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Solvent extraction of trivalent europium and americium into nitrobenzene by using hydrogen dicarbollylcobaltate and tetraisopropyl[oxybis(2,1-ethanediyiminocarbonyl)]-bisphosphoramidate

EMANUEL MAKRLÍK^{1*}, PETR VAŇURA², PAVEL SELUCKÝ³
and VASILIJ BRUSKO⁴

¹Faculty of Environmental Sciences, Czech University of Life Sciences, Prague, Kamýcká 129, 165 21 Prague 6-Suchbát, Czech Republic, ²Department of Analytical Chemistry, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic, ³Nuclear Research Institute, 250 68 Řež, Czech Republic and ⁴JSC NIIneftpromchim, N. Erschova st., 29, Kazan, 420061, Russia

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Abstract: Solvent extraction of micro-amounts of Eu^{3+} and Am^{3+} from water into nitrobenzene by means of a mixture of hydrogen dicarbollylcobaltate (H^+B^-) and tetraisopropyl[oxybis(2,1-ethanediyiminocarbonyl)]-bisphosphoramidate (L) was studied. The equilibrium data were explained assuming that the species HL^+ , ML_2^{3+} and ML_3^{3+} ($\text{M}^{3+} = \text{Eu}^{3+}$ or Am^{3+}) are extracted into the organic phase. Extraction and stability constants of the cationic complex species in nitrobenzene saturated with water were determined and discussed. From the experimental results, it is obvious that this effective ligand L for the Eu^{3+} and Am^{3+} could be considered as a potential extraction agent for nuclear waste treatment.

Keywords: liquid–liquid extraction; europium; americium; *N*-phosphorylated bis-urea; extraction and stability constants; water–nitrobenzene system.

INTRODUCTION

Dicarboxylic acid diamides are a subject of active research as potential extractants of actinides (in particular of minor actinides) from radioactive wastes. Important information concerning substituted malonic diamides has been reported.^{1,2} Lately, interest has shifted to the properties of tetraalkyldiglycolamides,^{3–6} with emphasis on tetraoctyldiglycolamide (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 has been discussed^{6,7} and the very high extractive capacity of this agent was shown to allow

* Corresponding author. E-mail: makrlik@centrum.cz
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its application as a solid extractant.⁸ Complexation of trivalent lanthanides and actinides with several novel diglycolamide-functionalized calixarenes has been studied recently.^{9–11} Besides, some of these functionalized calixarenes have been applied for the isolation of carrier-free ⁹⁰Y from ⁹⁰Sr.¹²

The dicarbollylcobaltate anion¹³ and some of its halogen derivatives have been employed often for the solvent extraction of various metal cations (*e.g.*, Cs⁺, Sr²⁺, Ba²⁺, Eu³⁺ and Am³⁺) from aqueous solutions into a polar organic phase, both under laboratory conditions for theoretical or analytical purposes,^{14–18} and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.^{19,20} In this context we must state that the very bulky lipophilic dicarbollylcobaltate anion is present practically only in the equilibrium polar organic phase of the investigated two-phase extraction system¹³ so that this univalent hydrophobic anion significantly facilitates the extraction of the mentioned cations from the aqueous phase into the organic one. Furthermore, a process involving chlorinated cobalt dicarbollide, polyethylene glycol, and diphenyl-*N,N*-dibutylcarbamoylmethyl phosphine oxide, also called UNEX, has been suggested for the simultaneous recovery of cesium, strontium, lanthanides, and actinides from highly acidic media into phenyltrifluoromethyl sulfone (abbrev. FS-13).^{19,20} It is necessary to emphasize that the FS-13 diluent was developed for the UNEX process as an alternative organic diluent to the highly polar nitrobenzene. Finally, FS-13 has the advantage of low viscosity and good solubility of metal solvates as well as the UNEX extractants.²⁰

