2 shows a plot of log D_{syn}/D_{TTA} vs [K22DD] for Am(III), Cm(III) and Eu(III). The magnitude of the synergistic effect on the extraction of each of these ions increases rapidly with increasing K22DD concentration, then levels off at the highest concentrations studied. It is also apparent from Figure 2 that the presence of K22DD enhances the extraction of Am(III) and Cm(III) more than the extraction of Eu(III). The extraction constant for each metal studied is reported in Table 1. The addition of K22DD to the TTA-chloroform phase increased the distribution of both the lanthanide and actinide ions by factors of 10^4-10^5.

Results of the slope analysis indicate that the composition of the synergistic complex is $M(TTA)_3 \cdot K22DD$. The HTTA dependence (Figure 3) was found to vary from 2.7 to 3.1 for the five metals studied. The pH dependence varied from 2.9 to 3.2 over the pH range of 4.0 to 5.0. Finally, the K22DD dependence approached one, and there was no indication of more than one K22DD molecule per metal ion even at the highest concentration of synergist. In the case of the HTTA and pH dependencies, the slight deviations of the slopes from 3.0 could be caused by the formation of mixed or slightly soluble complexes or by activity effects in the organic phase.

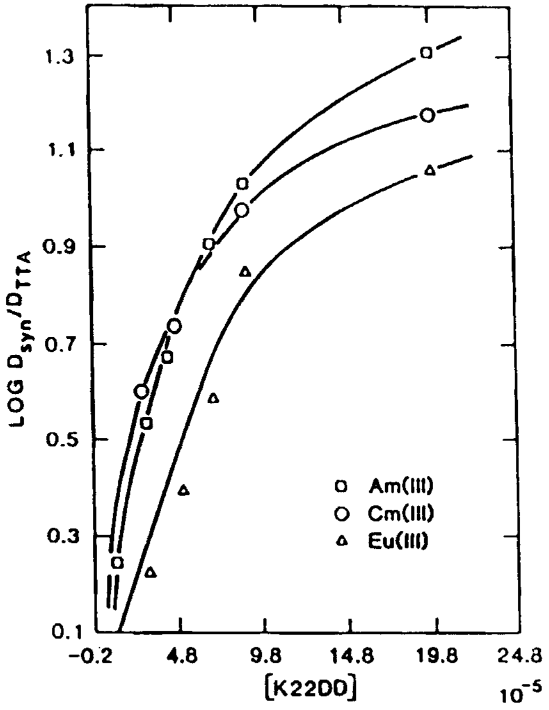


Fig. 2. Effect of the concentration of K22DD on the synergistic extraction of Am(III), Cm(III), and EU(III).

Table 1. Equilibrium values for the extraction of M(III) into HTTA/K22DD/Chloroform mixtures at 25°C

Metal	Log K_{TTA}[1]	Log K_{TTA}[2]	Log K_{syn}
Ce	-9.95	-9.63	-4.70
Pm	-9.28	-9.62	-5.08
Eu	-8.58	-8.48	-3.87
Am	-9.10	-9.01	-3.95
Cm	-9.10	-9.06	-4.10

[1] Measured using HTTA alone.

[2] Calculated from the synergistic extraction data.

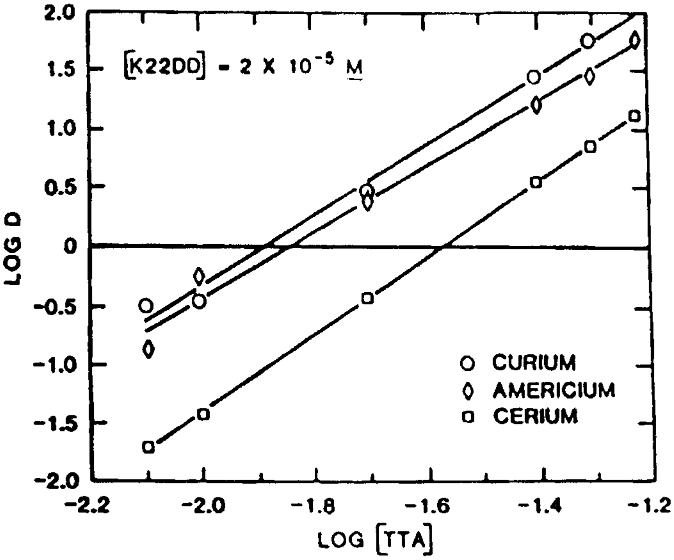


Fig. 3. Dependence of the distribution coefficient on the concentration of TTA.

The organic phase stability constant, β_{org}, for K22DD, along with the available data for tert-butylcyclohexyl-15-crown-5 (15-C-5) (11), a crown ether, and 5,6,14,15-dibenzo-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane (222BB) (11), a cryptand, are reported in Table 2. For K-5, 15-C-5 and K22DD the magnitude of β_{org} is greater for the trivalent actinides than for the trivalent lanthanides of similar ionic size. The data available for trioctylphosphine (TOPO) does not show a similar effect for Am(III) and Eu(III). The log β_{org} values for TOPO/HTTA in chloroform were 5.37 for Am(III) (12) and 5.40 for Eu(III) (13). Similar results for TBP/HTTA in chloroform have also been reported (14). All of the synergists shown in Table 2 enhance the extraction of Am and Cm in a similar manner.

The importance of the nitrogen donor groups in the synergistic mechanism can be clearly seen by comparing 15-C-5, which has no nitrogen donor groups, to K22DD. Each compound has a fixed cavity of similar size with K22DD being slightly larger. For each of the trivalent metals studied, K22DD shows an enhancement that is greater than that shown by 15-C-5 by a factor of 10^2. Other workers have reported similar results using other ligands containing soft donor atoms such as nitrogen and sulfur (15).

Table 2. Comparison of K22DD with other neutral macrocyclic synergistic agents

Metal	Ionic radius (nm)(11)	Log β_{org} K-5(7)	15-C-5(10)	222BB(10)	K22DD
Ce	0.101	4.15	2.61	4.64	4.93
Pm	0.098	3.97	----	----	4.54
Eu	0.095	3.62	2.61	4.73	4.61
Am	0.098	4.35	2.95	4.74	5.06
Cm	0.097	4.21	2.89	4.76	4.96

Comparison of K22DD with K-5 shows an increased stability for the aza-crown ether, which has a fixed cavity size. The extra stability could be a result of stronger bonding by the nitrogen donor groups in K22DD due to its relatively fixed stereochemistry compared to the more flexible K-5 molecule. Another factor could be the different basicity between the aliphatic nitrogen groups in K22DD and the aromatic nitrogen groups in K-5. More detailed studies of the two systems will be necessary to further understand the effects of these variables.

The results of this study reinforces the idea that nitrogen donor groups can be an important factor in the synergistic activity of macrocyclic compounds. Little evidence for significant size selectivity of these compounds for the trivalent lanthanides and actinides was observed. However, the significant differences in the organic phase stability constants of the synergistic complexes of the two families of elements provides promise that these molecules may be useful in the development of group separations based on synergistic solvent extraction processes.

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