Scientific paper

N,N,N',N'-Tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide as Very Effective Extraction Agent for Trivalent Europium and Americium

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Abstract

Solvent extraction of microamounts of Eu^{3+} and Am^{3+} from water into nitrobenzene by means of a mixture of hydrogen dicarbollylcobaltate (H^+B^-) and *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide (L) was studied. The equilibrium data were explained assuming that the species HL^+, H_2L^{2+}, HL_2^+, ML_2^{3+}, and ML_3^{3+} ($M^{3+} = Eu^{3+}$, Am^{3+}; L = *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide) are extracted into the nitrobenzene 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 evident that this effective *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide receptor for the Eu^{3+} and Am^{3+} cations could be considered as a potential extraction agent for nuclear waste treatment.

Keywords: Europium and americium; *N,N,N',N'*-Tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide; Extraction and stability constants; Water–nitrobenzene system; Solvent extraction.

1. Introduction

Removal of heavy metals from wastes and soils is a very urgent environmental and technological problem. Solvent extraction is one of the most popular methods for separation of hazardous metals and for radioactive waste processing. One of the most challenging tasks in high-level waste (HLW) processing is the separation of americium and curium from lanthanides. High selectivity of actinides/lanthanides separation has been achieved when polynitrogen extractants were employed.[1–9] However, in spite of very high separation factors for americium/europium separation, some ligands proposed so far have demonstrated some disadvantages (e. g., low chemical stability, slow kinetics, and limited solubility in diluents).

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.[10,11] Lately, interest has shifted to the properties of tetraalkyl-diglycolamides,[12–15] 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.[12–14] The ability of TODGA to extract many other metals has been discussed [15,16] and the very high extractive capacity of this agent was shown to allow its application as a solid extractant.[17] Complexation of trivalent lanthanides and actinides with several novel diglycolamide-functionalized calixarenes has been studied recently.[18–20] Besides, some of these functionalized calixarenes have been applied for the isolation of carrier-free ^{90}Y from ^{90}Sr.[21]

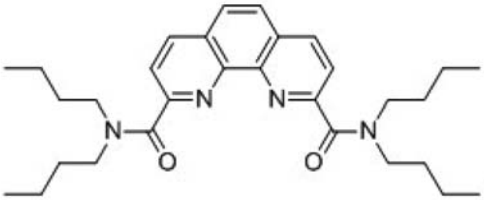
The dicarbollylcobaltate anion[22] and some of its halogen derivatives have been employed often for the solvent extraction of various metal cations (e. g., Cs^+, Sr^{2+}, Ba^{2+}, Eu^{3+}, and Am^{3+}) from aqueous solutions into a polar organic phase, both under laboratory conditions for theoretical or analytical purposes,[23–27] and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.[28,29] 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).[28,29] 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.[29] However, in Russia, nitrobenzene derivatives (e.g., 3-nitro-α,α,α-trifluorotoluene, also denoted by F-3) have been successfully utilized as diluents for cobalt dicarbollide processes.[28]

Recently, diamides of 1,10-phenanthroline-2,9-dicarboxylic acid have been proposed as selective extractants for trivalent americium and curium. The mixture of *N,N,N'N'*-tetraoctyl-1,10-phenanthroline-2,9-dicarboxamide and Br-cosan effectively extracts americium with a separation factor ($SF_{Am/Eu}$) over forty.[30] 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.[31]

In the current work, the solvent extraction of microamounts of trivalent europium and americium into nitrobenzene by using hydrogen dicarbollylcobaltate (H^+B^-)[22] and *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide (abbrev. L; see Scheme 1) was investigated. In this context we must add that the solvent extraction of these trivalent cations into nitrobenzene by means of the mentioned electroneutral *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide ligand (L) is nearly negligible; therefore, the mixture of H^+B^- and L was employed. Moreover, we intended to find the composition of the species in the organic phase of the water–nitrobenzene extraction system and to determine the corresponding equilibrium constants.

