SOLVENT EFFECT ON SYNERGISTIC EXTRACTION OF AMERICIUM(III)/
2-THENOYLTRIFLUOROACETONE/CROWN ETHER

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Abstract Extraction behavior of Am^{3+} with six kinds of crown ethers(CE) and 2-thenoyltrifluoroacetone(HTTA) in benzene, cyclohexane and 1,2-dichloroethane was studied. Synergistic extraction of $\text{Am}(\text{TTA})_3(\text{CE})$ was observed using benzene and cyclohexane and adduct formation constants were determined. We found the steric effect of CE is important as well as basicity of CE for the evaluation of the adduct formation constants. Ion-pair extraction of $\text{Am}(\text{TTA})_2(\text{CE})_n^+$ was observed with 1,2-dichloroethane.

Key words synergistic extraction, americium, crown ether,
2-thenoyltrifluoroacetone, solvent effect

Synergistic extraction is useful for the separation or concentration of metal ions with high coordination numbers such as actinides and lanthanides. There have been developed synergistic extraction systems, e.g., $\text{Am}(\text{III})/\text{HTTA}/\text{CE}[1-3]$, as well as lanthanides(III), actinides(III), (IV), or (VI)/ β -diketone or pyrazolone/TBP[4], alkylphosphine oxide[5], or heterocyclic amine[6]. Nakamura et. al.[6] reported that enhanced selectivity in the mutual separation of lanthanides could be obtained by using bidentate neutral ligand as an adduct. More enhancement of selectivity is, therefore, expected by employing multidentate adduct. CEs are the multidentate neutral ligands capable of separating metal ions of the same valency with different ionic radius. Although several works have been carried out on the synergistic extraction of actinides and lanthanides with CEs[7,8], the systematic elucidation on the extraction mechanism, the solvent effect and the chemical form or the stability of extracted species has not yet been achieved. In the present paper, the extraction of Am^{3+} was investigated using benzene(Bz), cyclohexane(Cy) and 1,2-dichloroethane(DCE) solution of HTTA and CEs, i.e., 15-crown-5 (15C5), 18-crown-6 (18C6), dicyclohexano-18C6(DC18C6), dibenzo-18C6(DB18C6), dicyclohexano-24-crown-8(DC24C8) and dibenzo-24C8(DB24C8) to elucidate the synergistic extraction mechanism.

EXPERIMENTAL

Chemicals Stock solution of Am^{3+} was prepared using hydrochloric acid solution of ^{241}Am . After removing the excess acid by evaporation, the residue was dissolved in concentrated perchloric acid and then evaporated to dryness. The perchloric acid treatment was repeated twice. The final residue obtained was dissolved with 10^{-3}M perchloric acid to result in 10^{-6}M Am^{3+} . The HTTA(Dojindo Lab.) purified by recrystallization and CEs(Aldrich Inc.) without further purification were employed. Spectroscopic grade organic solvents(Dojindo Lab.) were used without further purification.

Procedure Five ml of an organic solution of HTTA(10^{-3} ~ 0.1M) with or without CE (10^{-8} ~ 0.5M) and 5ml of an aqueous solution of 0.1M LiClO_4 and 10^{-3}M acetate buffer, unless otherwise noted, were placed in extraction vial(30ml) whose inner surface had been treated with dimethyldichlorosilane and methanol. After shaking for 30 min to attain pre-equilibrium, $50\mu\text{l}$ of Am -working solution was added to the aqueous phase and the vial was shaken again for 1h. After centrifugation and phase separation 2 ml of each phase was taken for γ -activity measurement with an $\text{NaI}(\text{Tl})$ well-type scintillation detector. The aqueous pH was measured after the phase separation. A distribution ratio of Am^{3+} was determined as the ratio of radioactivities of ^{241}Am in the organic

phase to that in the aqueous phase. The partition coefficients of CE (P_{CE}) between organic and aqueous solutions were determined by the measurement of concentration of CE in both phase by the ion-pair extraction-spectrophotometry using potassium picrate[9].

RESULTS AND DISCUSSION

The extraction constants ($K_{ex,0}$) of Am^{3+} by HTTA without CE in Bz, Cy and DCE were determined in order to evaluate the synergistic effect of Am^{3+} with HTTA and CE, and were obtained as follows: $\log K_{ex,0} = -8.13 \pm 0.26$ for Bz, -7.28 ± 0.21 for Cy and -8.38 ± 0.14 for DCE. Here, the reported values of partition coefficients of HTTA (P_{HTTA}) to be 1.63[10] for aq/Bz and 0.56[11] for aq/Cy were employed and P_{HTTA} for aq/DCE was determined to be 1.68. The acid dissociation constant of HTTA, pK_a , to be 6.23[12] reported was employed for the calculation.