Recently, diamides of 1,10-phenanthroline-2,9-dicarboxylic acid have been proposed as selective extractants for trivalent europium and curium. The mixture of *N*²,*N*²,*N*⁹,*N*⁹-tetraoctyl-1,10-phenanthroline-2,9-dicarboxamide and Br-Cosan effectively extracts americium with a separation factor ($SF_{Am/Eu}$) over forty.²¹ High $SF_{Am/Eu}$ values (up to 51) have been also demonstrated for metal extraction by 1,10-phenanthroline-2,9-dicarboxamides from perchloric media.²²

In the present work, the solvent extraction of micro-amounts of trivalent europium and americium into nitrobenzene by using hydrogen dicarbollylcobaltate (H^+B^-)¹³ and tetraisopropyl[oxybis(2,1-ethanediyiminocarbonyl)]-bisphosphoramidate (abbrev. L; see Fig. 1) was investigated. In this context, we must emphasize that the mentioned electroneutral ligand denoted by L can be involved into a *N*-phosphorylated group, whose syntheses and complexation properties have been already published.²³ Further, we intended to find the composition

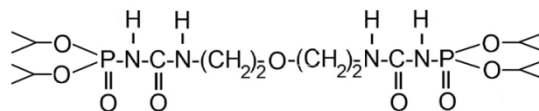


Fig. 1. Structural formula of tetraisopropyl[oxybis(2,1-ethanediyiminocarbonyl)]-bisphosphoramidate (abbrev. L).

of the species in the organic phase of the water–nitrobenzene extraction system and to determine the corresponding equilibrium constants. It means that the main aim of our study is discovering the respective extraction mechanisms and quantitative characterization of the investigated two-phase extraction systems.

EXPERIMENTAL

Chemicals

Tetraisopropyl[oxybis(2,1-ethanediyiminocarbonyl)]bisphosphoramidate (puriss., $\geq 99\%$; abbrev. L; see Fig. 1) was supplied by Kazan State University (Kazan, Russia), and it was employed as received. Cesium dicarbollylcobaltate, Cs^+B^- , was synthesized by the method published by Hawthorne *et al.*²⁴ Other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. A nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-)¹³ was prepared from Cs^+B^- by the procedure described elsewhere.²⁵ The carrier-free radionuclides $^{152,154}\text{Eu}^{3+}$ and $^{241}\text{Am}^{3+}$ were obtained from Polatom, Poland; their radionuclidic purities were 99.9%.

Extraction

The extraction experiments in the two-phase systems water– HNO_3 – $^{152,154}\text{Eu}^{3+}$ (ca. 30 kBq)–nitrobenzene–L– H^+B^- and water– HNO_3 – $^{241}\text{Am}^{3+}$ (ca. 30 kBq)–nitrobenzene–L– H^+B^- were performed in 10 mL polypropylene testtubes with polypropylene stoppers, using 2 mL of each phase. In these extraction systems, the respective initial aqueous phases additionally contained 1×10^{-6} mol L^{-1} of $\text{Eu}(\text{NO}_3)_3$. The testtubes filled with the solutions were shaken for 1 h at 25 ± 1 °C, using a laboratory shaker. However, under these conditions, the equilibria in the systems under study were established after approximately 15 min of shaking. Then the phases were separated by centrifugation. Finally, 1 mL samples were taken from each phase and their γ -activities were measured by means of a well-type NaI(Tl) scintillation detector connected to a γ -analyzer Triathler (Hidex, Turku, Finland).

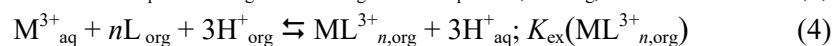
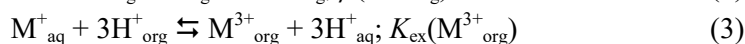
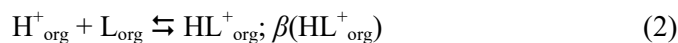
The equilibrium distribution ratios of europium and americium, D , were determined as the ratios of the corresponding measured radioactivities of $^{152,154}\text{Eu}^{3+}$ and $^{241}\text{Am}^{3+}$ in the nitrobenzene and aqueous samples (the uncertainties of these distribution ratios were always lower than 3%).