2. Experimental

N,N,N',N' - Tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide (puriss., ≥ 99%; abbrev. L; see Scheme 1) was supplied by St. Petersburg State University, Russia, and it was employed as received. Cesium dicarbollylcobaltate, Cs^+B^-, was synthesized by the method published by Hawthorne et al.[32] Other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. A nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-)[22] was prepared from Cs^+B^- by the procedure described elsewhere.[33] The carrier-free radionuclides $^{152,154}Eu^{3+}$ and $^{241}Am^{3+}$ were obtained from Polatom, Poland; their radionuclidic purities were 99.9%.



Scheme 1. Structural formula of *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide (abbrev. L).

The extraction experiments in the two–phase systems water–HNO_3–$^{152,154}Eu^{3+}$ (ca. 20 kBq) –nitrobenzene – L (*N,N,N',N'* – tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide) – H^+B^- and water–HNO_3–$^{241}Am^{3+}$ (ca. 20 kBq) –nitrobenzene – L (*N,N,N',N'* – tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide) – H^+B^- were performed in 10 mL polypropylene test-tubes with polypropylene stoppers, using 2 mL of each phase. In these extraction systems, the respective initial aqueous phases additionally contained 2×10^{-6} mol/L of $Eu(NO_3)_3$. The test-tubes filled with the solutions were shaken for 30 min at 25 ± 1 °C, using a laboratory shaker. However, under these conditions, the equilibria in the systems under study were established after approximately 5 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 $^{152,154}Eu^{3+}$ and $^{241}Am^{3+}$ in the nitrobenzene and aqueous samples (the uncertainties of these distribution ratios were always lower than 3%).

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 *N,N,N',N'* – tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide) ligand in the initial nitrobenzene phase, log c(L), are presented in Figures 1 and 2, as well as in Tables 1 and 2, respectively. The initial concentrations of hydrogen dicarbollylcobaltate (H^+B^-) in the organic phase, c_B = 0.0025 and 0.005 mol/L, as well as the initial concentration of HNO_3 in the aqueous phase, $c(HNO_3)$ = 0.05 mol/L, are always related to the volume of one phase. The occurrence of the characteristic maxima on these dependences can be explained qualitatively in terms of the competition between the charged trivalent complexes $ML^{3+}_{n,org}$ ($M^{3+} = Eu^{3+}$, Am^{3+}) and the protonized ligand L (i.e., HL^+_{org}, $H_2L^{2+}_{org}$, and $HL^+_{2,org}$; in detail, see the text below) during the balancing of the dicarbollylcobaltate electrostatic charge in the organic phase, analogously as in our previous work.[34]

Regarding the results of our previous papers,[22,25–27,35] the considered water–HNO_3–M^{3+} (microamounts; $M^{3+} = Eu^{3+}$, Am^{3+})–nitrobenzene– *N,N,N',N'*-tetrabutyl-1,10-

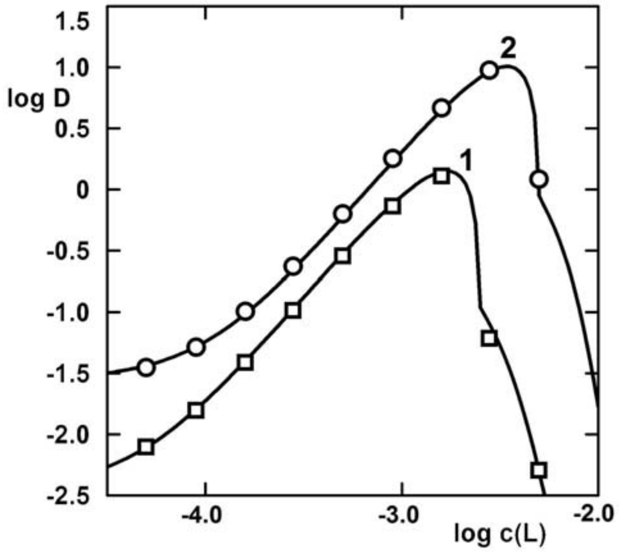


Figure 1. Log D as a function of log c(L), where L = *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide, for the system water – HNO_3–Eu^{3+}(microamounts)–nitrobenzene– *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide (L)–H^+B^-; **1** $c(HNO_3)$ = 0.05 mol/L, c_B = 0.0025 mol/L; **2** $c(HNO_3)$ = 0.05 mol/L, c_B = 0.005 mol/L. The curves were calculated using the constants given in Table 5.

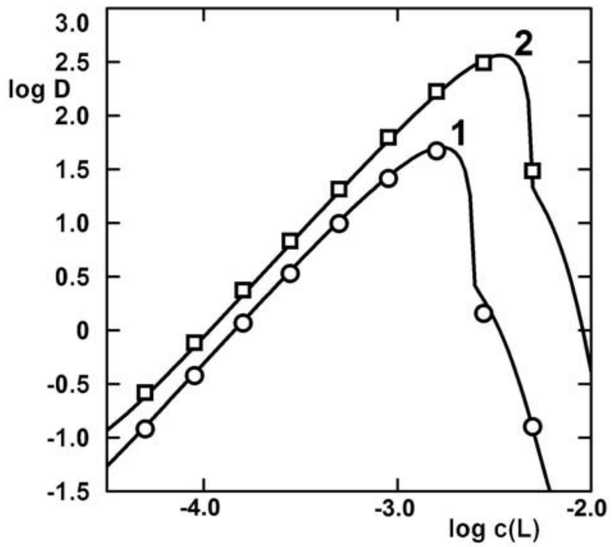


Figure 2. Log D as a function of log c(L), where L = *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide, for the system water – HNO_3–Am^{3+}(microamounts)–nitrobenzene– *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide (L)–H^+B^-; **1** $c(HNO_3)$ = 0.05 mol/L, c_B = 0.0025 mol/L; **2** $c(HNO_3)$ = 0.05 mol/L, c_B = 0.005 mol/L. The curves were calculated using the constants given in Table 6.

Table 1. Logarithm of the europium distribution ratio (log D) as a function of logarithm of the numerical value of the analytical concentration of the *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide ligand in the initial nitrobenzene phase (log c(L)); the values of log c(L) and log D are given for all experimental points.

$c(HNO_3)$ = 0.05 mol/L, c_B = 0.0025 mol/L
–4.301, –2.105; –4.046–1.805; –3.796, –1.413; –3.553, –0.987;
–3.301, –0.545; –3.046 –0.140; –2.796, 0.109; –2.553, –1.215;
–2.301 –2.297

$c(HNO_3)$ = 0.05 mol/L, c_B = 0.005 mol/L
–4.301, –1.455; –4.046, –1.288; –3.796, –0.994; –3.553, –0.630;
–3.301, –0.201; –3.046, 0.252; –2.796, 0.666; –2.553, 0.977;
–2.301, 0.084

Table 2. Logarithm of the americium distribution ratio (log D) as a function of logarithm of the numerical value of the analytical concentration of the *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide ligand in the initial nitrobenzene phase (log c(L)); the values of log c(L) and log D are given for all experimental points.

$c(HNO_3)$ = 0.05 mol/L, c_B = 0.0025 mol/L
–4.301, –0.921; –4.046, –0.422; –3.796, 0.065; –3.553, 0.526;
–3.301, 0.992; –3.046, 1.414; –2.796, 1.669; –2.553, 0.156;
–2.301, –0.901

$c(HNO_3)$ = 0.05 mol/L, c_B = 0.005 mol/L
–4.301, –0.584; –4.046, –0.117; –3.796, 0.372; –3.553, 0.831;
–3.301, 1.313; –3.046, 1.796; –2.796, 2.223; –2.553, 2.491;
–2.301, 1.482

phenanthroline-2,9-dicarboxamide (L)–H^+B^- systems can be described by the set of reactions:

