

Short communication

Synergistic Extraction of Calcium and Strontium Into Nitrobenzene by Using Hydrogen Dicarbolylcobaltate and 1,2-Bis(Diphenylphosphino)Ethane Dioxide

Emanuel Makrlík,^{1,*} Petr Vaňura,² Pavel Selucký³ and Zdeněk Spíchal⁴

¹ Faculty of Environmental Sciences, Czech University of Life Sciences, Prague, Kamýcká 129, 165 21 Prague 6, Czech Republic

² Department of Analytical Chemistry, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic

³ Nuclear Research Institute, 250 68 Řež, Czech Republic

⁴ Department of Inorganic Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

* Corresponding author: E-mail: makrlík@centrum.cz

Received: 15-06-2012

Abstract

Extraction of microamounts of calcium and strontium by a nitrobenzene solution of hydrogen dicarbolylcobaltate (H^+B^-) in the presence of 1,2-bis(diphenylphosphino)ethane dioxide (DPPEtDO, L) has been investigated. The equilibrium data have been explained assuming that the species HL^+ , HL_2^+ , ML_2^{2+} and ML_3^{2+} ($M^{2+} = Ca^{2+}, Sr^{2+}$) are extracted into the organic phase. The values of extraction and stability constants of the cationic complexes in nitrobenzene saturated with water have been determined. In the considered nitrobenzene medium, it was found that the stability constants of the complexes CaL_2^{2+} and CaL_3^{2+} , where L is DPPEtDO, are somewhat higher than those of the corresponding complex species SrL_2^{2+} and SrL_3^{2+} with the same ligand L.

Keywords: Calcium, strontium, hydrogen dicarbolylcobaltate, 1,2-bis(diphenylphosphino)ethane dioxide, extraction and stability constants, water-nitrobenzene system

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,^{2–13} and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.^{14,15}

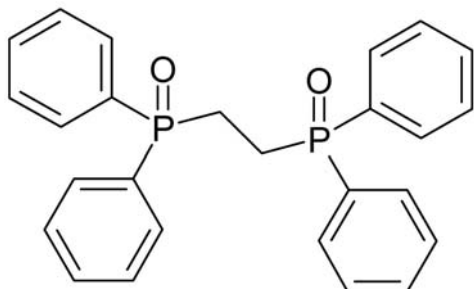
Bidentate phosphonates, phosphine oxides and malonamides have been intensively studied for the extraction of trivalent lanthanides and actinides from acidic media.^{16–18} A process using octyl-phenyl-*N,N*-diisobutylcar-

bamoylmethyl phosphine oxide (i.e. “classical” CMPO) and called TRUEX was apparently used in the United States,¹⁶ whereas malonic diamides $(RR'NCO)_2CHR''$ (DIAMEX) were proposed in France.¹⁷

Moreover, *N,N,N',N'*-tetrakis(2-methylpyridyl) ethylenediamine (TPEN),¹⁹ TODGA (*N,N,N',N'*-tetraoctyl diglycolamide),^{20–22} CMPO substituted calixarenes,²³ substituted 2,6-dipicolinamides,^{13,24–26} diamides of 2,2'-dipyridyl-6,6'-dicarboxylic acid,²⁷ substituted bis-tetrazolyl pyridines²⁸ and *N,N,N',N'*-tetraoctyl-3,6-dioxaoctanediamide (DOODA)²⁹ have been also applied for the extraction separation of trivalent lanthanides and minor actinides from acidic aqueous solutions.

Recently, extractive properties of a synergistic mixture of hydrogen dicarbolylcobaltate (H^+B^-)¹ and 1,2-

bis(diphenylphosphino)ethane dioxide (abbrev. DPPEtDO; see Scheme 1) toward Eu^{3+} and Am^{3+} have been investigated in the water–nitrobenzene system.³⁰ On the other hand, in the current work, the solvent extraction of microamounts of calcium and strontium by a nitrobenzene solution of this synergistic mixture was studied. We intended to find the composition of the species in the organic phase and to determine the corresponding equilibrium constants.



Scheme 1. Structural formula of 1,2-bis(diphenylphosphino)ethane dioxide (abbrev. DPPEtDO or L, respectively).

2. Experimental

Preparation of 1,2-(diphenylphosphino)ethane dioxide (see Scheme 1) was presented in Ref. 31. Cesium dicarbollycobaltate, Cs^+B^- , was synthesized by means of the method published by Hawthorne et al.³² A nitrobenzene solution of hydrogen dicarbollycobaltate (H^+B^-)¹ was prepared from Cs^+B^- by the procedure described elsewhere.³³ The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The water used for the extraction experiments was double-distilled and then it was deionized as well. 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–DPPEtDO– H^+B^- systems were performed in 10 mL polypropylene test-tubes with polypropylene 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 DPPEtDO 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, $c_{\text{B}} = 0.001$ 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.

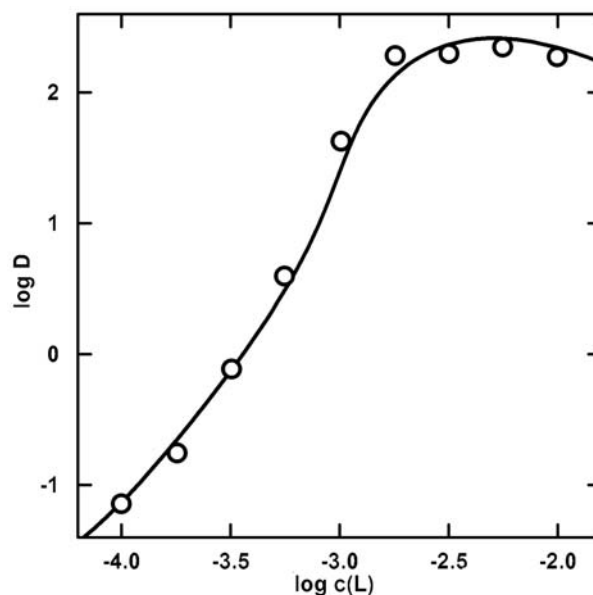
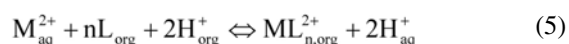
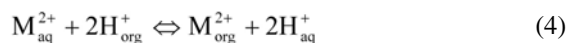


Figure 1. $\log D$ as a function of $\log c(\text{L})$, where $\text{L} = \text{DPPEtDO}$, for the system water–HCl– Ca^{2+} (microamounts)–nitrobenzene–DPPEtDO– H^+B^- ; $c(\text{HCl}) = 0.01$ mol/L, $c_{\text{B}} = 0.001$ mol/L. The curve was calculated using the constants given in Table 3.

With respect to the results of previous papers,^{2,4,34,35} the considered water–HCl– M^{2+} (microamounts; $\text{M}^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+}$)–nitrobenzene–DPPEtDO (L)– H^+B^- systems can be described by the set of reactions:



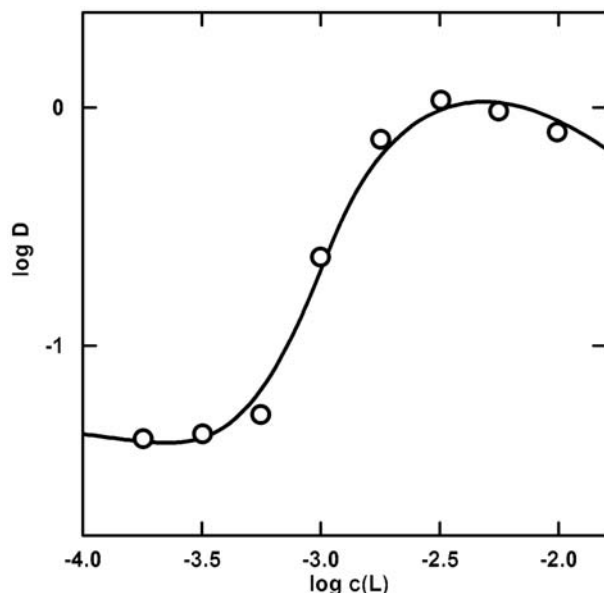


Figure 2. Log D as a function of log c(L), where L = DPPEtDO, for the system water–HCl–Sr²⁺ (microamounts)–nitrobenzene–DPPEtDO–H⁺B⁻; c(HCl) = 0.01 mol/L, c_B = 0.001 mol/L. The curve was calculated using the constants given in Table 4.

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 DPPEtDO 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 LETAGROP³⁸ used for determination of the “best” values of the extraction constants $K_{\text{ex}}(\text{ML}_{n,\text{org}}^{2+})$ ($\text{M}^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+}$; L = DPPEtDO). 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 $\log K_D = 2.06$,³⁰ $\log \beta(\text{HL}_{\text{org}}^+) = 4.88$,³⁰ $\log \beta(\text{HL}_{2,\text{org}}^+) = 7.33$,³⁰ $\log K_{\text{ex}}(\text{Ca}_{\text{org}}^{2+}) = 0.2$,³⁹ and $\log K_{\text{ex}}(\text{Sr}_{\text{org}}^{2+}) = 0.7$,³⁶ 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+} ($\text{M}^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+}$; L = DPPEtDO) 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 DPPEtDO.

Calcium complexes in the organic phase	log K _{ex} ^a	U ^b
CaL ₂ ²⁺	13.61 (14.12)	7.31
CaL ₃ ²⁺	17.49 (17.83)	1.76
CaL ₂ ²⁺ , CaL ₃ ²⁺	12.54 (12.83), 17.23 (17.61)	0.03

^a The values of the extraction constants are given for each complex. The reliability interval of the constants is given as 3 σ(K), where σ(K) is the standard deviation of the constant K.³⁸ These values are expressed in the logarithmic scale using the approximate relation $\log K \pm \{\log [K + 1.5\sigma(K)] - \log [K - 1.5\sigma(K)]\}$. For σ(K) > 0.2K, the previous relation is not valid and then only the upper limit is given in the parenthesis in the form $\log K (\log [K + 3\sigma(K)])$.³⁸

^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 DPPEtDO.

Strontium complexes in the organic phase	log K _{ex} ^a	U ^b
SrL ₂ ²⁺	11.80 (12.19)	2.30
SrL ₃ ²⁺	14.98 (15.25)	0.53
SrL ₂ ²⁺ , SrL ₃ ²⁺	10.99 (11.33), 14.82 (15.04)	0.02

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

Knowing the values $\log K_{\text{ex}}(\text{Ca}_{\text{org}}^{2+}) = 0.2$,³⁹ and $\log K_{\text{ex}}(\text{Sr}_{\text{org}}^{2+}) = 0.7$,³⁶ as well as the extraction constants $\log K_{\text{ex}}(\text{CaL}_{2,\text{org}}^{2+}) = 12.54$, $\log K_{\text{ex}}(\text{CaL}_{3,\text{org}}^{2+}) = 17.23$, $\log K_{\text{ex}}(\text{SrL}_{2,\text{org}}^{2+}) = 10.99$ and $\log K_{\text{ex}}(\text{SrL}_{3,\text{org}}^{2+}) = 14.82$ determined here (see Tables 1 and 2), the stability constants of the complexes ML_2^{2+} and ML_3^{2+} ($\text{M}^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+}$; L = DPPEtDO) 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:

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

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

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

Moreover, Figure 3 depicts the contributions of the species H^+ , 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 $\text{Sr}_{\text{org}}^{2+}$, $\text{SrL}_{2,\text{org}}^{2+}$, $\text{SrL}_{3,\text{org}}^{2+}$, 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 $\text{HL}_{2,\text{org}}^+$, $\text{CaL}_{3,\text{org}}^{2+}$ and $\text{SrL}_{3,\text{org}}^{2+}$ are present in significant concentrations only at relatively high amounts of the DPPEtDO ligand in the systems under consideration.

Finally, it should be noted that the stability constants of the complex species $\text{ML}_{2,\text{org}}^{2+}$ and $\text{ML}_{3,\text{org}}^{2+}$ ($\text{M}^{2+} = \text{Ca}^{2+}$, Sr^{2+} ; $\text{L} = \text{DPPEtDO}$) in nitrobenzene saturated with water are $\log \beta(\text{CaL}_{2,\text{org}}^{2+}) = 12.34$, $\log \beta(\text{SrL}_{2,\text{org}}^{2+}) = 10.29$, $\log \beta(\text{CaL}_{3,\text{org}}^{2+}) = 17.03$ and $\log \beta(\text{SrL}_{3,\text{org}}^{2+}) = 14.12$, as given in Tables 3 and 4. Thus, in the considered nitrobenzene medium, the stability constants of the CaL_n^{2+} complexes, where $n = 2, 3$ and L is DPPEtDO, are somewhat higher than those of the corresponding complexes SrL_n^{2+} .

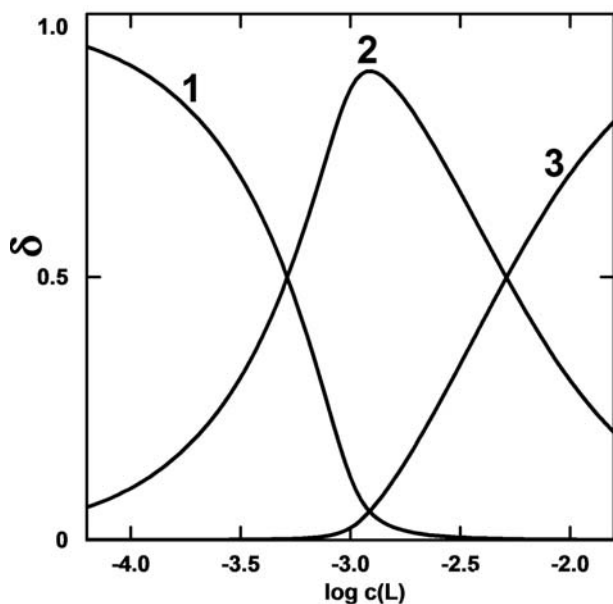


Figure 3. Distribution diagram of hydrogen cation in the equilibrium nitrobenzene phase of the water–HCl– Ca^{2+} (microamounts)–nitrobenzene–DPPEtDO– H^+B^- extraction system in the forms of H^+ , HL^+ and HL_2^+ ; $c(\text{HCl}) = 0.01 \text{ mol/L}$, $c_{\text{B}} = 0.001 \text{ mol/L}$.
 $1 \delta(\text{H}^+) = [\text{H}_{\text{org}}^+]/c(\text{H}^+)_{\text{org}}$, $2 \delta(\text{HL}^+) = [\text{HL}_{\text{org}}^+]/c(\text{H}^+)_{\text{org}}$,
 $3 \delta(\text{HL}_2^+) = [\text{HL}_{2,\text{org}}^+]/c(\text{H}^+)_{\text{org}}$,

$$\text{where } c(\text{H}^+)_{\text{org}} = [\text{H}_{\text{org}}^+] + [\text{HL}_{\text{org}}^+] + [\text{HL}_{2,\text{org}}^+].$$

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

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

Equilibrium	log K
$\text{L}_{\text{aq}} \rightleftharpoons \text{L}_{\text{org}}$	2.06 ^a
$\text{H}_{\text{org}}^+ + \text{L}_{\text{org}} \rightleftharpoons \text{HL}_{\text{org}}^+$	4.88 ^a
$\text{H}_{\text{org}}^+ + 2\text{L}_{\text{org}} \rightleftharpoons \text{HL}_{2,\text{org}}^+$	7.33 ^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
$\text{Ca}_{\text{aq}}^{2+} + 2\text{L}_{\text{org}} + 2\text{H}_{\text{org}}^+ \rightleftharpoons \text{CaL}_{2,\text{org}}^{2+} + 2\text{H}_{\text{aq}}^+$	12.54
$\text{Ca}_{\text{aq}}^{2+} + 3\text{L}_{\text{org}} + 2\text{H}_{\text{org}}^+ \rightleftharpoons \text{CaL}_{3,\text{org}}^{2+} + 2\text{H}_{\text{aq}}^+$	17.23
$\text{Ca}_{\text{org}}^{2+} + 2\text{L}_{\text{org}} \rightleftharpoons \text{CaL}_{2,\text{org}}^{2+}$	12.34
$\text{Ca}_{\text{org}}^{2+} + 3\text{L}_{\text{org}} \rightleftharpoons \text{CaL}_{3,\text{org}}^{2+}$	17.03

^a Ref. 30; ^b Ref. 39.

Table 4. Equilibrium constants in the water–HCl– Sr^{2+} (microamounts)–nitrobenzene–DPPEtDO– H^+B^- system.

Equilibrium	log K
$\text{L}_{\text{aq}} \rightleftharpoons \text{L}_{\text{org}}$	2.06 ^a
$\text{H}_{\text{org}}^+ + \text{L}_{\text{org}} \rightleftharpoons \text{HL}_{\text{org}}^+$	4.88 ^a
$\text{H}_{\text{org}}^+ + 2\text{L}_{\text{org}} \rightleftharpoons \text{HL}_{2,\text{org}}^+$	7.33 ^a
$\text{Sr}_{\text{aq}}^{2+} + 2\text{H}_{\text{org}}^+ \rightleftharpoons \text{Sr}_{\text{org}}^{2+} + 2\text{H}_{\text{aq}}^+$	0.7 ^b
$\text{Sr}_{\text{aq}}^{2+} + 2\text{L}_{\text{org}} + 2\text{H}_{\text{org}}^+ \rightleftharpoons \text{SrL}_{2,\text{org}}^{2+} + 2\text{H}_{\text{aq}}^+$	10.99
$\text{Sr}_{\text{aq}}^{2+} + 3\text{L}_{\text{org}} + 2\text{H}_{\text{org}}^+ \rightleftharpoons \text{SrL}_{3,\text{org}}^{2+} + 2\text{H}_{\text{aq}}^+$	14.82
$\text{Sr}_{\text{org}}^{2+} + 2\text{L}_{\text{org}} \rightleftharpoons \text{SrL}_{2,\text{org}}^{2+}$	10.29
$\text{Sr}_{\text{org}}^{2+} + 3\text{L}_{\text{org}} \rightleftharpoons \text{SrL}_{3,\text{org}}^{2+}$	14.12

^a Ref. 30; ^b Ref. 36.

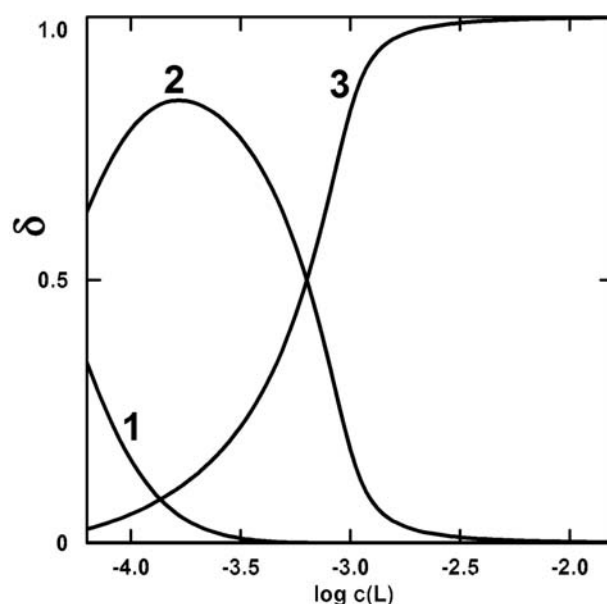


Figure 4. Distribution diagram of calcium in the equilibrium nitrobenzene phase of the water–HCl– Ca^{2+} (microamounts)–nitrobenzene–DPPEtDO– H^+B^- extraction system in the forms of Ca^{2+} , CaL_2^{2+} and CaL_3^{2+} ; $c(\text{HCl}) = 0.01 \text{ mol/L}$, $c_{\text{B}} = 0.001 \text{ mol/L}$.
 $1 \delta(\text{Ca}^{2+}) = [\text{Ca}_{\text{org}}^{2+}]/c(\text{Ca}^{2+})_{\text{org}}$, $2 \delta(\text{CaL}_2^{2+}) = [\text{CaL}_{2,\text{org}}^{2+}]/c(\text{Ca}^{2+})_{\text{org}}$,
 $3 \delta(\text{CaL}_3^{2+}) = [\text{CaL}_{3,\text{org}}^{2+}]/c(\text{Ca}^{2+})_{\text{org}}$,

$$\text{where } c(\text{Ca}^{2+})_{\text{org}} = [\text{Ca}_{\text{org}}^{2+}] + [\text{CaL}_{2,\text{org}}^{2+}] + [\text{CaL}_{3,\text{org}}^{2+}].$$

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

In conclusion, Table 5 summarizes the stability constants of the complex species HL^+ , HL_2^+ and ML_n^{2+} ($n = 2, 3$; $M^{2+} = Ca^{2+}, Sr^{2+}$) with four electroneutral ligands L, denoted by the symbols DPPEDO, DPPEtDO, DBDECMP and “classical” CMPO (see Schemes 1 and 2), in nitrobenzene saturated with water. From the data reviewed in this table it follows that in the mentioned nitrobenzene medium, the stability constants of the corresponding cationic

Table 5. Stability constants of the complex species HL^+ , HL_2^+ and ML_n^{2+} [$n = 2, 3$; $M^{2+} = Ca^{2+}, Sr^{2+}$; L = 1,2-bis(diphenylphosphino)ethylene dioxide (DPPEDO), 1,2-bis(diphenylphosphino)ethane dioxide (DPPEtDO), dibutyl diethylcarbamoylmethylene phosphonate (DBDECMP), octyl-phenyl-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (“classical” CMPO)] in nitrobenzene saturated with water at 25 °C.

Quantity	L			
	DPP-EDO ^a	DPP-EtDO ^b	DBDE-CMP ^d	“classical” CMPO ^e
$\log \beta (HL_{org}^+)$	5.06	4.88 ^c	4.22	6.16
$\log \beta (HL_{2,org}^+)$	7.89	7.33 ^c	6.74	9.29
$\log \beta (CaL_{2,org}^{2+})$	12.32	12.34	11.07	14.46
$\log \beta (CaL_{3,org}^{2+})$	17.24	17.03	14.72	19.52
$\log \beta (SrL_{2,org}^{2+})$	10.11	10.29	10.44	13.09
$\log \beta (SrL_{3,org}^{2+})$	15.15	14.12	13.48	17.31

^a Ref. 35; ^b This work; ^c Ref. 30; ^d Ref. 3; ^e Ref. 8.

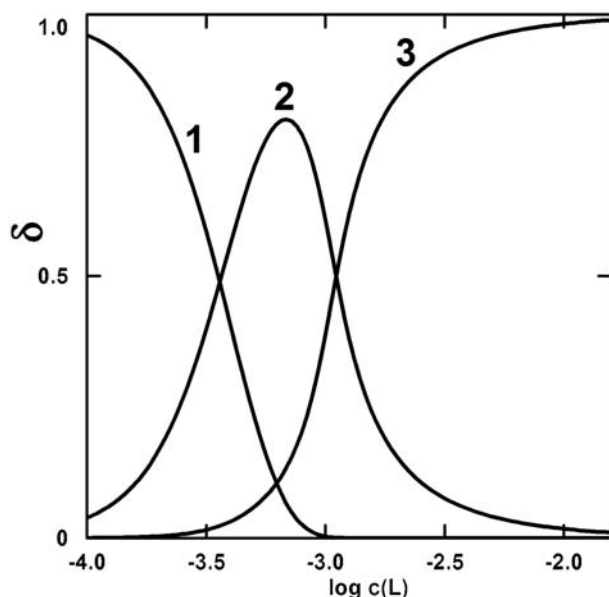
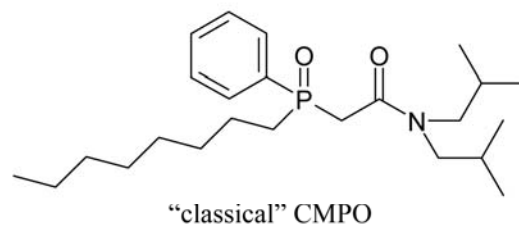
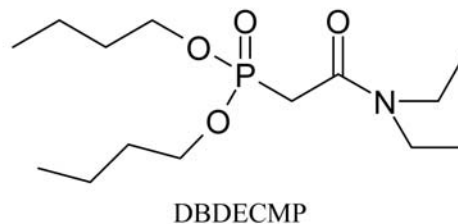
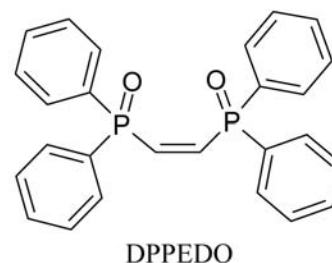


Figure 5. Distribution diagram of strontium in the equilibrium nitrobenzene phase of the water–HCl– Sr^{2+} (microamounts) –nitrobenzene–DPPEtDO– H^+B^- extraction system in the forms of Sr^{2+} , SrL_2^{2+} , and SrL_3^{2+} ; $c(HCl) = 0.01$ mol/L, $c_B = 0.001$ mol/L. $1 \delta(Sr^{2+}) = [Sr_{org}^{2+}]/c(Sr^{2+})_{org}$, $2 \delta(SrL_2^{2+}) = [SrL_{2,org}^{2+}]/c(Sr^{2+})_{org}$, $3 \delta(SrL_3^{2+}) = [SrL_{3,org}^{2+}]/c(Sr^{2+})_{org}$, where $c(Sr^{2+})_{org} = [Sr_{org}^{2+}] + [SrL_{2,org}^{2+}] + [SrL_{3,org}^{2+}]$. The distribution curves were calculated using the constants given in Table 4.

species HL^+ , HL_2^+ , ML_2^{2+} and ML_3^{2+} ($M^{2+} = Ca^{2+}, Sr^{2+}$; L = DPPEDO, DPPEtDO) are comparable, while the stabilities of the HL^+ , HL_2^+ , ML_2^{2+} and ML_3^{2+} ($M^{2+} = Ca^{2+}, Sr^{2+}$) in this nitrobenzene medium, where L is “classical” CMPO, are substantially higher than those of the respective complexes involving the DPPEDO, DPPEtDO or DBDECMP ligands.



Scheme 2. Structural formulas of 1,2-bis(diphenylphosphino)ethylene dioxide (abbrev. DPPEDO), dibutyl diethylcarbamoylmethylene phosphonate (DPPECMP) and octyl-phenyl-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (“classical” CMPO).

4. Acknowledgements

This work was supported by the Grant Agency of Faculty of Environmental Sciences, Czech University of Life Sciences, Prague, Project No.: 42900/1312/3114 “Environmental Aspects of Sustainable Development of Society,” and by the Czech Ministry of Education, Youth, and Sports, Project MSM 6046137307.

5. References

1. E. Makrlík, P. Vaňura, *Talanta* **1985**, 32, 423–429.
2. E. Makrlík, P. Vaňura, P. Selucký, *J. Solution Chem.* **2010**, 39, 692–700.
3. E. Makrlík, P. Vaňura, P. Selucký, *Acta Chim. Slov.* **2010**, 57, 470–474.

4. E. Makrlík, P. Vaňura, P. Selucký, *Acta Chim. Slov.* **2010**, *57*, 485–490.
5. E. Makrlík, P. Vaňura, P. Selucký, *Acta Chim. Slov.* **2010**, *57*, 922–926.
6. E. Makrlík, P. Toman, P. Vaňura, R. Rathore, *Acta Chim. Slov.* **2010**, *57*, 948–952.
7. E. Makrlík, P. Vaňura, P. Selucký, *Acta Chim. Slov.* **2011**, *58*, 176–180.
8. E. Makrlík, P. Vaňura, P. Selucký, Z. Spíchal, *Acta Chim. Slov.* **2011**, *58*, 600–604.
9. E. Makrlík, P. Toman, P. Vaňura, R. Rathore, *Acta Chim. Slov.* **2011**, *58*, 611–615.
10. E. Makrlík, P. Vaňura, P. Selucký, Z. Spíchal, *Acta Chim. Slov.* **2011**, *58*, 860–865.
11. E. Makrlík, P. Vaňura, Z. Sedláková, *J. Radioanal. Nucl. Chem.* **2010**, *283*, 157–161.
12. E. Makrlík, P. Vaňura, *J. Radioanal. Nucl. Chem.* **2010**, *283*, 497–501.
13. E. Makrlík, P. Vaňura, P. Selucký, V. A. Babain, I. V. Smirnov, *J. Radioanal. Nucl. Chem.* **2010**, *283*, 839–844.
14. V. N. Romanovskiy, I. V. Smirnov, V. A. Babain, T. A. Todd, R. S. Herbst, J. D. Law, K. N. Brewer, *Solvent Extr. Ion Exch.* **2001**, *19*, 1–21.
15. J. D. Law, R. S. Herbst, T. A. Todd, V. N. Romanovskiy, V. A. Babain, V. M. Esimantovskiy, I. V. Smirnov, B. N. