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Calcium ionophore I as very effective extraction agent for trivalent europium and americium

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Abstract: The 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 calcium ionophore I (marked as the ligand L) was investigated. The equilibrium data have been explained assuming that the species HL^+, HL_2^+,ML_2^{3+} and ML_3^{3+} (M^{3+}: Eu^{3+} or Am^{3+}) are extracted into the organic phase. The extraction and stability constants of the cationic complex species in nitrobenzene saturated with water have been determined and discussed. It was proven experimentally that the ligand L could be considered as a very strong receptor for Eu^{3+} and Am^{3+}.

Keywords: liquid–liquid extraction; europium and americium; calcium ionophore I; extraction and stability constants; water–nitrobenzene system.

INTRODUCTION

Organic complexing agents with the prevailing hydrophobic character form the inclusion complexes with inorganic metal cations. That's why they found use especially as components for the ion-selective electrodes involving liquid membranes. Theory and many applications of the ion-selective electrodes have been successfully summarized in several reviews.[1–3]

The dicarbollylcobaltates[4] (Fig. 1) 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 experimental purposes,[5–9] and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.[10,11] Generally, only the Cs^+ can be extracted into the organic phase as a simple cation. For the extraction of multivalent cations the mixture of dicarbollylcobaltate extractant with the above mentioned neutral organic complexing ligands must be used.

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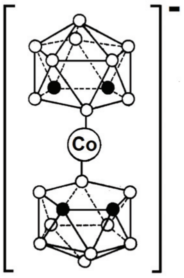

Fig. 1. Structural formula of dicarbollylcobaltates anion; ○, B–H groups; ●, C–H groups.

In this context, we must state that the very bulky lipophilic dicarbollylcobaltate is present almost only in the equilibrium organic phase of the investigated two-phase extraction system[4], 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 (FS-13).[10,11] 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, while in Russia trifluoronitrotoluene (abbrev. F-3) is used for the same purposes. Finally, FS-13 has the advantage of low viscosity and good solubility of metal solvates as well as the UNEX extractants.[11]

Dicarboxylic acid diamides are a subject of active research as potential extractants of actinides (in particular of minor actinides) from radioactive wastes. The important information concerning the substituted malonic diamides has been reported.[12,13] Lately, the interest has shifted to the properties of tetralkyl-diglycolamides,[14–17] with the emphasis on tetraoctyl-diglycolamide (TODGA), suggested as an extractant of Pu(IV), Np(IV), Am(III) and Cm(III) in solutions with hydrocarbon diluents.[14–16] The ability of TODGA to extract many other metals has been discussed[17–19] and the very high extraction capacity of this agent was shown to allow its application as a solid extractant.[19] The complexation of trivalent lanthanides and actinides with several diglycolamide-functionalized calixarenes has been studied.[20–22] Besides, some of these functionalized calixarenes have been applied for the isolation of carrier-free ^{90}Y from ^{90}Sr.[23]

Recently, the diamides of 1,10-phenanthroline-2,9-dicarboxylic acid have been intended as selective extractants for trivalent americium and curium. The mixture of *N*,*N*,*N'N'*-tetraoctyl-1,10-phenanthroline-2,9-dicarboxamide and brominated dicarbollylcobaltate effectively extracts americium with a separation factor ($SF_{Am/Eu}$) over forty.[24] High $SF_{Am/Eu}$ values (up to 51) have been also demonstrated in metal extraction by 1,10-phenanthroline-2,9-dicarboxamides from perchloric media.[25]

Very high separation factors, $SF_{\mathrm{Am/Eu}}$ (40–100), were reached during the extraction from nitric acid solution by the nitrobenzene solutions of 1,2-dicarbollylcobaltate in the presence of substituted 1,10-phenanthroline-2,9-dicarboxamides.[26–28]

In addition, as follows from Fig. 2, the calcium ionophore I ((*R*,*R*)-*N*,*N*′-bis-[11-(ethoxycarbonyl)undecyl]-*N*,*N*′,4,5-tetramethyl-3,6-dioxaoctane-diamide) contains two ethereal oxygens, two substituted amide moieties and two ethyl ester groups, so that this compound could be an efficient agent especially for the solvent extraction of lanthanides and actinides. It must be pointed out that this reagent is commercially available.