RESULTS AND DISCUSSION

The dependences of the logarithm of the europium and americium distribution ratios ($\log D$) on the logarithm of the total concentration of the electroneutral Tetraisopropyl[oxybis(2,1-ethanediyiminocarbonyl)]bisphosphoramidate ligand (L) in the initial nitrobenzene phase, $\log c(\text{L})$, are presented in Figs. 2 and 3. The initial concentrations of hydrogen dicarbollylcobaltate (H^+B^-) in the organic phase, $c_{\text{B}} = 0.0005$ and 0.001 mol L^{-1} , as well as the initial concentrations of HNO_3 in the aqueous phase, $c(\text{HNO}_3) = 0.20$ and 0.40 mol L^{-1} , are always related to the volume of one phase.

Regarding the results of our previous papers,^{13,16–18,26} the considered two-phase water– HNO_3 – M^{3+} (microamounts; $\text{M}^{3+} = \text{Eu}^{3+}$, Am^{3+})–nitrobenzene–L– H^+B^- systems can be described by the set of reactions:





to which the following equilibrium constants correspond:

$$K_{\text{D}} = \frac{[\text{L}_{\text{org}}]}{[\text{L}_{\text{aq}}]} \quad (5)$$

$$\beta(\text{HL}^+_{\text{org}}) = \frac{[\text{HL}^+_{\text{org}}]}{[\text{H}^+_{\text{org}}][\text{L}_{\text{org}}]} \quad (6)$$

$$K_{\text{ex}}(\text{M}^3+_{\text{org}}) = \frac{[\text{M}^3+_{\text{org}}][\text{H}^+_{\text{aq}}]^3}{[\text{M}^3+_{\text{aq}}][\text{H}^+_{\text{org}}]^3} \quad (7)$$

$$K_{\text{ex}}(\text{ML}^3+_{n,\text{org}}) = \frac{[\text{ML}^3+_{n,\text{org}}][\text{H}^+_{\text{aq}}]^3}{[\text{M}^3+_{\text{aq}}][\text{L}_{\text{org}}]^n[\text{H}^+_{\text{org}}]^3} \quad (8)$$

The subscripts “aq” and “org” denote the aqueous and organic phases, respectively. At this point we must add that Eq. (3) characterizes the investigated two-phase systems at $[\text{L}_{\text{org}}] \rightarrow 0$.

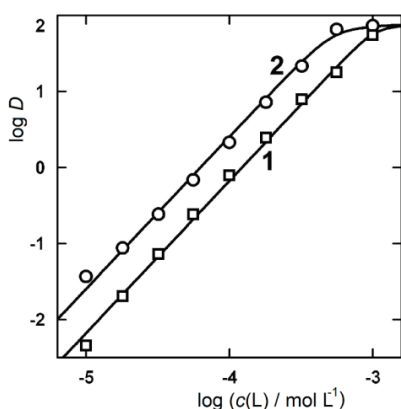


Fig. 2. Log D as a function of log $c(L)$ for the system water– HNO_3 – Eu^{3+} (microamounts)–nitrobenzene– L – H^1B ; **1** $c(\text{HNO}_3) = 0.40 \text{ mol L}^{-1}$, $c_{\text{B}} = 0.001 \text{ mol L}^{-1}$; **2** $c(\text{HNO}_3) = 0.20 \text{ mol L}^{-1}$, $c_{\text{B}} = 0.0005 \text{ mol L}^{-1}$. The curves were calculated using the constants given in Table I.

A subroutine UBBE, based on the relations given above, the mass balance of the ligand L and the electroneutrality conditions in both phases of the system under consideration, was formulated^{25,26} and introduced into a more general least-squares minimizing program LETAGROP²⁷ used for determination of the “best” values of the extraction constants $K_{\text{ex}}(\text{ML}^3+_{n,\text{org}})$ ($\text{M}^3+ = \text{Eu}^{3+}, \text{Am}^{3+}$). The minimum of the sum of squares of deviations in log D , *i.e.*, the minimum of the expression:

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

was sought.

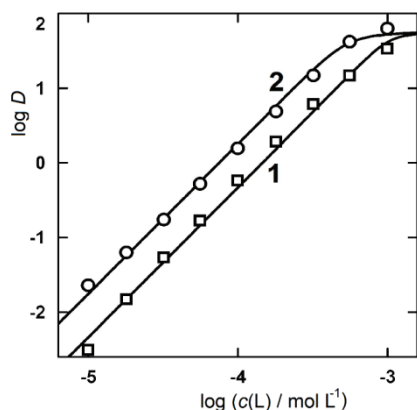


Fig. 3. Log D as a function of $\log c(L)$ for the system water– HNO_3 – Am^{3+} (microamounts)–nitrobenzene– L – H^+B^- ; **1** $c(\text{HNO}_3) = 0.40 \text{ mol L}^{-1}$, $c_{\text{B}} = 0.001 \text{ mol L}^{-1}$; **2** $c(\text{HNO}_3) = 0.20 \text{ mol L}^{-1}$, $c_{\text{B}} = 0.0005 \text{ mol L}^{-1}$. The curves were calculated using the constants given in Table II.

The values $\log K_{\text{D}} = 1.6$, $\log \beta(\text{HL}^+_{\text{org}}) = 4.6$, $\log K_{\text{ex}}(\text{Eu}^{3+}_{\text{org}}) = 1.3^{28}$ and $\log K_{\text{ex}}(\text{Am}^{3+}_{\text{org}}) = 1.5^{28}$ were used for the respective calculations. The results are listed in Tables I and II. From the results given in these tables it is evident that the extraction data can be best explained assuming the complexes ML_2^{3+} and ML_3^{3+} ($\text{M}^{3+} = \text{Eu}^{3+}, \text{Am}^{3+}$) to be extracted into the nitrobenzene phase because in these cases presented in Tables III and IV, the error - square sums (U) are the smallest.

TABLE I. Equilibrium constants in the water– HNO_3 – Eu^{3+} (microamounts)–nitrobenzene– L – H^+B^- system

| Equilibrium | $\log K$ |
|---|------------------|
| $L_{\text{aq}} \rightleftharpoons L_{\text{org}}$ | 1.6 ^a |
| $\text{H}^+_{\text{org}} + L_{\text{org}} \rightleftharpoons \text{HL}^+_{\text{org}}$ | 4.6 ^b |
| $\text{Eu}^{3+}_{\text{aq}} + 3\text{H}^+_{\text{org}} \rightleftharpoons \text{Eu}^{3+}_{\text{org}} + 3\text{H}^+_{\text{aq}}$ | 1.3 ^c |
| $\text{Eu}^{3+}_{\text{aq}} + 2L_{\text{org}} + 3\text{H}^+_{\text{org}} \rightleftharpoons \text{EuL}_2^{3+}_{\text{org}} + 3\text{H}^+_{\text{aq}}$ | 18.69 |
| $\text{Eu}^{3+}_{\text{aq}} + 3L_{\text{org}} + 3\text{H}^+_{\text{org}} \rightleftharpoons \text{EuL}_3^{3+}_{\text{org}} + 3\text{H}^+_{\text{aq}}$ | 23.26 |
| $\text{Eu}^{3+}_{\text{org}} + 2L_{\text{org}} \rightleftharpoons \text{EuL}_2^{3+}_{\text{org}}$ | 17.39 |
| $\text{Eu}^{3+}_{\text{org}} + 3L_{\text{org}} \rightleftharpoons \text{EuL}_3^{3+}_{\text{org}}$ | 21.96 |

^aDetermined by the method of the concentration dependent distribution;²⁹ ^bdetermined by the method described elsewhere;²⁸ ^cinferred from literature³⁰