The distribution ratios (D) of Am^{3+} were determined between Bz solution containing HTTA and CE and aqueous solution of pH 3.1 - 4.9. The results of $\log D$ were plotted against pH in Fig. 1 at $C_{HTTA} = 0.01M$ and $C_{CE} = 0.01M$. Here C_{HTTA} and C_{CE} denote the initial concentration of HTTA and CE, respectively. The $\log D_0 - pH$ plots for the extraction of Am^{3+} with HTTA in the absence of CE was calculated from $K_{ex,0}$, and given by the dotted line in Fig. 1. The D of Am^{3+} with CE was larger than that without CE for all CEs examined, which indicates the synergistic effect. The plots for each CE gave a straight line with a slope of 2.7 for 15C5, 2.7 for 18C6, 2.6 for DC18C6, 2.8 for DB18C6, 2.8 for DC24C8 and 2.7 for DB24C8. The $\log D - \log [HTTA]_{org}$ plots gave straight line with slope, e.g., 2.8 for $Am^{3+}/HTTA/18C6$ system or 3.1 for $Am^{3+}/HTTA/DC24C8$ system, and the $\log D - \log [CE]_{org}$ plots had linear portion with slopes, i.e., 1.0 for 15C5, 0.91 for 18C6, 0.89 for DC18C6, 1.0 for DB18C6, 0.88 for DC24C8, and 0.92 for DB24C8 in $Am^{3+}/HTTA/CE$ extraction system. Here, $[HTTA]_{org}$ and $[CE]_{org}$ denote the concentrations of HTTA and CE in Bz which were calculated from C_{HTTA} , P_{HTTA} , pK_a , C_{CE} and P_{CE} . The P_{CE} values determined are given in Table 1. From results as above, the extracted species was found to be $Am(TTA)_3(CE)$. The adduct formation constants ($\beta_{s,1}$) defined by eq.(1) was calculated by eq.(2) and summarized in Table 1.

$$\beta_{s,1} = (D - D_0)/D_0[CE]_{org} \quad (2)$$

The strength of the adduct complex could not be explained only by consulting with the basicity of CE as pointed out previously[1]. For example, $\beta_{s,1}$ for DC18C6 determined is smaller than that for 18C6, although DC18C6 with electron-donating cyclohexano- substituent is expected to form the adduct complex more favorably than 18C6. This implies the steric hindrance due to a large substituent in the adduct complex formation. The $\beta_{s,1}$ values for CEs with DC- or DB- substituent and with different number of ether groups show that the larger $\beta_{s,1}$ is obtained for CE with the more ether groups such as DC24C8 or DB24C8. Considering that an ionic diameter of Am^{3+} is close to the size between cavities of 15C5 and 18C6, the size-fitting effect of CE may not play an important role in the formation of $Am(TTA)_3(CE)$.

Fig. 1. Effect of pH on $\log D$ for Am^{3+} in Bz with 0.01M HTTA and 0.01M CEs.
(Δ) 15C5; ($\circ$) 18C6; ($\bullet$) DC18C6;
($\bullet$) DB18C6; ($\blacksquare$) DC24C8;
($\blacksquare$) DB24C8.

Fig. 2. Effect of pH on log D for Am^{3+} in Cy with 0.01M HTTA and 0.01M CEs.
(Δ) 15C5; ($\circ$) 18C6; ($\bullet$) DC18C6; ($\blacksquare$) DC24C8.

Fig. 3. Effect of pH on log D for Am^{3+} in DCE with 0.01M HTTA and 0.01M CEs.
(Δ) 15C5; ($\circ$) 18C6; ($\bullet$) DC18C6; ($\bullet$) DB18C6; ($\blacksquare$) DC24C8; ($\blacksquare$) DB24C8.

TABLE 1. The $\beta_{s,1}$ for synergistic extraction of Am^{3+} in benzene and cyclohexane with HTTA and CEs and the P_{CE} of CEs between 0.1M LiClO_4 aqueous and organic solutions.