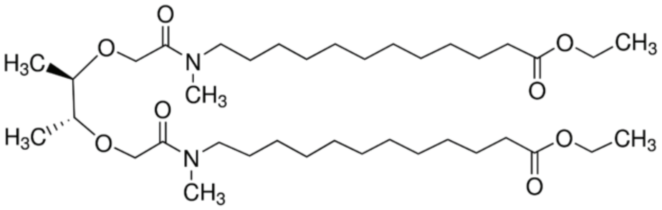

Fig. 2. Structural formula of calcium ionophore I.

Therefore, in the current work, the solvent extraction of microamounts of trivalent europium and americium from aqueous nitric acid solution into nitrobenzene by means of hydrogen dicarbollylcobaltate $(H^+B^-)^4$ and the calcium ionophore I was investigated. 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. It means that the main aim of our study is discovering the respective extraction mechanisms and the quantitative characterization of the investigated two-phase extraction system.

EXPERIMENTAL

Chemicals

Calcium ionophore I (puriss., ≥ 99%; Fig. 1) was purchased from Fluka and it was employed as received. Cesium dicarbollylcobaltate, Cs^+B^-, was synthesized by the method published by Hawthorne *et al.*[29] Other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. A nitrobenzene solution of hydrogen dicarbollylcobaltate $(H^+B^-)^4$ was prepared from Cs^+B^- by the procedure described elsewhere.[30] The carrier-free radionuclides $^{152,154}Eu^{3+}$ and $^{241}Am^{3+}$ were obtained from Polatom, Poland; their radionuclidic purities were 99.9 %.

Extraction

The extraction experiments in the two–phase water–HNO_3–$^{152,154}Eu^{3+}$ (*ca.* 20 kBq)––nitrobenzene–L–H^+B^- and water–HNO_3–$^{241}Am^{3+}$ (*ca.* 20 kBq)–nitrobenzene–L–H^+B^- systems 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 phase additionally contained 1×10^{-7} mol L^{-1} of $Eu(NO_3)_3$. The test-tubes 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 $^{152,154}Eu^{3+}$ and $^{241}Am^{3+}$ 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 calcium ionophore I, denoted in the following figures (Figs. 3–7) as ligand L in the initial nitrobenzene phase, $\log c(L)$, are presented in Figs. 3 and 4. The initial concentrations of hydrogen dicarbollylcobaltate in the organic phase, $c_B = 0.0005$ mol L^{-1}, as well as the initial concentrations of HNO_3 in the aqueous phase, $c(HNO_3)$ of 0.02 and 0.05 mol L^{-1}, are always related to the volume of one phase.

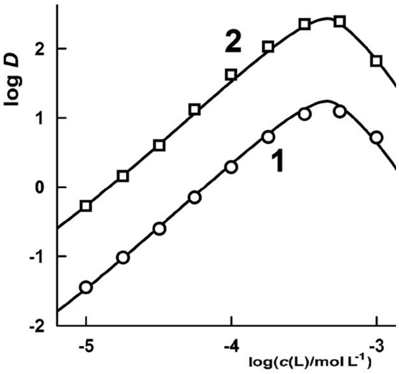

Fig. 3. Log D as a function of $\log c(L)$ for the system water–HNO_3–Eu^{3+}(microamounts)–nitrobenzene–L–H^+B^-; **1** $c(HNO_3) = 0.05$ mol L^{-1}, $c_B = 5\times10^{-4}$ mol L^{-1}; **2** $c(HNO_3) = 0.02$ mol L^{-1}, $c_B = 5\times10^{-4}$ mol L^{-1}. The curves were calculated using the constants given in Table III.

Regarding the results of our previous papers,[4,7-9,31] the considered water––HNO_3–M^{3+} (microamounts; M^{3+}: Eu^{3+} or Am^{3+})–nitrobenzene–(L)–H^+B^- systems can be described by the set of reactions:

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

$$H_{org}^{+} + L_{org} \leftrightarrows HL_{org}^{+};\ \beta HL_{org}^{+} \tag{2}$$

$$H_{org}^{+} + 2L_{org} \leftrightarrows HL_{2,org}^{+};\ \beta HL_{2org}^{+} \tag{3}$$

$$M_{aq}^{3+} + 3H_{org}^{+} \leftrightarrows M_{org}^{3+} + 3H_{aq}^{+};\ K_{ex}\, M_{org}^{3+} \tag{4}$$

$$M_{aq}^{3+} + nL_{org}^{+} + 3H_{org}^{+} \leftrightarrows ML_{n,org}^{3+} + 3H_{aq}^{+};\ K_{ex}\, ML_{n,org}^{3+} \tag{5}$$

to which the following equilibrium constants correspond:

$$K_{\mathrm{D}} = \frac{[\mathrm{L}_{\mathrm{org}}]}{[\mathrm{L}_{\mathrm{aq}}]} \tag{6}$$