Knowing the values $\log K_{\text{ex}}(\text{Eu}^{3+}_{\text{org}}) = 1.3$ and $\log K_{\text{ex}}(\text{Am}^{3+}_{\text{org}}) = 1.5$,³⁰ as well as the extraction constants $\log K_{\text{ex}}(\text{EuL}_2^{3+}_{\text{org}}) = 18.69$, $\log K_{\text{ex}}(\text{EuL}_3^{3+}_{\text{org}}) = 23.26$, $\log K_{\text{ex}}(\text{AmL}_2^{3+}_{\text{org}}) = 18.90$, and $\log K_{\text{ex}}(\text{AmL}_3^{3+}_{\text{org}}) = 23.64$ (Tables I and II), the stability constants of the complexes ML_2^{3+} and ML_3^{3+} ($\text{M}^{3+} = \text{Eu}^{3+}$ or Am^{3+}) in the nitrobenzene phase defined as:

$$\beta(\text{ML}^{3+}_{2,\text{org}}) = \frac{[\text{ML}^{3+}_{2,\text{org}}]}{[\text{M}^{3+}_{\text{org}}][\text{L}_{\text{org}}]^2} \quad (10)$$

$$\beta(\text{ML}^{3+}_{3,\text{org}}) = \frac{[\text{ML}^{3+}_{3,\text{org}}]}{[\text{M}^{3+}_{\text{org}}][\text{L}_{\text{org}}]^3} \quad (11)$$

can be calculated employing the following simple relations:

$$\log \beta(\text{ML}^{3+}_{2,\text{org}}) = \log K_{\text{ex}}(\text{ML}^{3+}_{2,\text{org}}) - \log K_{\text{ex}}(\text{M}^{3+}_{\text{org}}) \quad (12)$$

$$\log \beta(\text{ML}^{3+}_{3,\text{org}}) = \log K_{\text{ex}}(\text{ML}^{3+}_{3,\text{org}}) - \log K_{\text{ex}}(\text{M}^{3+}_{\text{org}}) \quad (13)$$

The respective equilibrium constants are summarized in Tables I and II. It should be noted that the stability constants of the cationic complexes ML_2^{3+} and ML_3^{3+} ($\text{M}^{3+} = \text{Eu}^{3+}, \text{Am}^{3+}$) in water-saturated nitrobenzene are $\log \beta(\text{EuL}_2^{3+}_{\text{org}}) = 17.39$, $\log \beta(\text{AmL}_2^{3+}_{\text{org}}) = 17.40$, $\log \beta(\text{EuL}_3^{3+}_{\text{org}}) = 21.96$, and $\log \beta(\text{AmL}_3^{3+}_{\text{org}}) = 22.14$, as given in Tables I and II. This means that the stability constants of the corresponding complexes EuL_n^{3+} and AmL_n^{3+} , where $n = 2, 3$, in the mentioned nitrobenzene medium are comparable.

TABLE II. Equilibrium constants in the water– HNO_3 – Am^{3+} (microamounts)–nitrobenzene– $\text{L-H}^+\text{B}^-$ system

| Equilibrium | $\log K$ |
|--|------------------|
| $L_{\text{aq}} \rightleftharpoons L_{\text{org}}$ | 1.6 ^a |
| $H^+_{\text{org}} + L_{\text{org}} \rightleftharpoons HL^+_{\text{org}}$ | 4.6 ^b |
| $\text{Am}^{3+}_{\text{aq}} + 3\text{H}^+_{\text{org}} \rightleftharpoons \text{Am}^{3+}_{\text{org}} + 3\text{H}^+_{\text{aq}}$ | 1.5 ^c |
| $\text{Am}^{3+}_{\text{aq}} + 2\text{L}_{\text{org}} + 3\text{H}^+_{\text{org}} \rightleftharpoons \text{AmL}_2^{3+}_{\text{org}} + 3\text{H}^+_{\text{aq}}$ | 18.90 |
| $\text{Am}^{3+}_{\text{aq}} + 3\text{L}_{\text{org}} + 3\text{H}^+_{\text{org}} \rightleftharpoons \text{AmL}_3^{3+}_{\text{org}} + 3\text{H}^+_{\text{aq}}$ | 23.64 |
| $\text{Am}^{3+}_{\text{org}} + 2\text{L}_{\text{org}} \rightleftharpoons \text{AmL}_2^{3+}_{\text{org}}$ | 17.40 |
| $\text{Am}^{3+}_{\text{org}} + 3\text{L}_{\text{org}} \rightleftharpoons \text{AmL}_3^{3+}_{\text{org}}$ | 22.14 |

^aDetermined by the method of the concentration dependent distribution; ²⁹ ^bdetermined by the method described elsewhere; ²⁸ ^cinferred from literature³⁰

TABLE III. Comparison of various models of europium extraction from aqueous solution of HNO_3 by nitrobenzene solution of H^+B^- in the presence of the ligand L; 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 .³¹ 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 $\sigma(K) > 0.2K$, the previous expression is not valid and then only the upper limit is given in the parentheses in the form of $\log K (\log [K + 3\sigma(K)])$; ³¹ $U = \Sigma(\log D_{\text{calc}} - \log D_{\text{exp}})^2$, the error-square sum

| Europium complexes in the organic phase | $\log K_{\text{ex}}$ | U |
|---|------------------------|------|
| EuL_2^{3+} | 19.17 (19.39) | 2.80 |
| EuL_3^{3+} | 24.32 (24.71) | 6.73 |
| $\text{EuL}_2^{3+}, \text{EuL}_3^{3+}$ | 18.69±0.12, 23.26±0.17 | 0.05 |

TABLE IV. Comparison of various models of americium extraction from aqueous solution of HNO₃ by nitrobenzene solution of H⁺B⁻ in the presence of the ligand L

| Americium complexes in the organic phase | log K_{ex} | U |
|---|------------------------|------|
| AmL ₂ ³⁺ | 19.02(19.24) | 2.86 |
| AmL ₃ ³⁺ | 24.30 (24.60) | 6.61 |
| AmL ₂ ³⁺ , AmL ₃ ³⁺ | 18.90±0.12, 23.64±0.14 | 0.05 |

Moreover, Figs. 4 and 5 show the contributions of the cations M³⁺_{org}, ML₂³⁺_{org} and ML₃³⁺_{org} (M³⁺ = Eu³⁺ or Am³⁺) to the total trivalent metal cation concentrations in the corresponding equilibrium organic phase. From Figs. 4 and 5 it follows that the species EuL₃³⁺_{org} and AmL₃³⁺_{org} are present in significant concentrations only at relatively high amounts of the ligand L in the systems under study.

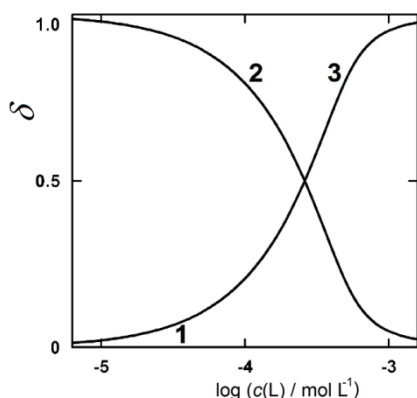


Fig. 4. Distribution diagram of europium in the equilibrium nitrobenzene phase of the water–HNO₃–Eu³⁺ (microamounts)–nitrobenzene–L–H⁺B⁻ extraction system in the forms of Eu³⁺, EuL₂³⁺ and EuL₃³⁺; $c(\text{HNO}_3) = 0.40 \text{ mol L}^{-1}$, $c_B = 0.001 \text{ mol L}^{-1}$. **1** – $\delta(\text{Eu}^{3+}) = [\text{Eu}^{3+}_{\text{org}}]/c(\text{Eu}^{3+})_{\text{org}}$, **2** – $\delta(\text{EuL}_2^{3+}) = [\text{EuL}_2^{3+}_{\text{org}}]/c(\text{Eu}^{3+})_{\text{org}}$, **3** – $\delta(\text{EuL}_3^{3+}) = [\text{EuL}_3^{3+}_{\text{org}}]/c(\text{Eu}^{3+})_{\text{org}}$, where $c(\text{Eu}^{3+})_{\text{org}} = [\text{Eu}^{3+}_{\text{org}}] + [\text{EuL}_2^{3+}_{\text{org}}] + [\text{EuL}_3^{3+}_{\text{org}}]$. The distribution curves were calculated using the constants given in Table I.

