Solvent Extraction of Microamounts of Europium and Americium into Nitrobenzene by Using Hydrogen Dicarbollylcobaltate in the Presence of "classical" CMPO

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Abstract

Extraction of microamounts of europium and americium by a nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-) in the presence of octyl-phenyl – N,N – diisobutylcarbamoylmethyl phosphine oxide ("classical" CMPO, L) has been investigated. The equilibrium data have been explained assuming that the complexes HL^+, HL_2^+, ML_2^{3+}, ML_3^{3+} and ML_4^{3+}, ($M^{3+} = Eu^{3+}$, Am^{3+}) are extracted into the organic phase. The values of extraction and stability constants of the species in nitrobenzene saturated with water have been determined.

Keywords: Europium, americium, hydrogen dicarbollylcobaltate, CMPO, extraction and stability constants, water-nitrobenzene system

1. Introduction

Partitioning of transuranium elements, such as americium and curium, from high-level liquid radioactive waste (HLLW) and subsequent transmutation of these nuclides to shorter-lived nuclides largely facilitates safety and low cost of nuclear waste management.

A new class of extractants (bidentate phosphonates, phosphine oxides and malonamides) for the extraction of tervalent lanthanides and actinides from acidic media has been intensively studied.[1–3] A process using octyl-phenyl-N,N-diisobutylcarbamoylmethyl phosphine oxide (i.e. "classical" CMPO) and called TRUEX was apparently used in the United States,[1] while N, N-tetraalkyl alkyl propane diamides (RR´NCO)$_2$CHR´´ (DIAMEX) were proposed in France.[2]

In the present work, the solvent extraction of microamounts of europium and americium by a nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-)[4] in the presence of octyl-phenyl-N,N-diisobutylcarbamoylmethyl phosphine oxide ("classical" CMPO, L) was stu-

died. We intended to find the composition of the species in the nitrobenzene phase and to determine the corresponding equilibrium constants.

2. Experimental

Octyl-phenyl-N,N-diisobutylcarbamoylmethyl phosphine oxide (abbrev. "classical" CMPO) was supplied by Alpha – Ventron. Cesium dicarbollylcobaltate, Cs^+B^-, was synthesized in the Institute of Inorganic Chemistry, Řež, Czech Republic, using the method published by Hawthorne et al.[5] A nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-) was prepared from Cs^+B^- by the procedure described in Reference 6. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclides [241]Am[3+] and [152,154]Eu^{3+} (Polatom, Poland) were of standard radiochemical purity.

The extraction experiments in the two–phase water–HCl–M[3+](microamounts; $M^{3+} = Eu^{3+}$, Am^{3+})–nitrobenzene–"classical" CMPO–H^+B^- systems were performed in 10 mL glass test-tubes covered with polyethylene

stoppers, using 2 mL of each phase. The test-tubes filled with the solutions were shaken for 2 h at 25 ± 1 °C, using a laboratory shaker. Under these conditions, the equilibria in the systems under study were established after 20 min of shaking. Then the phases were separated by centrifugation. Afterwards, 1 mL samples were taken from each phase and their γ-activities were measured using a well-type NaI(T1) scintillation detector connected to a γ-analyzer NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratios of europium and americium, D, were determined as the ratios of the corresponding measured radioactivities of $^{152,154}Eu^{3+}$ and $^{241}Am^{3+}$ in the nitrobenzene and aqueous samples.

3. Results and Discussion

The dependences of the logarithm of the europium and americium distribution ratios (log D) on the logarithm of the numerical value of the total (analytical) concentration of the "classical" CMPO ligand in the initial nitrobenzene phase, log c(L), are given in Figures 1 and 2, respectively. The initial concentration of hydrogen dicarbollylcobaltate in the nitrobenzene phase, $c_B = 0.001$ mol L^{-1}, as well as the initial concentration of HCl in the aqueous phase, c(HCl) = 0.20 mol L^{-1}, are always related to the volume of one phase.

Regarding the results of previous papers,[7–14] the considered water–HCl–M^{3+} (microamounts; M^{3+} = Eu^{3+}, Am^{3+})–nitrobenzene–"classical" CMPO (L)–H^+B^- systems can be described by the set of reactions

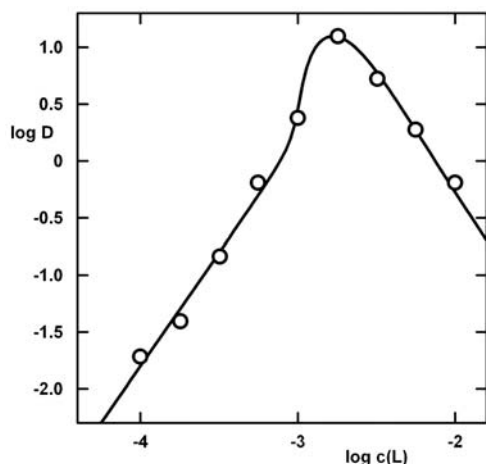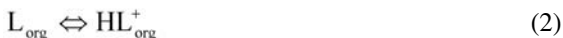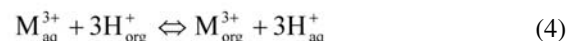$$L_{aq} \Leftrightarrow L_{org} \tag{1}$$

$$L_{org} \Leftrightarrow HL^+_{org} \tag{2}$$

$$H^+_{org} + 2L_{org} \Leftrightarrow HL^+_{2,org} \tag{3}$$

$$M^{3+}_{aq} + 3H^+_{org} \Leftrightarrow M^{3+}_{org} + 3H^+_{aq} \tag{4}$$

$$M^{3+}_{aq} + nL_{org} + 3H^+_{org} \Leftrightarrow ML^{3+}_{n,org} + 3H^+_{aq} \tag{5}$$

to which the following equilibrium constants correspond:

$$K_D = \frac{[L_{org}]}{[L_{aq}]} , \tag{6}$$

$$\beta(HL^+_{org}) = \frac{[HL^+_{org}]}{[H^+_{org}][L_{org}]} , \tag{7}$$

$$\beta(HL^+_{2,org}) = \frac{[HL^+_{2,org}]}{[H^+_{org}][L_{org}]^2} , \tag{8}$$

$$K_{ex}(M^{3+}_{org}) = \frac{[M^{3+}_{org}][H^+_{aq}]^3}{[M^{3+}_{aq}][H^+_{org}]^3} , \tag{9}$$

$$K_{ex}(ML^{3+}_{n,org}) = \frac{[ML^{3+}_{n,org}][H^+_{aq}]^3}{[M^{3+}_{aq}][L_{org}]^n[H^+_{org}]^3} . \tag{10}$$

The subscripts "aq" and "org" denote the aqueous and organic phases, respectively.

A subroutine UBBE, based on the relations given above, the mass balance of the "classical" CMPO ligand and the electroneutrality conditions in both phases of the system under consideration, was formulated[15,16] and introduced into a more general least-squares minimizing program LETAGROP[17] used for determination of the "best"
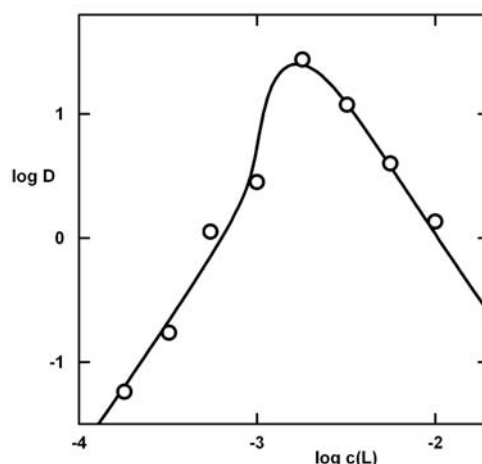

Figure 1. Log D as a function of log c(L) for the system water–HCl– Eu^{3+} (microamounts)–nitrobenzene–"classical"CMPO– H^+B^-. c(HCl) = 0.20 mol L^{-1}, $c_B = 0.001$ mol L^{-1}. The curve was calculated using the constants given in Table 3.