CE	$\log \beta_{s,1}$		$\log P_{\text{CE}}$		
	Bz	Cy	Bz	Cy	DCE
15C5	4.59 ± 0.19	5.15 ± 0.21	-0.93 ± 0.02	-2.61 ± 0.03	-0.03 ± 0.01
18C6	4.98 ± 0.18	5.39 ± 0.13	-1.31 ± 0.06	-2.91 ± 0.05	0.01 ± 0.01
DC18C6	4.50 ± 0.16	4.69 ± 0.10	2.36 ± 0.01	1.08 ± 0.02	2.78 ± 0.02
DB18C6	3.53 ± 0.08	-	3.02 ± 0.03	1.18 ± 0.03	3.81 ± 0.20
DC24C8	4.55 ± 0.11	5.27 ± 0.19	2.17 ± 0.01	0.38 ± 0.01	2.76 ± 0.02
DB24C8	4.02 ± 0.12	-	3.20 ± 0.01	0.97 ± 0.02	3.96 ± 0.07

Bz:benzene; Cy:cyclohexane; DCE:1,2-dichloroethane

According to the same procedure as that for Fig. 1 but with Cy or DCE instead of Bz, D_s for the extraction of Am^{3+} were determined. Plots of $\log D$ - pH obtained with Cy and DCE containing are given in Figs. 2 and 3, respectively ($C_{\text{HTTA}} = 0.01\text{M}$, $C_{\text{CE}} = 0.01\text{M}$). Identically to the extraction in Bz, the synergistic effect by CE can be observed with Cy, and the extracted species was confirmed to be $\text{Am}(\text{TTA})_3(\text{CE})$. The adduct formation constants for four kinds of CEs were determined and added in Table 1. The $\beta_{s,1}$ value with the CE in Cy was larger than that with the respective CE in Bz, which agrees with a general concept that the adduct complex is liable to be formed in the solvent of less polarity.

The most remarkable feature of the extraction behavior with DCE as shown in Fig. 3 is that the slope of $\log D$ - pH plots are 2.0 for 18C6, 1.9 for DC18C6, 2.4 for 15C5, 2.3 for DC24C8 and 2.4 for DB24C8, instead of 3 observed in Figs. 1 and 2. The slope of $\log D$ - $\log [\text{HTTA}]_{\text{org}}$ plot was 2.0, when extraction was carried out using DCE with 18C6 ($C_{\text{HTTA}} = 10^{-3} - 0.03\text{M}$, $C_{\text{CE}} = 0.01\text{M}$, pH 3.5). These suggest that Am^{3+} can be extracted as ionic species, i.e., $\text{Am}(\text{TTA})_2(\text{CE})_n^+$ containing two TTA^- into DCE phase having comparatively high dielectric constant. In this connection, $\log D$ was less than -4 when the Am^{3+}

was extracted at pH 3.6 using DCE containing 0.01M CE in the absence of HTTA. Although the slopes of the $\log D - \log [CE]_{org}$ plots with 0.01M HTTA and 10^{-8} - 0.1M CE were scatter between 0.5 to 1.3, it is presumed that the extracted species may contain one molecule of CE. When tetraphenylborate or chloride ions was employed in the place of perchlorate ion as the counter anion (X^-) in the aqueous solution, $\log D$ with 18C6 were 1.7 for 10^{-3} M tetraphenylborate, 0.6 for 0.1M perchlorate and -1.7 for 0.1M chloride ions ($C_{HTTA} = 0.01M$, $C_{CE} = 0.01M$, pH 3.1), which supports the ion-pair extraction of $Am(TTA)_2(CE)^+$ with X^- . The slope of $\log D - pH$ plot for DB18C6 in Fig. 3 is exceptionally ca. 3 indicating synergistic extraction of $Am(TTA)_3(CE)$ even with DCE, although the synergistic effect observed is not pronounced in comparison with that observed in aq/Bz system. It is noteworthy that larger D values can be obtained at lower pH region in the ion-pair extraction of $Am(TTA)_2(CE)^+$ using DCE with HTTA and 18C6 or DC18C6 than in the synergistic extraction of $Am(TTA)_3(CE)$ using Bz or Cy. Furthermore extractability depends more strongly on the kind of CE using DCE than using Bz or Cy. In the ion-pair extraction system with DCE, D for 18C6 is larger than D for 15C5 and D for DC18C6 is larger than D for DC24C8, which implies that the size-fitting effect between Am^{3+} and CE may be involved in the formation of $Am(TTA)_2(CE)^+$ complex.

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