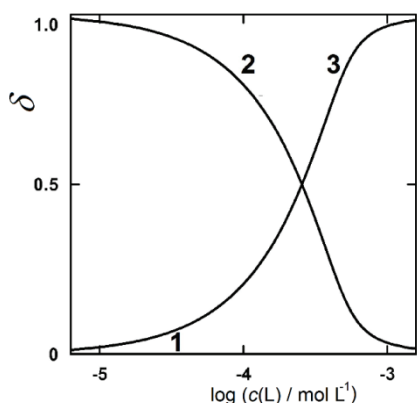


Fig. 5. Distribution diagram of americium in the equilibrium nitrobenzene phase of the water–HCl–Am³⁺ (microamounts)–nitrobenzene–L–H⁺B⁻ extraction system in the forms of Am³⁺, AmL₂³⁺ and AmL₃³⁺; $c(\text{HNO}_3) = 0.40 \text{ mol L}^{-1}$, $c_B = 0.001 \text{ mol L}^{-1}$. **1** – $\delta(\text{Am}^{3+}) = [\text{Am}^{3+}_{\text{org}}]/c(\text{Am}^{3+})_{\text{org}}$, **2** – $\delta(\text{AmL}_2^{3+}) = [\text{AmL}_2^{3+}_{\text{org}}]/c(\text{Am}^{3+})_{\text{org}}$, **3** – $\delta(\text{AmL}_3^{3+}) = [\text{AmL}_3^{3+}_{\text{org}}]/c(\text{Am}^{3+})_{\text{org}}$, where $c(\text{Am}^{3+})_{\text{org}} = [\text{Am}^{3+}_{\text{org}}] + [\text{AmL}_2^{3+}_{\text{org}}] + [\text{AmL}_3^{3+}_{\text{org}}]$. The distribution curves were calculated using the constants given in Table II.

On the other hand, the contributions of the cations Eu³⁺_{org} and Am³⁺_{org} are very small, as also follows from Figs. 4 and 5.

Finally, Table V summarizes the stability constants of the complex species ML_2^{3+} and ML_3^{3+} ($M^{3+} = Eu^{3+}$ or Am^{3+}) with two electroneutral ligands L (L = tetraisopropyl[oxybis(2,1-ethanediyiminocarbonyl)]-bisphosphoramidate, or 1,1'-(1,2-ethenediyil)-bis[1,1-diphenylphosphine oxide] (DPPEDO)) in water-saturated nitrobenzene. From the data reviewed in this table it is apparent that in the considered nitrobenzene medium, the stabilities of the complexes $ML_2^{3+}_{org}$ and $ML_3^{3+}_{org}$ ($M^{3+} = Eu^{3+}$ or Am^{3+}) containing the tetraisopropyl[oxybis(2,1-ethanediyiminocarbonyl)]bisphosphoramidate ligand are somewhat higher than those of the respective cationic complexes $ML_2^{3+}_{org}$ and $ML_3^{3+}_{org}$ ($M^{3+} = Eu^{3+}$ or Am^{3+}) with the ligand DPPEDO. It means that complexation ability towards Eu^{3+} and Am^{3+} of the tetraisopropyl[oxybis(2,1-ethanediyiminocarbonyl)]bisphosphoramidate ligand under study is also higher than that of the DPPEDO ligand.