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

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

$$2H^+_{org} + L_{org} \leftrightarrows H_2L^{2+}_{org} \tag{3}$$

$$H^+_{org} + 2L_{org} \leftrightarrows HL^+_{2,org} \tag{4}$$

$$M^{3+}_{aq} + 3H^+_{org} \rightleftarrows M^{3+}_{org} + 3H^+_{aq} \tag{5}$$

$$M^{3+}_{aq} + nL_{org} + 3H^+_{org} \rightleftarrows ML^{3+}_{n,org} + 3H^+_{aq} \tag{6}$$

to which the following equilibrium constants correspond:

$$K_D = \frac{[L_{org}]}{[L_{aq}]} \tag{7}$$

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

$$\beta(H_2L^{2+}_{org}) = \frac{[HL^{2+}_{2,org}]}{[H^+_{org}]^2[L_{org}]} \tag{9}$$

$$\beta(HL^+_{2,org}) = \frac{[HL^+_{2,org}]}{[H^+_{org}][L_{org}]^2} \tag{10}$$

$$K_{ex}(M^{3+}_{org}) = \frac{[M^{3+}_{org}][H^+_{aq}]^3}{[M^{3+}_{aq}][H^+_{org}]^3} \tag{11}$$

$$K_{ex}(ML^{3+}_{n,org}) = \frac{[ML^{3+}_{n,org}][H^+_{aq}]^3}{[M^{3+}_{aq}][L_{org}]^n[H^+_{org}]^3} \tag{12}$$

The subscripts "aq" and "org" denote the aqueous and organic phases, respectively. At this point we must add that Eq. (5) characterizes the investigated two-phase systems for $[L_{org}] \to 0$.

A subroutine UBBE, based on the relations given above, the mass balance of the *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide (L) ligand and the electroneutrality conditions in both phases of the system under consideration, was formulated [36,37] and introduced into a more general least-squares minimizing program LETAGROP [38] used for determination of the "best" values of the extraction constants $K_{ex}(ML^{3+}_{n,org})$ ($M^{3+} = Eu^{3+}$, Am^{3+}; L = *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide). The minimum of the sum of uncertainties in log D, i.e., the minimum of the expression

$$U = \sum(\log D_{calc} - \log D_{exp})^2 \tag{13}$$

was sought.

The values log K_D = 2.2 (see Table 5, footnote a), $\log\beta(HL^+_{org})$ = 9.4 (Table 5, footnote b), $\log\beta(H_2L^{2+}_{org})$ = 11.0 (Table 5, footnote b), $\log\beta(HL^+_{2,org})$ = 12.7 (Table 5, footnote b), log $K_{ex}(Eu^{3+}_{org})$ = 1.3 (inferred from Ref. 40), and $K_{ex}(Am^{3+}_{org})$ = 1.5 (inferred from Ref. 40) were used for the respective calculations. The results are listed in Tables 3 and 4. From these tables 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 = = *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide) to be extracted into the nitrobenzene phase.

Table 3. Comparison of various models of europium extraction from aqueous solution of HNO_3 by nitrobenzene solution of H^+B^- in the presence of *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide (L).

Europium complexes in the organic phase	logK$_{ex}$[a]	U[b]
EuL_2^{3+}	24.31 (24.79)	23.50
EuL_3^{3+}	32.84 (33.39)	17.60
EuL_2^{3+}, EuL_3^{3+}	23.76 ± 0.21, 31.12(31.41)	0.03

[a] The values of the extraction constants are given for each complex. The reliability interval of the constants is given as 3σ(K), where σ(K) is the standard deviation of the constant K.[38] 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) > 0.2 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 +3σ(K)]).[38]

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

Table 4. Comparison of various models of americium extraction from aqueous solution of HNO_3 by nitrobenzene solution of H^+B^- in the presence of *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide (L).

Americium complexes in the organic phase	logK$_{ex}$[a]	U [b]
AmL_2^{3+}	25.92 (26.59)	20.14
AmL_3^{3+}	34.46 (35.17)	16.98
AmL_2^{3+}, AmL_3^{3+}	25.15 ± 0.22, 32.24(32.52)	0.02

[a] See Table 3, footnote a. [b] See Table 3, footnote b.

Knowing the values $K_{ex}(Eu^{3+}_{org})$ = 1.3 and log $K_{ex}(Am^{3+}_{org})$, which were inferred from Ref. 40, as well as the extraction constants log $K_{ex}(EuL^{3+}_{2,org})$ = 23.76, log $K_{ex}(EuL^{3+}_{3,org})$ = 31.12, log $K_{ex}(AmL^{3+}_{2,org})$ = 25.15, and log $K_{ex}(AmL^{3+}_{3,org})$ = 32.24 (Tables 5 and 6), the stability constants of the complexes ML_2^{3+} and ML_3^{3+} ($M^{3+} = Eu^{3+}$, Am^{3+}; L = *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide) in the nitrobenzene phase defined as

$$\beta(ML^{3+}_{2,org}) = \frac{[ML^{3+}_{2,org}]}{[M^{3+}_{org}][L_{org}]^2} \tag{14}$$

$$\beta(ML^{3+}_{3,org}) = \frac{[ML^{3+}_{3,org}]}{[M^{3+}_{org}][L_{org}]^3} \tag{15}$$

can be calculated employing the following simple relations:

$$\log \beta (ML^{3+}_{2,\,org}) = \log K_{ex} (ML^{3+}_{2,org}) - \log K_{ex} (M^{3+}_{org}) \quad (16)$$

$$\log \beta (ML^{3+}_{3,\,org}) = \log K_{ex} (ML^{3+}_{3,org}) - \log K_{ex} (M^{3+}_{org}) \quad (17)$$

The respective equilibrium constants are summarized in Tables 5 and 6. It should be noted that the stability constants of the cationic complex species ML_2^{3+} and ML_3^{3+} ($M^{3+} = Eu^{3+}, Am^{3+}$; L = *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide) in water-saturated nitrobenzene are $\log\beta(EuL^{3+}_{2,org}) = 22.46$, $\log\beta(AmL^{3+}_{2,org}) = 23.65$, $\log\beta(EuL^{3+}_{3,org}) = 29.82$, and $\log\beta(AmL^{3+}_{3,org}) = 30.74$, as given in Tables 5 and 6. This means that in the mentioned nitrobenzene medium, the stability constants of the complexes $AmL^{3+}_{2,org}$ and $AmL^{3+}_{3,org}$ are somewhat higher than those of the corresponding cationic complex species $EuL^{3+}_{2,org}$ and $EuL^{3+}_{3,org}$.

Moreover, Figure 3 presents the contributions of the species H^+_{org}, HL^+_{org}, $H_2L^{2+}_{org}$, and $HL^+_{2,org}$ to the total hydrogen cation concentration in the equilibrium nitrobenzene phase, whereas Figures 4 and 5 show the contributions of the cations M^{3+}_{org}, $ML^{3+}_{2,org}$, and $ML^{3+}_{3,org}$ ($M^{3+} = Eu^{3+}, Am^{3+}$; L = *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicar-

Table 5. Equilibrium constants in the water–HNO_3–Eu^{3+}(microamounts)–nitrobenzene– *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide (L) – H^+B^- system.

Equilibrium	**log K**
$L_{aq} \Leftrightarrow L_{org}$	2.2 [a]
$H^+_{org} + L_{org} \Leftrightarrow HL^+_{org}$	9.4 [b]
$2H^+_{org} + L_{org} \Leftrightarrow H_2L^{2+}_{org}$	11.0 [b]
$H^+_{org} + 2L_{org} \Leftrightarrow HL^+_{2,org}$	12.7 [b]
$Eu^{3+}_{aq} + 3H^+_{org} \Leftrightarrow Eu^{3+}_{org} + 3H^+_{aq}$	1.3 [c]
$Eu^{3+}_{aq} + 2L_{org} + 3H^+_{org} \Leftrightarrow EuL^{3+}_{2,org} + 3H^+_{aq}$	23.76
$Eu^{3+}_{aq} + 3L_{org} + 3H^+_{org} \Leftrightarrow EuL^{3+}_{3,org} + 3H^+_{aq}$	31.12
$Eu^{3+}_{org} + 2L_{org} \Leftrightarrow EuL^{3+}_{2,org}$	22.46
$Eu^{3+}_{org} + 3L_{org} \Leftrightarrow EuL^{3+}_{3,org}$	29.82

[a] Determined by the method of the concentration dependent distribution.[39] [b] Determined by the method described in Ref. 34. [c] Inferred from Ref. 40.

Table 6. Equilibrium constants in the water–HCl–Am^{3+}(microamounts)–nitrobenzene– *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide (L) –H^+B^- system.

