

Synergistic Extraction of Calcium and Strontium into Nitrobenzene by Using Hydrogen Dicarbolylcobaltate and *N,N'*-Dimethyl-*N,N'*-Diphenyl-2,6-Dipicolinamide

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Abstract

Extraction of microamounts of calcium and strontium by a nitrobenzene solution of hydrogen dicarbolylcobaltate (H^+B^-) in the presence of *N,N'*-dimethyl-*N,N'*-diphenyl-2,6-dipicolinamide (MePhDPA, L) has been investigated. The equilibrium data have been explained assuming that the species HL^+ , HL_2^+ , ML_2^{2+} and ML_3^{2+} ($\text{M}^{2+} = \text{Ca}^{2+}$, Sr^{2+}) are extracted into the organic phase. The values of extraction and stability constants of the cationic complex species in nitrobenzene saturated with water have been determined.

Keywords: Calcium, strontium, hydrogen dicarbolylcobaltate, *N,N'*-dimethyl-*N,N'*-diphenyl-2,6-dipicolinamide, complexation, water-nitrobenzene system, extraction and stability constants

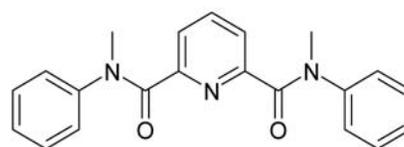
1. Introduction

The dicarbolylcobaltate anion¹ and some of its halogen derivatives are very useful reagents for the extraction of various metal cations (especially Cs^+ , Sr^{2+} , Ba^{2+} , Eu^{3+} and Am^{3+}) from aqueous solutions into a polar organic phase, both under laboratory conditions for purely theoretical or analytical purposes,^{2–19} and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.^{20,21}

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 have been reported.^{22,23} Lately, interest has shifted to the properties of tetraalkyl-diglycolamides,^{24–27} 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.^{24–26} The ability of TODGA to extract many other metals was discussed^{27,28} and the very high extractive capacity of this agent was shown to allow its application as a solid extractant.²⁹

Recently, the extractive properties of some 2,6-dipicolinamides have been investigated.^{30–34} In the current work, the solvent extraction of microamounts of cal-



Scheme 1. Structural formula of *N,N'*-dimethyl-*N,N'*-diphenyl-2,6-dipicolinamide (abbrev. MePhDPA or L, respectively).

cium and strontium by a nitrobenzene solution of hydrogen dicarbollycobaltate (H^+B^-)¹ in the presence of *N,N'*-dimethyl-*N,N'*-diphenyl-2,6-dipicolinamide (MePhDPA) (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.

2. Experimental

N,N'-Dimethyl-*N,N'*-diphenyl-2,6-dipicolinamide (MePhDPA) was produced as described in References 35 and 36. Cesium dicarbollycobaltate, Cs^+B^- , was synthesized by means of the method published by Hawthorne et al.³⁷ A nitrobenzene solution of hydrogen dicarbollycobaltate (H^+B^-)¹ was prepared from Cs^+B^- by the procedure described elsewhere.³⁸ The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclides $^{45}\text{Ca}^{2+}$ and $^{85}\text{Sr}^{2+}$ (DuPont, Belgium) were of standard radiochemical purity.

The extraction experiments in the two-phase water–HCl– M^{2+} (microamounts; $\text{M}^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+}$)–nitrobenzene–MePhDPA– H^+B^- systems were performed in 10 mL glass test-tubes 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. In the case of the systems involving $^{45}\text{Ca}^{2+}$, after evaporating aliquots (1 mL) of the respective phases on Al plates, their β -activities were measured by using the apparatus NRB-213 (Tesla Přemyšlení, Czech Republic). On the other hand, in the case of the systems with $^{85}\text{Sr}^{2+}$, 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 NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratios of calcium and strontium, D , were determined as the ratios of the corresponding measured radioactivities of $^{45}\text{Ca}^{2+}$ and $^{85}\text{Sr}^{2+}$ in the nitrobenzene and aqueous samples.

3. Results and Discussion

The dependences of the logarithm of the calcium and strontium distribution ratios ($\log D$) on the logarithm of the numerical value of the total (analytical) concentration of the MePhDPA ligand in the initial nitrobenzene phase, $\log c(\text{L})$, are given in Figures 1 and 2, respectively. The initial concentration of hydrogen dicarbollycobaltate in the organic phase, $c_{\text{B}} = 0.003$ mol/L, as well as the initial concentration of HCl in the aqueous phase, $c(\text{HCl}) = 0.01$ mol/L, are always related to the volume of one phase.

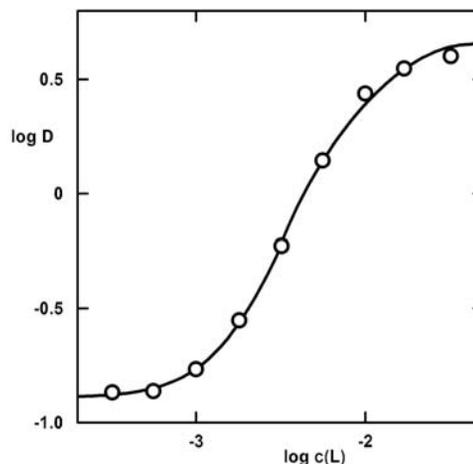


Figure 1. $\log D$ as a function of $\log c(\text{L})$, where $\text{L} = \text{MePhDPA}$, for the system water–HCl– Ca^{2+} (microamounts)–nitrobenzene–MePhDPA– H^+B^- ; $c(\text{HCl}) = 0.01$ mol/L, $c_{\text{B}} = 0.003$ mol/L. The curve was calculated using the constants given in Table 3.

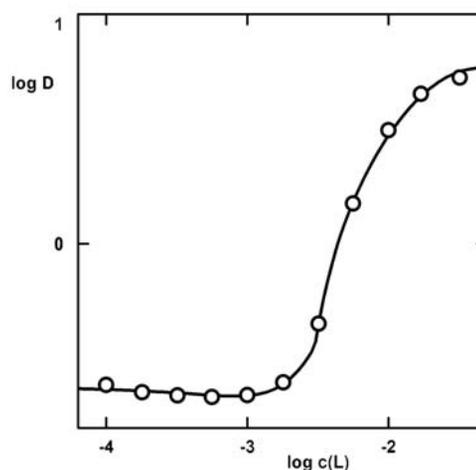


Figure 2. $\log D$ as a function of $\log c(\text{L})$, where $\text{L} = \text{MePhDPA}$, for the system water–HCl– Sr^{2+} (microamounts)–nitrobenzene–MePhDPA– H^+B^- ; $c(\text{HCl}) = 0.01$ mol/L, $c_{\text{B}} = 0.003$ mol/L. The curve was calculated using the constants given in Table 4.

With respect to the results of previous papers,^{3,5,12,34,39,40} the considered water–HCl– M^{2+} (microamounts; $\text{M}^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+}$)–nitrobenzene–MePhDPA(L)– H^+B^- systems can be described by the set of reactions:



to which the following equilibrium constants correspond:

$$K_D = \frac{[L_{\text{org}}]}{[L_{\text{aq}}]} \quad (6)$$

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

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

$$K_{\text{ex}}(\text{M}_{\text{org}}^{2+}) = \frac{[\text{M}_{\text{org}}^{2+}][\text{H}_{\text{aq}}^+]^2}{[\text{M}_{\text{aq}}^{2+}][\text{H}_{\text{org}}^+]^2} \quad (9)$$

$$K_{\text{ex}}(\text{ML}_{n,\text{org}}^{2+}) = \frac{[\text{ML}_{n,\text{org}}^{2+}][\text{H}_{\text{aq}}^+]^2}{[\text{M}_{\text{aq}}^{2+}][L_{\text{org}}]^n[\text{H}_{\text{org}}^+]^2} \quad (10)$$

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 MePhDPA ligand and the electroneutrality conditions in both phases of the system under consideration, was formulated^{41,42} and introduced into a more general least-squares minimizing program LETAGROP⁴³ used for determination of the “best” values of the extraction constants $K_{\text{ex}}(\text{ML}_{n,\text{org}}^{2+})$ ($\text{M}^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+}$; $\text{L} = \text{MePhDPA}$). The minimum of the sum of errors 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.

The values $\log K_D = 1.29$,³⁴ $\log \beta(\text{HL}_{\text{org}}^+) = 9.3$,³⁴ $\log \beta(\text{HL}_{2,\text{org}}^+) = 10.7$,³⁴ $\log K_{\text{ex}}(\text{Ca}_{\text{org}}^{2+}) = 0.244$ and $\log K_{\text{ex}}(\text{Sr}_{\text{org}}^{2+}) = 0.741$ were used for the respective calculations. The results are listed in Tables 1 and 2. From these tables it is evident that the extraction data can be best explained assuming the complexes ML_2^{2+} and ML_3^{2+} ($\text{M}^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+}$; $\text{L} = \text{MePhDPA}$) to be extracted into the nitrobenzene phase.

Table 1. Comparison of three different models of calcium extraction from aqueous solution of HCl by nitrobenzene solution of H^+B^- in the presence of MePhDPA.

Calcium complexes in the organic phase	log K_{ex}^a	U^b
CaL_2^{2+}	19.99 (20.30)	1.36
CaL_3^{2+}	22.54 (22.95)	2.10
$\text{CaL}_2^{2+}, \text{CaL}_3^{2+}$	19.49 ± 0.17, 22.26 ± 0.15	0.04

^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 .⁴³ 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 $\log K(\log[K + 3\sigma(K)])$.⁴³

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

Table 2. Comparison of three different models of strontium extraction from aqueous solution of HCl by nitrobenzene solution of H^+B^- in the presence of MePhDPA.

Strontium complexes in the organic phase	log K_{ex}^a	U^b
SrL_2^{2+}	20.01 (20.36)	1.87
SrL_3^{2+}	22.57 (22.86)	0.96
$\text{SrL}_2^{2+}, \text{SrL}_3^{2+}$	19.33 ± 0.15, 22.39 ± 0.10	0.03

^a See Table 1, footnote a; ^b See Table 1, footnote b.

Knowing the values $\log K_{\text{ex}}(\text{Ca}_{\text{org}}^{2+}) = 0.244$ and $\log K_{\text{ex}}(\text{Sr}_{\text{org}}^{2+}) = 0.7$,⁴¹ $\log K_{\text{ex}}(\text{CaL}_{2,\text{org}}^{2+}) = 19.49$ as well as the extraction constants $\log K_{\text{ex}}(\text{CrL}_{2,\text{org}}^{2+}) = 19.33$, $\log K_{\text{ex}}(\text{CaL}_{3,\text{org}}^{2+}) = 22.26$ and $\log K_{\text{ex}}(\text{SrL}_{3,\text{org}}^{2+}) = 22.39$ determined here (see Tables 1 and 2), the stability constants of the complexes ML_2^{2+} and ML_3^{2+} ($\text{M}^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+}$; $\text{L} = \text{MePhDPA}$) in the organic phase defined as

$$\beta(\text{ML}_{2,\text{org}}^{2+}) = \frac{[\text{ML}_{2,\text{org}}^{2+}]}{[\text{M}_{\text{org}}^{2+}][L_{\text{org}}]^2} \quad (12)$$

$$\beta(\text{ML}_{3,\text{org}}^{2+}) = \frac{[\text{ML}_{3,\text{org}}^{2+}]}{[\text{M}_{\text{org}}^{2+}][L_{\text{org}}]^3} \quad (13)$$

can be evaluated applying the following simple relations:

$$\log \beta(\text{ML}_{2,\text{org}}^{2+}) = \log K_{\text{ex}}(\text{ML}_{2,\text{org}}^{2+}) - \log K_{\text{ex}}(\text{M}_{\text{org}}^{2+}) \quad (14)$$

$$\log \beta(\text{ML}_{3,\text{org}}^{2+}) = \log K_{\text{ex}}(\text{ML}_{3,\text{org}}^{2+}) - \log K_{\text{ex}}(\text{M}_{\text{org}}^{2+}) \quad (15)$$

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

Table 3. Equilibrium constants in the water – HCl – Ca^{2+} (microamounts) – nitrobenzene – MePhDPA – H^+B^- system.

Equilibrium	log K
$\text{L}_{\text{aq}} \rightleftharpoons \text{L}_{\text{org}}$	1.29 ^a
$\text{H}_{\text{org}}^+ + \text{L}_{\text{org}} \rightleftharpoons \text{HL}_{\text{org}}^+$	9.3 ^a
$\text{H}_{\text{org}}^+ + 2\text{L}_{\text{org}} \rightleftharpoons \text{HL}_{2,\text{org}}^+$	10.7 ^a
$\text{Ca}_{\text{aq}}^{2+} + 2\text{H}_{\text{org}}^+ \rightleftharpoons \text{Ca}_{\text{org}}^{2+} + 2\text{H}_{\text{aq}}^+$	0.2 ^b
$\text{Ca}_{\text{aq}}^{2+} + 2\text{L}_{\text{org}} + 2\text{H}_{\text{org}}^+ \rightleftharpoons \text{CaL}_{2,\text{org}}^{2+} + 2\text{H}_{\text{aq}}^+$	19.49
$\text{Ca}_{\text{aq}}^{2+} + 3\text{L}_{\text{org}} + 2\text{H}_{\text{org}}^+ \rightleftharpoons \text{CaL}_{3,\text{org}}^{2+} + 2\text{H}_{\text{aq}}^+$	22.26
$\text{Ca}_{\text{org}}^{2+} + 2\text{L}_{\text{org}} \rightleftharpoons \text{CaL}_{2,\text{org}}^{2+}$	19.29
$\text{Ca}_{\text{org}}^{2+} + 3\text{L}_{\text{org}} \rightleftharpoons \text{CaL}_{3,\text{org}}^{2+}$	22.06

^a Ref. 34; ^b Ref. 44.

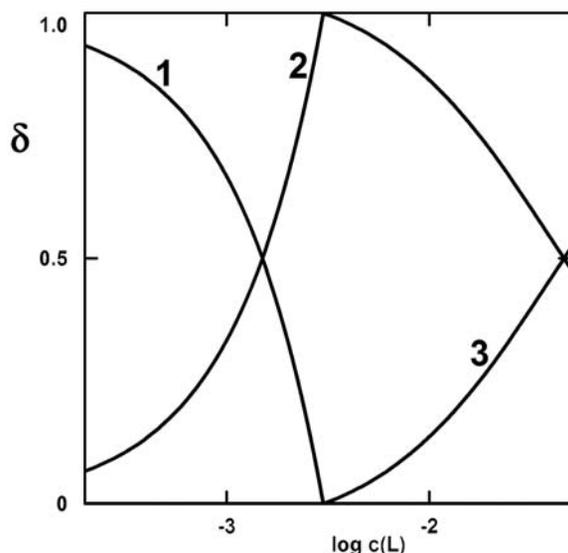
Moreover, Figure 3 depicts the contributions of the species H_{org}^+ , HL_{org}^+ and $\text{HL}_{2,\text{org}}^+$ to the total hydrogen cation concentration in the equilibrium nitrobenzene phase, whereas Figures 4 and 5 show the contributions of the cations $\text{Ca}_{\text{org}}^{2+}$, $\text{CaL}_{2,\text{org}}^{2+}$, $\text{CaL}_{3,\text{org}}^{2+}$ and $\text{Sr}_{\text{org}}^{2+}$, $\text{SrL}_{2,\text{org}}^{2+}$, $\text{SrL}_{3,\text{org}}^{2+}$,

Table 4. Equilibrium constants in the water – HCl – Sr²⁺ (microamounts) – nitrobenzene – MePhDPA – H⁺B⁻ system.

Equilibrium	log K
$L_{aq} \rightleftharpoons L_{org}$	1.29 ^a
$H^+_{org} + L_{org} \rightleftharpoons HL^+_{org}$	9.3 ^a
$H^+_{org} + 2L_{org} \rightleftharpoons HL^+_{2,org}$	10.7 ^a
$Sr^{2+}_{aq} + 2H^+_{org} \rightleftharpoons Sr^{2+}_{org} + 2H^+_{aq}$	0.7 ^b
$Sr^{2+}_{aq} + 2L_{org} + 2H^+_{org} \rightleftharpoons SrL^{2+}_{2,org} + 2H^+_{aq}$	19.33
$Sr^{2+}_{aq} + 3L_{org} + 2H^+_{org} \rightleftharpoons SrL^{2+}_{3,org} + 2H^+_{aq}$	22.39
$Sr^{2+}_{org} + 2L_{org} \rightleftharpoons SrL^{2+}_{2,org}$	18.63
$Sr^{2+}_{org} + 3L_{org} \rightleftharpoons SrL^{2+}_{3,org}$	21.69

^a Ref. 34; ^b Ref. 41.

respectively, to the total divalent metal cation concentration in the corresponding equilibrium organic phase. From Figures 3, 4 and 5 it follows that the cationic complex species $HL^+_{2,org}$, $CaL^{2+}_{3,org}$ and $SrL^{2+}_{3,org}$ are present in significant concentrations only at relatively high amounts of the MePhDPA ligand in the systems under consideration.

**Figure 3.** Distribution diagram of hydrogen cation in the equilibrium nitrobenzene phase of the water–HCl–Ca²⁺ (microamounts)–nitrobenzene–MePhDPA–H⁺B⁻ extraction system in the forms of H⁺, HL⁺ and HL₂⁺; c(HCl) = 0.01 mol/L, c_B = 0.003 mol/L.

$$1 \delta(H^+) = [H^+]_{org} / c(H^+)_{org}$$

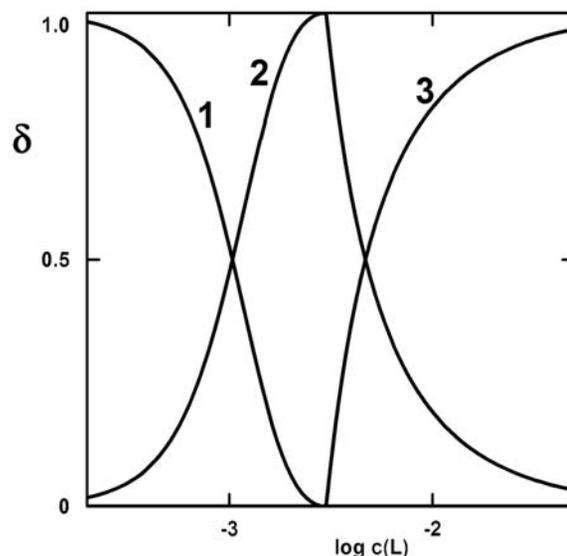
$$2 \delta(HL^+) = [HL^+]_{org} / c(H^+)_{org}$$

$$3 \delta(HL_2^+) = [HL_2^+]_{org} / c(H^+)_{org}$$

where $c(H^+)_{org} = [H^+]_{org} + [HL^+]_{org} + [HL_2^+]_{org}$.

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

Finally, it should be noted that the stability constants of the complex species $CaL^{2+}_{2,org}$, $SrL^{2+}_{2,org}$, $CaL^{2+}_{3,org}$ and $SrL^{2+}_{3,org}$, where L = MePhDPA, in nitrobenzene saturated with water are $\log \beta(CaL^{2+}_{2,org}) = 19.29$, $\log \beta(SrL^{2+}_{2,org}) = 18.63$, $\log \beta(CaL^{2+}_{3,org}) = 22.06$ and $\log \beta(SrL^{2+}_{3,org}) =$

**Figure 4.** Distribution diagram of calcium in the equilibrium nitrobenzene phase of the water–HCl–Ca²⁺ (microamounts) – nitrobenzene – MePhDPA – H⁺B⁻ extraction system in the forms of CaL²⁺, CaL₂²⁺ and CaL₃²⁺; c(HCl) = 0.01 mol/L, c_B = 0.003 mol/L.