Figure 2. Log D as a function of log c(L) for the system water–HCl–Am^{3+}(microamounts)–nitrobenzene–"classical" CMPO– H^+B^-. c(HCl) = 0.20 mol L^{-1}, $c_B = 0.001$ mol L^{-1}. The curve was calculated using the constants given in Table 4.

values of the extraction constants $K_{ex}(ML_{n,org}^{3+})$ (M^{3+} = Eu^{3+}, Am^{3+}). The minimum of the sum of errors in log D, i.e., the minimum of the expression

$$U = \sum(\log D_{calc} - \log D_{exp})^2 \qquad (11)$$

was sought.

The values log K_D = 3.14,[13] log $\beta(HL_{org}^+)$ = 6.16,[13] log $\beta(HL_{2,org}^+)$ = 9.29,[13] log $K_{ex}(Eu_{org}^{3+})$ = 1.3[14] and log $K_{ex}(Am_{org}^{3+})$ = 1.5[14] were used for the respective calculations. The results are listed in Tables 1 and 2. From these tables it is evident that the extraction data can be best explained assuming the complexes ML_2^{3+}, ML_3^{3+} and ML_4^{3+} (M^{3+} = Eu^{3+}, Am^{3+}; L = "classical" CMPO) to be extracted into the nitrobenzene phase.

Figure 3 presents the contributions of the species Eu_{org}^{3+}, $EuL_{2,org}^{3+}$, $EuL_{3,org}^{3+}$ and $EuL_{4,org}^{3+}$ to the total europium concentration in the equilibrium nitrobenzene phase, whereas Figure 4 shows the contributions of the cations Am_{org}^{3+}, $AmL_{2,org}^{3+}$, $AmL_{3,org}^{3+}$ and $AmL_{4,org}^{3+}$ to the total americium concentration in the equilibrium organic phase. From both of these figures it follows that the complexes $EuL_{4,org}^{3+}$ and $AmL_{4,org}^{3+}$ are present in significant concentrations only at relatively high amounts of the "classical" CMPO ligand in the systems under consideration.
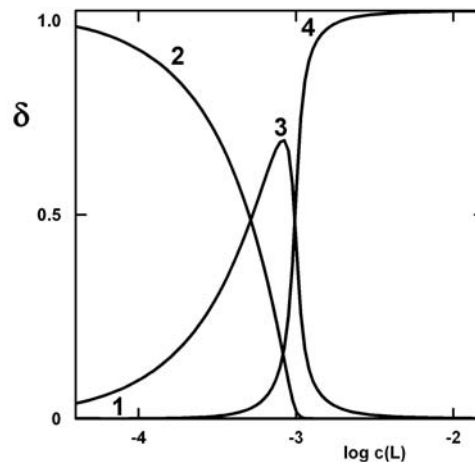

Figure 3. Distribution diagram of europium in the equilibrium nitrobenzene phase of the water–HCl–Eu^{3+}(microamounts)–nitrobenzene–"classical" CMPO–H^+B^- extraction system in the forms of Eu^{3+}, EuL_2^{3+}, EuL_3^{3+}, and EuL_4^{3+}. c(HCl) = 0.20 mol L^{-1}, c_B = 0.001 mol L^{-1}.
1 $\delta(Eu^{3+})$ = $[Eu_{org}^{3+}]/c(Eu^{3+})_{org}$,
2 $\delta(EuL_2^{3+})$ = $[EuL_{2,org}^{3+}]/c(Eu^{3+})_{org}$,
3 $\delta(EuL_3^{3+})$ = $[EuL_{3,org}^{3+}]/c(Eu^{3+})_{org}$,
4 $\delta(EuL_3^{3+})$ = $[EuL_{3,org}^{3+}]/c(Eu^{3+})_{org}$
where $c(Eu^{3+})_{org}$ = $[Eu_{org}^{3+}]$ + $[EuL_{2,org}^{3+}]$ + $[EuL_{3,org}^{3+}]$ + $[EuL_{3,org}^{3+}]$.
The distribution curves were calculated using the constants given in Table 3.

Table 1. Comparison of various models of europium extraction from aqueous solution of HCl by nitrobenzene solution of H^+B^- in the presence of "classical" CMPO.

Europium complexes in the organic phase	log K_{ex} [a]	U [b]
EuL_2^{3+}	22.21 (23.09)	65.80
EuL_3^{3+}	26.87 (27.37)	7.28
EuL_4^{3+}	31.52 (32.13)	14.10
EuL_2^{3+}, EuL_3^{3+}	transformed to EuL_3^{3+}	
EuL_3^{3+}, EuL_4^{3+}	26.14 (26.41), 30.40 (30.69)	0.52
EuL_2^{3+}, EuL_3^{3+}, EuL_4^{3+}	19.43 ± 0.24, 25.56 (25.87), 30.43 ± 0.14	0.05

[a] The values of the extraction constants are given for each complex. The reliability interval of the constants is given as $3\sigma(K)$, where $\sigma(K)$ is the standard deviation of the constant K.[17] These values are given in the logarithmic scale using the approximate expression log K ± {log [K + 1.5σ(K)] – log [K – 1.5σ(K)]}. For σ(K >0.2K, the previous expression is not valid and then only the upper limit is given in the parentheses in the form of log K(log [K + 3σ(K)]).[17]
[b] The error–square sum U = Σ (logD_{calc} – log D_{exp})^2.

Table 2. Comparison of various models of americium extraction from aqueous solution of HCl by nitrobenzene solution of H^+B^- in the presence of "classical" CMPO.

Americium complexes in the organic phase	log K_{ex} [a]	U [b]
AmL_2^{3+}	22.79 (23.70)	61.90
AmL_3^{3+}	27.14 (27.71)	8.55
AmL_4^{3+}	31.49 (32.04)	7.55
AmL_2^{3+}, AmL_3^{3+}	transformed to AmL_3^{3+}	
AmL_3^{3+}, AmL_4^{3+}	26.16 (26.41), 30.73 (30.96)	0.28
AmL_2^{3+}, AmL_3^{3+}, AmL_4^{3+}	19.48 (19.93), 25.82 (26.31), 30.73 (30.94)	0.07

[a] See Table 1, footnote *a*.   [b] See Table 1, footnote *b*.
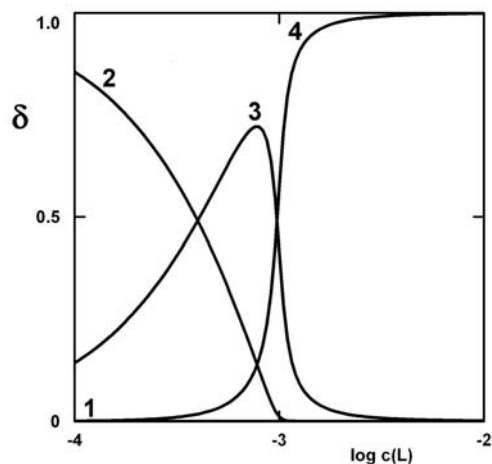
Figure 4. Distribution diagram of americium in the equilibrium nitrobenzene phase of the water–HCl–Am^{3+}(microamounts)–nitrobenzene–"classical" CMPO–H^+B^- extraction system in the forms of Am^{3+}, AmL_2^{3+}, AmL_3^{3+}, and AmL_4^{3+}. $c(HCl) = 0.20$ mol L^{-1}, $c_B = 0.001$ mol L^{-1}.