TABLE V. Stability constants of the complexes ML_2^{3+} and ML_3^{3+} ($M^{3+} = Eu^{3+}$, Am^{3+} ; L = tetraisopropyl[oxybis(2,1-ethanediyiminocarbonyl)]bisphosphoramidate, or 1,1'-(1,2-ethenediyil)-bis-[1,1-diphenylphosphine oxide] (DPPEDO)) in nitrobenzene saturated with water at 25 °C

| Quantity | L:DPPEDO ^a | Tetraisopropyl[oxybis(2,1-ethanediyil- iminocarbonyl)]bisphosphoramidate ^b |
|--------------------------------|-----------------------|--|
| $\log \beta(EuL_2^{3+}_{org})$ | 15.42 | 17.39 |
| $\log \beta(EuL_3^{3+}_{org})$ | 19.74 | 21.96 |
| $\log \beta(AmL_2^{3+}_{org})$ | 15.10 | 17.40 |
| $\log \beta(AmL_3^{3+}_{org})$ | 20.15 | 22.14 |

^aRef. 32; ^bthis work

CONCLUSIONS

In the present work, the solvent extraction of trivalent europium and americium from acidic aqueous solutions into nitrobenzene was studied by means of hydrogen dicarbollylcobaltate (H^+B^-) and tetraisopropyl[oxybis(2,1-ethanediyiminocarbonyl)]-bisphosphoramidate (L). It was proven that the cationic species HL^+ , ML_2^{3+} and ML_3^{3+} ($M^{3+} = Eu^{3+}$ or Am^{3+}) are extracted into the organic phase of the water–nitrobenzene system. The stability constants of the corresponding complexes EuL_n^{3+} and AmL_n^{3+} , where $n = 2$ or 3, were found to be comparable in nitrobenzene saturated with water. It was evidenced experimentally that this ligand L can be considered in the nitrobenzene medium as the very strong receptor for the Eu^{3+} and Am^{3+} . On the basis of the previous facts, it is obvious that the investigated electroneutral ligand L could be also considered as a potential extraction agent for nuclear waste treatment.

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ИЗВОД

ТЕЧНО-ТЕЧНА ЕКСТРАКЦИЈА ТРОВАЛЕНТНОГ ЕУРОПИЈУМА И АМЕРИЦИЈУМА У НИТРОБЕНЗЕН ПОМОЋУ ВОДНИК ДИКАРБОЛИЛКОБАЛТАТА И ТЕТРАИЗОПРОПИЛ[ОКСИБИС(2,1-ЕТАНДИИЛИМИНОКАРБОНИЛ)]БИСФОСФОРАМИДАТА

EMANUEL MAKRLÍK¹, PETR VAŇURA², PAVEL SELUCKÝ³ и VASILIJ BRUSKO⁴

¹Faculty of Environmental Sciences, Czech University of Life Sciences, Prague, Kamýcká 129, 165 21 Prague 6-Suchdol, Czech Republic, ²Department of Analytical Chemistry, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic, ³Nuclear Research Institute, 250 68 Řež, Czech Republic и ⁴JSC NIIneftpromchim, N. Erschova st., 29, Kazan, 420061, Russia

Испитивана је екстракција течно–течно микро–количина Eu^{3+} и Am^{3+} из воде у нитробензен помоћу смеше водоник–дикарболилкобалтата (H^+B) и тетраизопропил[оксисис(2,1-етандиилиминокарбонил)]бисфосфорамидата (L). Равнотеже су објашњене претпоставком да су врсте HL^+ , ML_2^{3+} и ML_2^{3+} ($\text{M}^{3+} = \text{Eu}^{3+}$ или Am^{3+}) екстраховане у органску фазу. Одређене су и дискутоване константе екстракције и стабилности катјонских комплексних врста у нитробензену засићеном водом. Из експерименталних резултата произилази да би ефективни лиганд L за Eu^{3+} и Am^{3+} могао бити узет у обзир као потенцијални екстракциони агенс у третирању нуклеарног отпада.

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