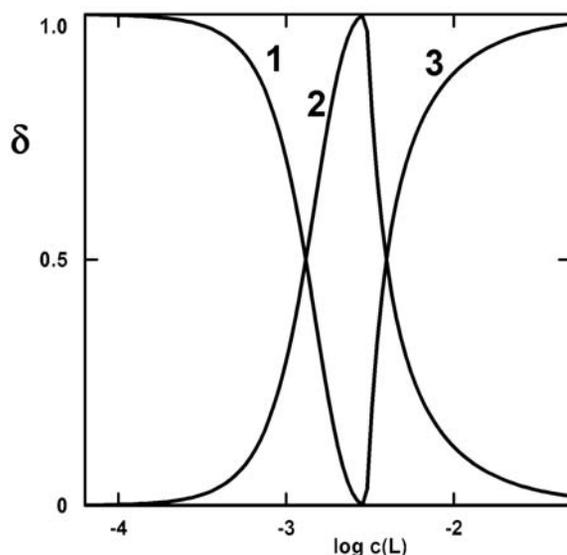
$$1 \delta(CaL^{2+}) = [CaL^{2+}]_{org} / c(Ca^{2+})_{org}$$

$$2 \delta(CaL_2^{2+}) = [CaL_2^{2+}]_{org} / c(Ca^{2+})_{org}$$

$$3 \delta(CaL_3^{2+}) = [CaL_3^{2+}]_{org} / c(Ca^{2+})_{org}$$

where $c(Ca^{2+})_{org} = [Ca^{2+}]_{org} + [CaL_2^{2+}]_{org} + [CaL_3^{2+}]_{org}$.

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

**Figure 5.** Distribution diagram of strontium in the equilibrium nitrobenzene phase of the water–HCl–Sr²⁺ (microamounts) – nitrobenzene – MePhDPA – H⁺B⁻ extraction system in the forms of SrL²⁺, SrL₂²⁺ and SrL₃²⁺; c(HCl) = 0.01 mol/L, c_B = 0.003 mol/L.

$$1 \delta(SrL^{2+}) = [SrL^{2+}]_{org} / c(Sr^{2+})_{org}$$

$$2 \delta(SrL_2^{2+}) = [SrL_2^{2+}]_{org} / c(Sr^{2+})_{org}$$

$$3 \delta(SrL_3^{2+}) = [SrL_3^{2+}]_{org} / c(Sr^{2+})_{org}$$

where $c(Sr^{2+})_{org} = [Sr^{2+}]_{org} + [SrL_2^{2+}]_{org} + [SrL_3^{2+}]_{org}$.

The distribution curves were calculated using the constants given in Table 4.

21.69, as given in Tables 3 and 4. Thus, in the considered nitrobenzene medium, the stability constants of corresponding complexes $ML_{2,org}^{2+}$ and $ML_{3,org}^{2+}$ ($M^{2+} = Ca^{2+}, Sr^{2+}$; $L = MePhDPA$) are comparable.

In conclusion, it is necessary to emphasize that the stability constants of the complexes CaL_3^{2+} , SrL_3^{2+} and EuL_3^{3+} with the MePhDPA ligand in water-saturated nitrobenzene are $\log \beta(CaL_{3,org}^{2+}) = 22.06$ (Table 3), $\log \beta(SrL_{3,org}^{2+}) = 21.69$ (Table 4) and $\log \beta(EuL_{3,org}^{3+}) = 33.28$.³⁴ This means that the stability of these three complexes in the mentioned medium increases in the series of $Ca^{2+} < Sr^{2+} \ll Eu^{3+}$.

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Povzetek

Raziskovali smo ekstrakcijo mikrokoličin kalcija in stroncija z raztopino vodikovega dikarbolilkobaltata (H^+B^-) v nitrobenzenu in v prisotnosti *N,N'*-dimetil-*N,N'*-difenil-2,6-dipikolinamida (MePhDPA, L). Dobljene podatke za dosežena ravnotežja smo razložili ob predpostavki, da se ionske zvrsti HL^+ , HL_2^+ , ML_2^{2+} in ML_3^{2+} ($M^{2+} = Ca^{2+}, Sr^{2+}$) prene-sejo v organsko fazo. Za nitrobenzen, nasičen z vodo, smo določili konstante ekstrakcije in konstante stabilnosti vseh zvrsti kationskih kompleksov.