Equilibrium	**log K**
$L_{aq} \Leftrightarrow L_{org}$	2.2 [a]
$H^+_{org} + L_{org} \Leftrightarrow HL^+_{org}$	9.4 [b]
$2H^+_{org} + L_{org} \Leftrightarrow H_2L^{2+}_{org}$	11.0 [b]
$H^+_{org} + 2L_{org} \Leftrightarrow HL^+_{2,org}$	12.7 [b]
$Am^{3+}_{aq} + 3H^+_{org} \Leftrightarrow Am^{3+}_{org} + 3H^+_{aq}$	1.5 [c]
$Am^{3+}_{aq} + 2L_{org} + 3H^+_{org} \Leftrightarrow AmL^{3+}_{2,org} + 3H^+_{aq}$	25.15
$Am^{3+}_{aq} + 3L_{org} + 3H^+_{org} \Leftrightarrow AmL^{3+}_{3,org} + 3H^+_{aq}$	32.24
$Am^{3+}_{org} + 2L_{org} \Leftrightarrow AmL^{3+}_{2,org}$	23.65
$Am^{3+}_{org} + 3L_{org} \Leftrightarrow AmL^{3+}_{3,org}$	30.74

[a] Determined by the method of the concentration dependent distribution.[39] [b] Determined by the method described in Ref. 34. [c] Inferred from Ref. 40.

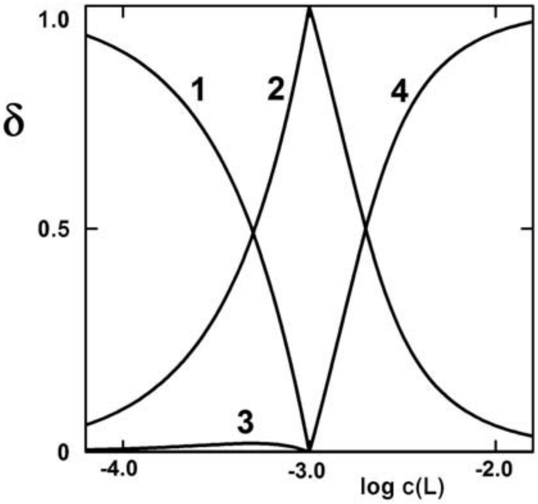


Figure 3. Distribution diagram of hydrogen cation in the equilibrium nitrobenzene phase of the water–HNO_3–Eu^{3+}(microamounts)–nitrobenzene– *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide (L)– H^+B^- extraction system in the forms of H^+, H_2L^{2+}, and HL_2^+; $c(HNO_3) = 0.05$ mol/L, $c_B = 0.0025$ mol/L. **1** $\delta(H^+) = [H^+_{org}]/c(H^+)_{org}$, **2** $\delta(HL^+) = [HL^+_{org}]/c(H^+)_{org}$, **3** $\delta(H_2L^{2+}) = 2\,[H_2L^{2+}_{org}]/c(H^+)_{org}$, **4** $\delta(HL_2^+) = [HL^+_{2,org}]/c(H^+)_{org}$, where $c(H^+)_{org} = [H^+_{org}] + [HL^+_{org}] + 2[H_2L^{2+}_{org}] + [HL^+_{2,org}]$. The distribution curves were calculated using the constants given in Table 5.