1 $\delta(Am^{3+}) = [Am_{org}^{3+}]/c(Am^{3+})_{org}$,
2 $\delta(AmL_2^{3+}) = [AmL_{2,org}^{3+}]/c(Am^{3+})_{org}$,
3 $\delta(AmL_3^{3+}) = [AmL_{3,org}^{3+}]/c(Am^{3+})_{org}$,
4 $\delta(AmL_4^{3+}) = [AmL_{3,org}^{3+}]/c(Am^{3+})_{org}$
where $c(Am^{3+})_{org} = [Am_{org}^{3+}] + [AmL_{2,org}^{3+}] + [AmL_{3,org}^{3+}] + [AmL_{3,org}^{3+}]$. The distribution curves were calculated using the constants given in Table 4.

Knowing the values log $K_{ex}(Eu_{org}^{3+}) = 1.3^{14}$ and log $K_{ex}(An_{org}^{3+}) = 1.5^{14}$, as well as the extraction constants log $K_{ex}(EuL_{2,org}^{3+}) = 19.43$, log $K_{ex}(EuL_{3,org}^{3+}) = 25.56$, log $K_{ex}(EuL_{4,org}^{3+}) = 30.43$, log $K_{ex}(AmL_{2,org}^{3+}) = 19.48$, log $K_{ex}(AmL_{3,org}^{3+}) = 25.82$ and log $K_{ex}(AmL_{4,org}^{3+}) = 30.73$ determined here (Tables 1 and 2), the stability constants of the complexes ML_2^{3+}, ML_3^{3+} and ML_4^{3+} ($M^{3+} = Eu^{3+}$, Am^{3+}; L = "classical" CMPO) in the nitrobenzene phase defined as

$$\beta(ML_{2,org}^{3+}) = \frac{[ML_{2,org}^{3+}]}{[M_{org}^{3+}][L_{org}]^2} , \qquad (12)$$

$$\beta(ML_{3,org}^{3+}) = \frac{[ML_{3,org}^{3+}]}{[M_{org}^{3+}][L_{org}]^3} , \qquad (13)$$

$$\beta(ML_{4,org}^{3+}) = \frac{[ML_{4,org}^{3+}]}{[M_{org}^{3+}][L_{org}]^4} , \qquad (14)$$

can be evaluated applying the simple relations:

$$\log\beta(ML_{2,org}^{3+}) = \log K_{ex}(ML_{2,org}^{3+}) - \log K_{ex}(M_{org}^{3+}), \quad (15)$$

$$\log\beta(ML_{3,org}^{3+}) = \log K_{ex}(ML_{3,org}^{3+}) - \log K_{ex}(M_{org}^{3+}), \quad (16)$$

$$\log\beta(ML_{4,org}^{3+}) = \log K_{ex}(ML_{4,org}^{3+}) - \log K_{ex}(M_{org}^{3+}). \quad (17)$$

The respective equilibrium constants are summarized in Tables 3 and 4.

Table 3. Equilibrium constants in the water–HCl–Eu^{3+} (microamounts)–nitrobenzene–"classical" CMPO–H^+B^- system.

Equilibrium	log K
$L_{aq} \Leftrightarrow L_{org}$	3.14 [a]
$H_{org}^+ + L_{org} \Leftrightarrow HL_{org}^+$	6.16 [a]
$H_{org}^+ + 2L_{org} \Leftrightarrow HL_{2,org}^+$	9.29 [a]
$Eu_{aq}^{3+} + 3H_{org}^+ \Leftrightarrow Eu_{org}^{3+} + 3H_{aq}^+$	1.3 [b]
$Eu_{aq}^{3+} + 2L_{org} + 3H_{org}^+ \Leftrightarrow EuL_{2,org}^{3+} + 3H_{aq}^+$	19.43
$Eu_{aq}^{3+} + 3L_{org} + 3H_{org}^+ \Leftrightarrow EuL_{3,org}^{3+} + 3H_{aq}^+$	25.56
$Eu_{aq}^{3+} + 4L_{org} + 3H_{org}^+ \Leftrightarrow EuL_{4,org}^{3+} + 3H_{aq}^+$	30.43
$Eu_{org}^{3+} + 2L_{org} \Leftrightarrow EuL_{2,org}^{3+}$	18.13
$Eu_{org}^{3+} + 3L_{org} \Leftrightarrow EuL_{3,org}^{3+}$	24.26
$Eu_{org}^{3+} + 4L_{org} \Leftrightarrow EuL_{4,org}^{3+}$	29.13

