Short communication

Extractive Properties of Synergistic Mixture of Hydrogen Dicarbollylcobaltate and N, N, N', N' - Tetraisobutyl - 2, 6 - Dipicolinamide in the Water - Nitrobenzene System with Regard to Eu³⁺ and Am³⁺

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Received: 17-01-2008

Abstract

Extraction of microamounts of europium and americium by a nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-) in the presence of N, N, N', N' - tetraisobutyl - 2, 6 - dipicolinamide [T(iBu)DPA, L] has been investigated. The equilibrium data have been explained assuming that the cations HL⁺, HL⁺₂, ML³⁺₂ and ML³⁺₃ (M³⁺ = Eu³⁺, Am³⁺) 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, N, N, N', N' - tetraisobutyl - 2, 6 - dipicolinamide, water-nitrobenzene system, extraction and stability constants

1. Introduction

The spent fuels contain both fissile and fertile residues of significant energy value and radioactive products, which make them very irradiant and which release an important amount of heat (mainly due to ⁹⁰Sr and ¹³⁷Cs, after five years of cooling). The radiotoxicity of these fuels can last for millions of years. Reprocessing is of great interest to recover uranium and plutonium, which can be recycled in the form of new nuclear fuels, and to optimize the conditioning of waste.

Reprocessing operations and particularly dismantling facilities generate medium level activity liquid wastes. A great part of these high salinity solutions has to be disposed of in stable geological formations or in longterm storage after embedding due to the presence of these long-lived nuclides, mainly actinides, ⁹⁰Sr and ¹³⁷Cs. It would be desirable to remove them from the contaminated liquid wastes before embedding in order to allow a large part of these wastes to be directed to a surface repository, and a very small part containing most of the long lived nuclides to be disposed of or stored after conditioning.

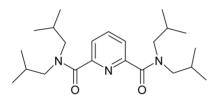
In order to minimize the volume of medium level activity waste or to separate long lived nuclides from high level activity waste, it is paramount importance to find compounds able to remove especially cesium, strontium and actinides (with high efficiency and selectivity) from acidic or high salinity media.

Dicarboxylic acid diamides are a subject of active research as potential extractants of actinides (in particular of minor actinides) from radioactive wastes. Important informations concerning substituted malonic diamides were

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reported.^{1,2} Lately, interest has shifted to the properties of tetraalkyl-diglycolamides,^{3–6} with emphasis on tetraoctyl-diglycolamide (TODGA) suggested as an extractant of Pu (IV), Np (IV), Am (III) and Cm (III) in solutions with hydrocarbon diluents.^{3–5} The ability of TODGA to extract many other metals was discussed^{6,7} and the very high extractive capacity of this agent was shown to allow its application as a solid extractant.⁸

Recently, the extraction properties of some 2, 6 - dipicolinamides have been investigated.⁹⁻¹² In the present work, the solvent extraction of microamounts of europium and americium by a nitrobenzene solution of hydrogen dicarbollylcobaltate $(H^+B^-)^{13}$ in the presence of N, N, N', N' - tetraisobutyl - 2, 6 - dipicolinamide [T(iBu)DPA, L] (see Scheme 1) was studied. We intended to find the composition of the species in the nitrobenzene phase and to determine the corresponding equilibrium constants.



Scheme 1: Structural formula of N, N, N', N' - tetraisobutyl - 2, 6 - dipicolinamide [abbrev. T(iBu)DPA].

2. Experimental

N, N, N', N' - tetraisobutyl - 2, 6 - dipicolinamide [abbrev. T(iBu)DPA] was produced as described in References 14 and 15. Cesium dicarbollylcobaltate, Cs⁺B⁻, was synthesized by means of the method published by Hawthorne et al.¹⁶ A nitrobenzene solution of hydrogen dicarbollylcobaltate (H⁺B⁻) was prepared from Cs⁺B⁻ by the procedure described elsewhere.¹⁷ The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclides ²⁴¹Am³⁺ and ^{152,154}Eu³⁺ (Polatom, Poland) were of standard radiochemical purity.

The extraction experiments in the two-phase water-HCl–M³⁺ (microamounts; M³⁺ = Eu³⁺, Am³⁺)-nitrobenzene-T(iBu)DPA-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 approximately 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 welltype 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 Eu³⁺ and 241 Am³⁺ 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 T(iBu)DPA 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, $c_B = 0.01 \text{ mol } L^{-1}$, as well as the initial concentration of HCl in the aqueous phase,

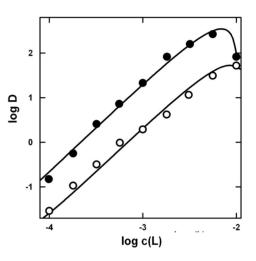


Figure 1: Log D as a function of log c (L), where L = T(iBu)DPA, for the system water-HCl–M³⁺(microamounts; M³⁺ = Eu³⁺, Am³⁺)-nitrobenzene-T(iBu)DPA–H⁺B⁻. c(HCl) = 0.20 mol L⁻¹, c_B = 0.01 mol L⁻¹; O Eu³⁺, • Am³⁺. The curves were calculated using the constants given in Tables 2 and 3.

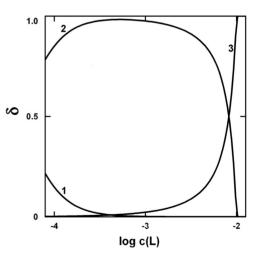


Figure 2: Distribution diagram of europium in the equilibrium nitrobenzene phase of the water-HCl-Eu³⁺(microamounts)-nitrobenzene-T(iBu)DPA- H⁺B⁻ extraction system in the forms of Eu³⁺, EuL₂³⁺ and EuL₃³⁺. c(HCl) = 0.20 mol L⁻¹, c_B = 0.01 mol L⁻¹. *I* δ (Eu³⁺) = [Eu₃³⁺] /c(Eu³⁺)_{org}, 2 δ (EuL₂³⁺) = [EuL_{2,org}³⁺] /c(Eu³⁺)_{org}, 4 δ (EuL₃³⁺) = [EuL_{3,org}³⁺] /c(Eu³⁺)_{org}, where c(Eu³⁺)_{org} = [Eu₃³⁺] + [EuL_{2,org}³⁺] + [EuL_{3,org}³⁺].

The distribution curves were calculated using the constants given in Table 2.

 $c(HCl) = 0.20 \text{ mol } L^{-1}$, are always related to the volume of one phase.

Regarding the previous results,^{18–23} the considered water- M^{3+} (microamounts; $M^{3+} = Eu^{3+}$, Am^{3+})-nitrobenzene-T(iBu)DPA(L)-H⁺B⁻ systems can be described by the set of reactions

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

$$H_{\rm org}^{+} + L_{\rm org} \Leftrightarrow HL_{\rm org}^{+}$$
(2)

$$H_{org}^{+} + 2L_{org} \Leftrightarrow HL_{2,org}^{+}$$
 (3)

$$M_{aq}^{3+} + 3H_{org}^{+} \Leftrightarrow M_{org}^{3+} + 3H_{aq}^{+}$$
(4)

$$M_{aq}^{3+} + nL_{org} + 3H_{org}^{+} \Leftrightarrow ML_{n,org}^{3+} + 3H_{aq}^{+}$$
(5)

to which the following equilibrium constants correspond:

$$K_{\rm D} = \frac{[L_{\rm org}]}{[L_{\rm so}]} \tag{6}$$

$$\beta(\mathrm{HL}_{\mathrm{org}}^{+}) = \frac{[\mathrm{HL}_{\mathrm{org}}^{+}]}{[\mathrm{H}_{\mathrm{org}}^{+}][\mathrm{L}_{\mathrm{org}}]}$$
(7)

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

$$K_{ex}(M_{org}^{3+}) = \frac{[M_{org}^{3+}][H_{aq}^{+}]^{3}}{[M_{aq}^{3+}][H_{org}^{+}]^{3}}$$
(9)

$$K_{ex}(ML_{n,org}^{3+}) = \frac{[ML_{n,org}^{3+}][H_{aq}^{+}]^{3}}{[M_{aq}^{3+}][L_{org}]^{n}[H_{org}^{+}]^{3}}$$
(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 T(iBu)DPA ligand and the electroneutrality conditions in both phases of the system under consideration, was formulated^{24,25} and introduced into a more general least-squares minimizing program LETAGROP²⁶ used for determination of the "best" values of the extraction constants K_{ex} (ML³⁺_{n,org}) (M³⁺ = Eu³⁺, Am³⁺). The minimum of the sum of errors in log D, i.e., the minimum of the expression

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

was sought.

The values log $K_D = 1.57$ (see Table 2, footnote *a*), log β (HL⁺_{org}) = 9.4 (see Table 2, footnote *b*), log β (HL⁺_{2,org}) = 10.8(see Table 2, footnote *b*), log $K_{ex}(Eu_{org}^{3+}) = 1.3^{23}$ and log $K_{ex}(Am_{org}^{3+}) = 1.5^{23}$ were used for the respective calculations. The results are listed in Table 1. From this table it is evident that the extraction data can be best explained assuming the complexes ML_2^{3+} and $ML_3^{3+}[M^{3+} = Eu^{3+}, Am^{3+}; L = T(iBu)DPA]$ to be extracted into the nitrobenzene

Table 1: Comparison of various models of europium and americium extraction from aqueous solution of HCl by nitrobenzene solution of H^+B^- in the presence of T(iBu)DPA.

Europium and americiu complexes in the organic phase	$\log K_{ex}^{a}$	U ^b
	$Eu^{3+} - T(iBu)DPA$	
EuL ₂ ³⁺	25.41 (25.94)	8.30
$\operatorname{EuL}_{3}^{\overline{3}_{+}}$	35.14 (35.69)	6.70
$\operatorname{EuL}_2^{3+}$, $\operatorname{EuL}_3^{3+}$	25.06 (25.26), 33.76 (34.16)	0.04
	Am ³⁺ – T(iBu)DPA	
AmL ₂ ³⁺	26.29 (26.73)	4.53
$AmL_3^{\tilde{3}+}$	36.16 (36.70)	8.24
$AmL_{2}^{3+}, AmL_{3}^{3+}$	$26.04 \pm 0.15, 34.02 \ (34.32)$	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.²⁶ These values are given in the logarithmic scale using the approximate expression log K $\pm \{\log [K + 1.5\sigma(K)] - \log [K - 1.5\sigma(K)]\}$ For $\sigma(K) > 0.2$ K, 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 + $3\sigma(K)$].²⁶

^b The error-square sum U = $\sum (\log D_{calc} - \log D_{exp})^2$.

Table 2: Equilibrium constants in the water-HCl- Eu^{3+} (microamounts)-nitrobenzene-T(iBu)DPA-H⁺B⁻ system.

Equilibrium	log K
$L_{aq} \Leftrightarrow L_{org}$	1.57 ^a
$H_{org}^{+} + L_{org} \Leftrightarrow HL_{org}^{+}$	9.4 ^b
$H_{org}^{+} + 2L_{org} \Leftrightarrow HL_{2,org}^{+}$	10. 8 ^b
$Eu_{aq}^{3+} + 3H_{org}^{+} \Leftrightarrow Eu_{org}^{3+} + 3H_{aq}^{+}$	1.3 ^c
$\operatorname{Eu}_{\operatorname{aq}}^{3+} + 2L_{\operatorname{org}} + 3H_{\operatorname{org}}^{+} \Leftrightarrow \operatorname{Eu}_{2,\operatorname{org}}^{3+} + 3H_{\operatorname{aq}}^{+}$	25.06
$Eu_{aq}^{3+} + 3L_{org} + 3H_{org}^{+} \Leftrightarrow EuL_{3 org}^{3+} + 3H_{aq}^{+}$	33.76
$\operatorname{Eu}_{\operatorname{org}}^{3+} + 2L_{\operatorname{org}} \Leftrightarrow \operatorname{Eu}_{2,\operatorname{org}}^{3+}$	23.76
$\underline{\operatorname{Eu}}_{\operatorname{org}}^{3+} + 3L_{\operatorname{org}} \Leftrightarrow \operatorname{Eu}L_{3,\operatorname{org}}^{3+}$	32.46

^a Determined by the method of the concentration dependent distribution.²¹

^b Determined by the method described in detail in Ref. 22.

^c Ref. 23.

phase.

Knowing the values log $K_{ex}(Eu_{org}^{3+}) = 1.3^{23}$ and log $K_{ex}(Am_{org}^{3+}) = 1.5$,²³ as well as the extraction constants log $K_{ex}(EuL_{2org}^{3+}) = 25.06$, log $K_{ex}(EuL_{3,org}^{3+}) = 33.76$, log $K_{ex}(AmL_{2,org}^{3+}) = 26.04$, and log $K_{ex}(AmL_{3,org}^{3+}) = 34.02$ determined here (Table 1), the stability constants of the complexes ML_{2}^{3+} and ML_{3}^{3+} [$M^{3+} = Eu^{3+}$, Am^{3+} ; L = T(iBu)DPA] in the nitrobenzene phase defined as

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

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

can be evaluated applying the simple relations:

$$\log \beta(ML_{2,org}^{3+}) = \log K_{ex}(ML_{2,org}^{3+}) - \log K_{ex}(M_{org}^{3+})$$
(14)

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

The respective equilibrium constants are summarized in Tables 2 and 3.

Table 3: Equilibrium constants in the water-HCl-Am³⁺ (microa-mounts)-nitrobenzene-T(iBu)DPA – H^+B^- system.

Equilibrium	log K
$L_{aq} \Leftrightarrow L_{org}$	1.57 ^a
$H_{org}^{+} + L_{org}^{-} \Leftrightarrow HL_{org}^{+}$	9.4 ^b
$H^+_{org} + 2L^{org} \Leftrightarrow HL^+_{2,org}$	10. 8 ^b
$Am_{aq}^{3+} + 3H_{org}^{+} \Leftrightarrow Am_{org}^{3+} + 3H_{aq}^{+}$	1.5 ^c
$Am_{aq}^{3+} + 2L_{org} + 3H_{org}^{+} \Leftrightarrow AmL_{2,org}^{3+} + 3H_{aq}^{+}$	26.04
$Am_{aq}^{3+} + 3L_{org} + 3H_{org}^{+} \Leftrightarrow AmL_{3,org}^{3+} + 3H_{aq}^{+}$	34.02
$Am_{org}^{3+} + 2L_{org} \Leftrightarrow AmL_{2,org}^{3+}$	24.54
$Am_{org}^{3+} + 3L_{org}^{-} \Leftrightarrow AmL_{3,org}^{3+}$	32.52

^a Determined by the method of the concentration dependent distribution.²¹ ^b Determined by the method described in detail in Ref. 22. ^c Ref. 23.

Finally, Figures 2 and 3 depict the contributions of the species M_{org}^{3+} , $ML_{2,org}^{3+}$ and $ML_{3,org}^{3+}$ ($M^{3+} = Eu^{3+}$, Am^{3+}) to the total trivalent metal cation concentrations in the corresponding equilibrium organic phase. From both of these figures it follows that the complexes $EuL_{3,org}^{3+}$ and $AmL_{3,org}^{3+}$ are present in significant concentrations in the equilibrium nitrobenzene phase only at relatively high amounts of the T(iBu)DPA ligand in the systems under consideration.

In conclusion, it should be noted that the stability constants of the complex species ML_2^{3+} and ML_3^{3+} [$M^{3+} = Eu^{3+}$, Am^{3+} ; L = T(iBu)DPA] in water saturated nitrobenzene are log β (EuL_{2,org}^{3+}) =23.76, log β (EuL_{3,org}^{3+}) = 32.46, log β (AmL_{2,org}^{3+}) =24.54 and log β (AmL_{3,org}^{3+}) =32.53 as given in Tables 2 and 3. It means that in the mentioned medium the stability constants of the complexes EuL_{3,org}^{3+} and AmL_{3,org}^{3+} are practically the same, whereas the stability of EuL_{2,org}^{3+} is somewhat lower than that of the corresponding AmL_{2,org}^{3+} complex cation.

4. Acknowledgement

The present work was supported by the Czech Ministry of Education, Youth and Sports, Projects MSM 4977751303 and MSM 6046137307.

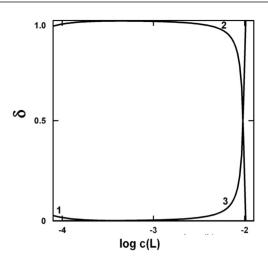


Figure 3: Distribution diagram of americium in the equilibrium nitrobenzene phase of the water-HCl–Am³⁺(microamounts)-nitrobenzene-T(iBu)DPA-H⁺B⁻ extraction system in the forms of AmL³⁺, AmL³⁺₂ and AmL³⁺₃. c(HCl) = 0.20 mol L⁻¹, c_B = 0.01 mol L⁻¹. *I* $\delta(Am^{3+}) = [Am^{3+}_{org}]/c(Am^{3+})_{org}$, *2* $\delta(AmL^{3+}_{2}) = [AmL^{3+}_{2,org}]/c(Am^{3+})_{org}$, where $c(Am^{3+})_{org} = [Am^{3+}_{2,org}] + [AmL^{3+}_{2,org}]/c(Am^{3+})_{org}$.

The distribution curves were calculated using the constants given in Table 3.

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Povzetek

Raziskovali smo ekstrakcijo mikrokoličin evropija ter americija z raztopinami hidrogen dicarbolilkobaltata (H^+B^-) v prisotnosti N, N, N', N' - tetraisobutil - 2, 6 - dipikolinamida [T(iBu)DPA, L] v nitrobenzen. Ravnotežja smo obravnavali ob predpostavki, da se kationi HL⁺, HL⁺₂, ML³⁺₃ in ML³⁺₃ ($M^{3+} = Eu^{3+}$, Am³⁺) ekstrahirajo v organsko fazo ter določili konstante porazdelitve ter konstante stabilnosti kompleksov.