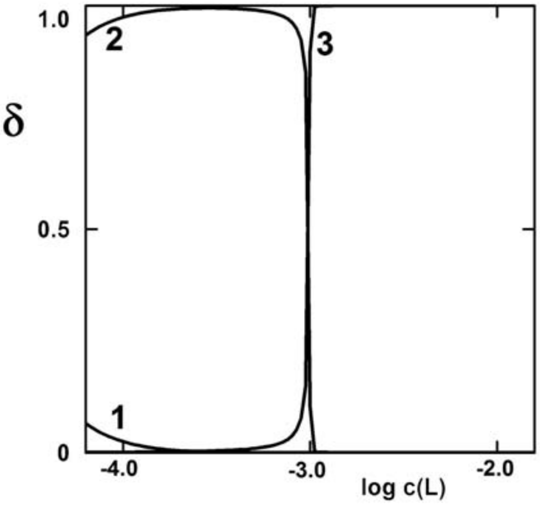


Figure 4. Distribution diagram of europium in the equilibrium nitrobenzene phase of the water–HNO_3–Eu^{3+}(microamounts)–nitrobenzene– *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide (L)– H^+B^- extraction system in the forms of Eu^{3+}, EuL_2^{3+}, and EuL_3^{3+}; $c(HNO_3) = 0.05$ mol/L, $c_B = 0.0025$ mol/L. **1** $\delta(Eu^{3+}) = [Eu^{3+}_{org}]/c(Eu^{3+})_{org}$, **2** $\delta(EuL_2^{3+}) = [EuL^{3+}_{2,org}]/c(Eu^{3+})_{org}$, **3** $\delta(EuL_3^{3+}) = [EuL^{3+}_{3,org}]/c(Eu^{3+})_{org}$, where $c(Eu^{3+})_{org} = [Eu^{3+}_{org}] + [EuL^{3+}_{2,org}] + [EuL^{3+}_{3,org}]$. The distribution curves were calculated using the constants given in Table 5.

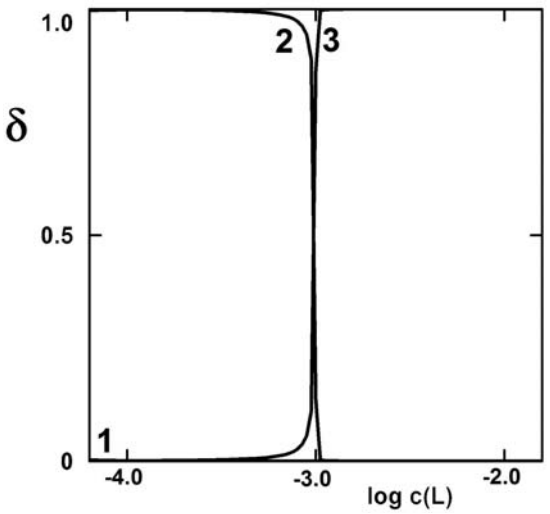
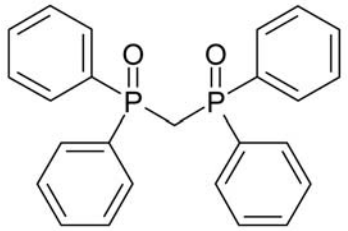


Figure 5. Distribution diagram of americium in the equilibrium nitrobenzene phase of the water– HNO_3–Am^{3+}(microamounts)–nitrobenzene– *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide (L)–H^+B^- extraction system in the forms of Am^{3+}, AmL_2^{3+}, and AmL_3^{3+}; $c(HNO_3)$ = 0.05 mol/L, c_B = 0.0025 mol/L. **1** $\delta(Am^{3+}) = [Am^{3+}_{org}]/c(Am^{3+})_{org}$, **2** $\delta(Am_2^{3+}) = [AmL^{3+}_{2,org}]/c(Am^{3+})_{org}$, **3** $\delta(AmL_3^{3+}) = [AmL^{3+}_{3,org}]/c(Am^{3+})_{org}$, where $c(Am^{3+})_{org} = [Am^{3+}_{org}] + [AmL^{3+}_{2,org}] + [AmL^{3+}_{3,org}]$. The distribution curves were calculated using the constants given in Table 6.

boxamide) to the total trivalent metal cation concentrations in the corresponding equilibrium organic phase. From Figures 3, 4, and 5 it follows that the species $HL^+_{2,org}$, $EuL^{3+}_{3,org}$, and $AmL^{3+}_{3,org}$ are present in significant concentrations only at relatively high amounts of the *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide (L) ligand in the systems under consideration. On the other hand, the contributions of the cations $H_2L^{2+}_{org}$, Eu^{3+}_{org}, and Am^{3+}_{org} are very small, as also follows from Figures 3, 4, and 5.

Finally, Table 7 summarizes the stability constants of the complex species ML_2^{3+} and ML_3^{3+} ($M^{3+} = Eu^{3+}, Am^{3+}$) with two electroneutral ligands L (L = *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide, bis(diphenylphosphino)methane dioxide (DPPMDO) – see Scheme 2) 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 $ML^{3+}_{2,org}$ and $ML^{3+}_{3,org}$ ($M^{3+} = Eu^{3+}, Am^{3+}$) containing *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide ligand are essentially higher than those of respective cationic complexes $ML^{3+}_{2,org}$ and $ML^{3+}_{3,org}$ ($M^{3+} = Eu^{3+}$, Am^{3+}) with the ligand DPPMDO. It means that complexation ability towards Eu^{3+} and Am^{3+} of the *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide ligand under study is also substantially higher than that of the DPPMDO ligand.



Scheme 2. Structural formula of bis(diphenylphosphino)methane dioxide (abbrev. DPPMDO).

In conclusion, we must state that the separation factors $SF_{Am/Eu}$, reached in the studied two–phase water–nitrobenzene extraction system, defined by means of the corresponding equilibrium distribution ratios, $D(Am^{3+})$ / $D(Eu^{3+})$, are in the range from 12 to 38. This fact follows from the results presented in Figures 1 and 2 or in Tables 1 and 2, respectively.

4. Conclusions

In the present work, the solvent extraction of trivalent europium and americium from acidic aqueous solutions into nitrobenzene was investigated by means of a mixture of hydrogen dicarbollylcobaltate (H^+B^-) and *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide (L). It was proven that the cationic species HL^+, H_2L^{2+}, HL_2^+, ML_2^{3+} and ML_3^{3+} ($M^{3+} = Eu^{3+}, Am^{3+}$; L = *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide) are extracted into the organic phase of the water–ni-

Table 7. Stability constants of the complexes ML_2^{3+} and ML_3^{3+} ($M^{3+} = Eu^{3+}, Am^{3+}$; L = *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide, bis(diphenylphosphino)methane dioxide (DPPMDO) – see Scheme 2) in nitrobenzene saturated with water at 25 °C.

	L	
Quantity	**DPPMDO** [a]	***N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide** [b]
log $\beta(EuL^{3+}_{2,org})$	17.76	22.46
log $\beta(EuL^{3+}_{3,org})$	24.59	29.82
log $\beta(AmL^{3+}_{2,org})$	17.73	23.65
log $\beta(AmL^{3+}_{3,org})$	24.72	30.74

[a] Ref. 27. [b] This work.

trobenzene system. It was found that in nitrobenzene saturated with water, the stability constants of the complexes $AmL^{3+}_{2,org}$ and $AmL^{3+}_{3,org}$ are somewhat higher than those of the corresponding cationic species $EuL^{3+}_{2,org}$ and $EuL^{3+}_{3,org}$. Finally, it was evidenced experimentally that the *N,N,N',N'*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide ligand can be considered in the nitrobenzene medium as the very strong receptor for the Eu^{3+} and Am^{3+} cations. On the basis of the previous facts it is obvious that this investigated electroneutral ligand L could be also considered as a potential extraction agent for nuclear waste treatment.

5. Acknowledgements

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Povzetek

Proučevali smo ekstrakcijo mikrokoličin Eu^{3+} in Am^{3+} iz vode v nitrobenzen s pomočjo mešanice hidrogen dikarbolilkobaltata (H^+B^-) in *N,N,N',N'*-tetrabutil-1,10-fenantrolin-2,9-dikarboksamida (L). Ravnotežje smo obravnavali s predpostavko, da se kompleksi HL^+, H_2L^{2+}, HL_2^+, ML_2^{3+}, in ML_3^{3+} ($M^{3+} = Eu^{3+}$, Am^{3+}) ekstrahirajo v fazo nitrobenzena. Določili smo konstante ekstrakcije in stabilnosti kationskih kompleksov v nitrobenzenu, nasičenem z vodo. Iz dobljenih eksperimentalnih podatkov je razvidno, da *N,N,N',N'*-tetrabutil-1,10-fenantrolin-2,9-dikarboksamid sodeluje kot receptor za Eu^{3+} in Am^{3+} ter bi ga torej lahko uporabljali pri ravnanju z z jedrskimi odpadki.