[a] Ref. 13. [b] Ref. 14.

Table 4. Equilibrium constants in the water–HCl–Am^{3+} (microamounts)–nitrobenzene–"classical" CMPO–H^+B^- system.

Equilibrium	log K
$L_{aq} \Leftrightarrow L_{org}$	3.14 [a]
$H_{org}^+ + L_{org} \Leftrightarrow HL_{org}^+$	6.16 [a]
$H_{org}^+ + 2L_{org} \Leftrightarrow HL_{2,org}^+$	9.29 [a]
$Am_{aq}^{3+} + 3H_{org}^+ \Leftrightarrow Am_{org}^{3+} + 3H_{aq}^+$	1.5 [b]
$Am_{aq}^{3+} + 2L_{org} + 3H_{org}^+ \Leftrightarrow AmL_{2,org}^{3+} + 3H_{aq}^+$	19.48
$Am_{aq}^{3+} + 3L_{org} + 3H_{org}^+ \Leftrightarrow AmL_{3,org}^{3+} + 3H_{aq}^+$	25.82
$Am_{aq}^{3+} + 4L_{org} + 3H_{org}^+ \Leftrightarrow AmL_{4,org}^{3+} + 3H_{aq}^+$	30.73
$Am_{org}^{3+} + 2L_{org} \Leftrightarrow AmL_{2,org}^{3+}$	17.98
$Am_{org}^{3+} + 3L_{org} \Leftrightarrow AmL_{3,org}^{3+}$	24.32
$Am_{org}^{3+} + 4L_{org} \Leftrightarrow AmL_{4,org}^{3+}$	29.23

[a] Ref. 13. [b] Ref. 14.

In conclusion, it should be noted that the stability constants of the complex species ML_2^{3+}, ML_3^{3+} and ML_4^{3+} ($M^{3+} = Eu^{3+}$, Am^{3+}; L = "classical" CMPO) in nitrobenzene saturated with water are log $\beta(EuL_{2,org}^{3+}) = 18.13$, log $\beta(AmL_{2,org}^{3+}) = 17.98$, log $\beta(EuL_{3,org}^{3+}) = 24.26$, log $\beta(AmL_{3,org}^{3+}) = 24.32$, log $\beta(EuL_{4,org}^{3+}) = 29.13$ and log $\beta(AmL_{4,org}^{3+}) = 29.23$ as follows from Tables 3 and 4. It means that the stability constants of the corresponding complexes EuL_n^{3+} and AmL_n^{3+}, where n = 2, 3, 4 and L is "classical" CMPO, in the mentioned medium are practically the same.

4. Acknowledgements

5. References

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Povzetek

Raziskovali smo ekstrakcijo mikrokoličin evropija in americija z raztopino vodikovega dikarbolilkobaltata (H^+B^-) v nitrobenzen ob prisotnosti oktil-fenil-N,N-diizobutilkarbamoilmetil fosfin oksida (CMPO, L). Dobljene rezultate smo obravnavali s predpostavko, da v organsko fazo preidejo kompleksi HL^+, HL_2^+, ML_2^{3+}, ML_3^{3+}, in ML_4^{3+}, (M^{3+} = Eu^{3+}, Am^{3+}) in določili konstante ekstakcije in stabilnosti kompleksov v nitrobenzenu, nasičenem z vodo.