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

$$\beta \mathrm{HL}_{2,\mathrm{org}}^{\ +} = \frac{[\mathrm{HL}_{2,\mathrm{org}}^{\ +}]}{[\mathrm{H}_{\mathrm{org}}^{\ +}][\mathrm{L}_{\mathrm{org}}]^2} \tag{8}$$

$$K_{ex}\ \mathrm{ML}_{n,\mathrm{org}}^{\ 3+} = \frac{[\mathrm{ML}_{n,\mathrm{org}}^{\ 3+}][\mathrm{H}^{+}_{\mathrm{aq}}]^3}{[\mathrm{M}_{\mathrm{aq}}^{\ 3+}][\mathrm{L}_{\mathrm{org}}]^n[\mathrm{H}_{\mathrm{org}}^{\ +}]^3} \tag{9}$$

The subscripts "aq" and "org" denote the aqueous and organic phases, respectively. At this point we must add that Eq. (4) characterizes the investigated two-phase systems at $[\mathrm{L}_{\mathrm{org}}] \to 0$.

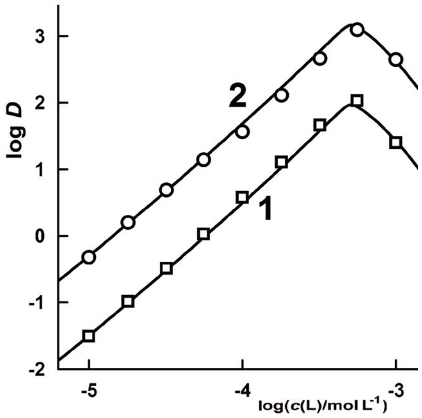

Fig. 4. Log D as a function of log c(L) for the system water–$\mathrm{HNO_3}$–Am^{3+}(microamounts)–nitrobenzene–L–$\mathrm{H^+B^-}$; **1** $c(\mathrm{HNO_3})$ = 0.05 mol $\mathrm{L^{-1}}$, c_{B} = = 0.0005 mol $\mathrm{L^{-1}}$; **2** $c(\mathrm{HNO_3})$ = 0.02 mol $\mathrm{L^{-1}}$, c_{B} = = 0.0005 mol $\mathrm{L^{-1}}$. The curves were calculated using the constants given in Table IV.

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[32,33] and introduced into a more general least-squares minimizing program LETAGROP,[34] used for determination of the "best" values of the extraction constants $K_{\mathrm{ex}}\ \mathrm{ML}_{n,\mathrm{org}}^{\ 3+}$($\mathrm{M}^{3+}$: Eu^{3+} or Am^{3+}). The present version of this program, written in Embarcadero Delphi, has graphic output allowing also the printing of the Figs. 3–7. The minimum of the sum of squares of deviations in log D, *i.e.*, the minimum of the expression:

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

was sought (Tables I and II). This value is the main criterion for the determination of the respective extraction mechanism. The other one is the visual fit of the experimental data with the calculated dependencies of log D on log c(L).

TABLE I. 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.[34] 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 $\log K$ ($\log [K + 3\sigma(K)]$)[34]

Europium complexes in the organic phase	$\log K_{ex}$	U[a]
EuL_2^{3+}	21.06(21.43)	11.07
EuL_3^{3+}	27.56(27.93)	11.99
EuL_2^{3+}, EuL_2^{3+}	20.63±0.06, 26.41±0.10	0.07

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

TABLE II. Comparison of various models of americium extraction from aqueous solution of HNO_3 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+}	21.34(21.76)	19.36
AmL_3^{3+}	27.85(28.13)	5.32
AmL_2^{3+}, AmL_2^{3+}	20.66±0.07, 27.20±0.09	0.08

The values $\log K_D = 3.8$, $\log \beta(HL_{org}^{+}) = 6.4$, $\log \beta(HL_{2,org}^{+}) = 9.7$ (Table III), $\log K_{ex}(Eu_{org}^{3+}) = 1.3$ and $\log K_{ex}(Am_{org}^{3+}) = 1.5$ (inferred from ref. 37) 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+} (M^{3+}: Eu^{3+} or Am^{3+}) to be extracted into the nitrobenzene phase because in the cases presented in Tables I and II, the error-square sums (U) are the smallest.

Knowing the values $\log K_{ex}(Eu_{org}^{3+}) = 1.3$ and $\log K_{ex}(Am_{org}^{3+}) = 1.5$ which were inferred from ref. 37, as well as the extraction constants summarized in Tables III and IV, the stability constants of the complexes ML_2^{3+} and ML_3^{3+} (M^{3+}: Eu^{3+} or Am^{3+}) in the nitrobenzene phase defined as:

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

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

can be calculated employing the following simple relations:

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

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

The respective equilibrium constants are summarized in Tables III and IV. It should be noted that the stability constants of the cationic complexes ML_2^{3+} and ML_3^{3+} (M^{3+}: Eu^{3+} or Am^{3+}) in water-saturated nitrobenzene are log $\beta(EuL_{2,org}^{3+})$ = = 19.33, log $\beta(AmL_{2,org}^{3+})$ = 19.16, log $\beta(EuL_{3,org}^{3+})$ = 25.11 and log $\beta(AmL_{3,org}^{3+})$ = 25.70. This means that the stability constants of the complexes $EuL_{2,org}^{3+}$ and $AmL_{2,org}^{3+}$ are comparable but the stability constant of the complex $AmL_{3,org}^{3+}$ is higher than that of $EuL_{3,org}^{3+}$.

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

Equilibrium	log *K*
$L_{aq} \Leftrightarrow L_{org}$	3.8[a]
$H_{org}^+ + L_{org} \Leftrightarrow HL_{org}^+$	6.4[b]
$H_{org}^+ + 2L_{org} \Leftrightarrow HL_{2,org}^+$	9.7[b]
$Eu_{aq}^{3+} + 3H_{org}^+ \Leftrightarrow Eu_{org}^{3+} + 3H_{aq}^+$	1.3[c]
$Eu_{aq}^{3+} + 2L_{org} + 3H_{org}^+ \Leftrightarrow EuL_{2,org}^{3+} + 3H_{aq}^+$	20.63
$Eu_{aq}^{3+} + 3L_{org} + 3H_{org}^+ \Leftrightarrow EuL_{3,org}^{3+} + 3H_{aq}^+$	26.41
$Eu_{org}^{3+} + 2L_{org} \Leftrightarrow EuL_{2,org}^{3+}$	19.33
$Eu_{org}^{3+} + 3L_{org} \Leftrightarrow EuL_{3,org}^{3+}$	25.11

[a] Determined by the method of the concentration dependent distribution;[36] [b] determined by the method described elsewhere;[35] [c] inferred from literature[37]

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

Equilibrium	log *K*
$L_{aq} \Leftrightarrow L_{org}$	3.8[a]
$H_{org}^+ + L_{org} \Leftrightarrow HL_{org}^+$	6.4[b]
$H_{org}^+ + 2L_{org} \Leftrightarrow HL_{2,org}^+$	9.7[b]
$Am_{aq}^{3+} + 3H_{org}^+ \Leftrightarrow Am_{org}^{3+} + 3H_{aq}^+$	1.5[c]
$Am_{aq}^{3+} + 2L_{org} + 3H_{org}^+ \Leftrightarrow AmL_{2,org}^{3+} + 3H_{aq}^+$	20.66
$Am_{aq}^{3+} + 3L_{org} + 3H_{org}^+ \Leftrightarrow AmL_{3,org}^{3+} + 3H_{aq}^+$	27.20
$Am_{org}^{3+} + 2L_{org} \Leftrightarrow AmL_{2,org}^{3+}$	19.16
$Am_{org}^{3+} + 3L_{org} \Leftrightarrow AmL_{3,org}^{3+}$	25.70

[a] Determined by the method of the concentration dependent distribution;[36] [b] determined by the method described elsewhere;[35] [c] inferred from literature[37]

Moreover, Fig. 5 presents the contributions of the species H_{org}^+, HL_{org}^+ and $HL_{2,org}^+$ to the total hydrogen cation concentration in the equilibrium nitrobenzene phase, whereas Figs 6 and 7 show the contributions of the cations M_{org}^{3+}, $ML_{2,org}^{3+}$ and $ML_{3,org}^{3+}$ to the total trivalent metal cation concentrations in the corresponding equilibrium organic phase. From Figs. 5–7 it follows that the species $HL_{2,org}^+$, $EuL_{3,org}^{3+}$ and $AmL_{3,org}^{3+}$ are present in significant concentrations only at relatively high amounts of the ligand L in the systems under study.

The distribution curves were calculated using the constants given in Tables III and IV.

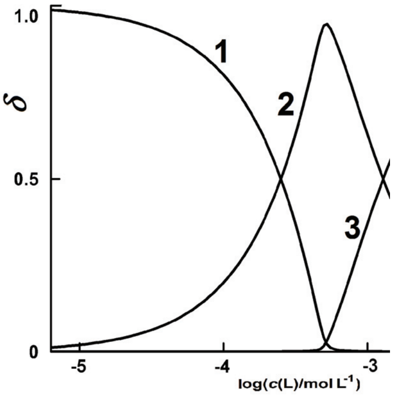

Fig. 5. Distribution diagram of hydrogen cation in the equilibrium nitrobenzene phase of the water–HNO$_3$–Eu^{3+}(microamounts)–nitrobenzene–L–H$^+$B$^-$ extraction system in the forms of H$^+$, HL$^+$ and HL$_2^+$; c(HNO$_3$) = 0.02 mol L^{-1}, c_B = 0.0005 mol L^{-1}. **1** H$^+$, [H$_{org}^+$]/c(H$^+$)$_{org}$, **2** HL$^+$, [HL$_{org}^+$]/c(H$^+$)$_{org}$, **3** HL$_2^+$, [HL$_{2,org}^+$]/c(H$^+$)$_{org}$, where c(H$^+$)$_{org}$ = [H$_{org}^+$] + [HL$_{org}^+$] + [HL$_{2,org}^+$]. The distribution curves were calculated using the constants given in Table III.

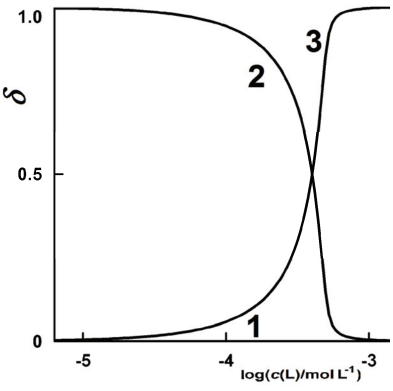

Fig. 6. Distribution diagram of europium in the equilibrium organic phase of the water–HNO$_3$–Eu^{3+} (microamounts)–nitrobenzene–L–H$^+$B$^-$ extraction system in the forms of Eu^{3+}, EuL$_2^{3+}$ and EuL$_3^{3+}$; c(HNO$_3$) = 0.02 mol L^{-1}, c_B = 0.0005 mol L^{-1}. **1** Eu^{3+}, [Eu$_{org}^{3+}$]/c(Eu^{3+})$_{org}$, **2** EuL$_2^{3+}$, [EuL$_{2,org}^{3+}$]/c(Eu^{3+})$_{org}$, **3** EuL$_3^{3+}$, [EuL$_{3,org}^{3+}$]/c(Eu^{3+})$_{org}$, where c(Eu^{3+})$_{org}$ = [Eu$_{org}^{3+}$] + [EuL$_{2,org}^{3+}$] + [EuL$_{3,org}^{3+}$].

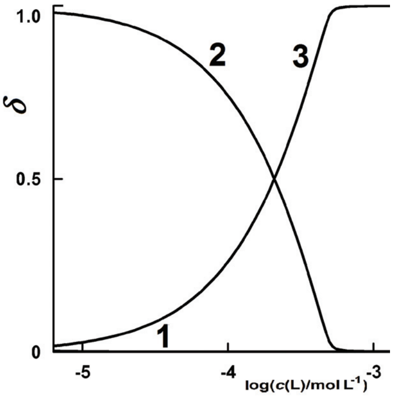

Fig. 7. Distribution diagram of americium in the equilibrium nitrobenzene phase of the water–HNO$_3$–Am^{3+}(microamounts)–nitrobenzene–L–H$^+$B$^-$ extraction system in the forms of Am^{3+}, Am$_2^{3+}$ and AmL$_3^{3+}$; c(HNO$_3$) = 0.02 mol L^{-1}, c_B = 0.0005 mol L^{-1}. **1** Am^{3+}, [Am$_{org}^{3+}$]/c(Am^{3+})$_{org}$, **2** AmL$_2^{3+}$, [AmL$_{2,org}^{3+}$]/c(Am^{3+})$_{org}$ **3** AmL$_3^{3+}$, [AmL$_{3,org}^{3+}$]/c(Am^{3+})$_{org}$, where c(Am^{3+})$_{org}$ = [Am$_{org}^{3+}$] + [AmL$_{2,org}^{3+}$] + AmuL$_{3,org}^{3+}$].

Synergistic factor defined as $S = D(\mathrm{Me}^{3+})/D_0(\mathrm{Me}^{3+})$, where D(Me^{3+}) is the maximal distribution ratio of the extracted metals in the systems under study and D_0(Me^{3+}) is the distribution ratio reached for the same concentrations of HNO$_3$ and dicarbollylcobaltate anion, but in the absence of calcium ionophore I, is very high, log S(Eu) = 6.0 and log S(Am) = 6.9. This means that the extraction system water–HNO_3–calcium ionophore I–dicarbollylcobaltate–nitrobenzene can be used for the separation of Eu^{3+} and Am^{3+} from the PUREX process raffinate. Value of separation factor α(Am/Eu) ≈ 5 allows also mutual separation of Am/Eu by the same extraction agents.

Finally, Table V summarizes the stability constants of the complex species HL^+, HL_2^+, $ML_{2,org}^{3+}$ and $ML_{3,org}^{3+}$ with the two electroneutral ligands (L = calcium ionophore I or magnesium ionophore II) 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 HL_{org}^+, $HL_{2,org}^+$, $ML_{2,org}^{3+}$ and $ML_{3,org}^{3+}$ containing the calcium ionophore I ligand are comparable with those of the respective cationic complexes HL_{org}^+, $HL_{2,org}^+$, $ML_{2,org}^{3+}$ and $ML_{3,org}^{3+}$ with the ligand magnesium ionophore II. It means that the complexation ability towards H^+, Eu^{3+} and Am^{3+} of the calcium ionophore I ligand under study is also comparable with that of the magnesium ionophore II. On the other hand, no separation of Am from Eu has been found in the system with magnesium ionophore II ($SF_{Am/Eu}$ ≈ 1).

TABLE V. Stability constants of the complexes HL^+, HL_2^+, ML_2^{3+} and ML_3^{3+} (M^{3+}: Eu^{3+} or Am^{3+}; L = magnesium ionophore II or calcium ionophore I) in nitrobenzene saturated with water at 25 °C

Quantity	Magnesium ionophore II[a]	Calcium ionophore I[b]
$\log \beta(HL_{org}^+)$	6.4	6.4
$\log \beta(HL_{2,org}^+)$	9.8	9.7
$\log \beta(EuL_{2,org}^{3+})$	18.91	19.33
$\log \beta(EuL_{3,org}^{3+})$	25.40	25.11
$\log \beta(AmL_{2,org}^{3+})$	18.99	19.16
$\log \beta(AmL_{3,org}^{3+})$	25.46	25.70

[a]Ref. 38; [b]this work

CONCLUSIONS

In the present work, the solvent extraction of trivalent europium and americium from nitric acid solutions into nitrobenzene was studied using hydrogen dicarbollylcobaltate (H^+B^-) and calcium ionophore I. It was evidenced that the cationic species HL^+, HL_2^+, and ML^{3+}, 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 $EuL_{n,org}^{3+}$ and $AmL_{n,org}^{3+}$, where $n = 2$ or 3, were found to be comparable in nitrobenzene saturated with water. From the very high stabilities of the proven ML_2^{3+} and ML_3^{3+} cationic complexes in the organic phase of the studied water–nitrobenzene system it is obvious that this very efficient ligand L for Eu^{3+} and Am^{3+} could be considered as a potential extraction agent for nuclear waste treatment.

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ИЗВОД

КАЛЦИЈУМОВА ЈОНОФОРА I КАО ВЕОМА ЕФЕТКИВАН ЕКСТРАКЦИОНИ АГЕНС ТРОВАЛЕНТНОГ ЕУРОПИЈУМА И АМЕРИЦИЈУМА

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Испитивана је екстракција микроколичина Eu^{3+} и Am^{3+} из воде у нитробензен помоћу смеше хидроген-дикарболилкобалтата (H^+B^-) и калцијумове јонофоре I (означен као лиганд L). Равнотеже су објашњене на бази екстракције врста HL^+, HL_2^+, ML_2^{3+} и ML_3^{3+} (M^{3+}: Eu^{3+} или Am^{3+}) у органску фазу. Одређене су и дискутоване равнотежне константе екстракције и стабилности катјонских комплексних врста у нитробензену засићеном водом. Експериментално је доказано да лиганд L може бити разматран као веома снажан рецептор за катјоне Eu^{3+} и Am^{3+}.

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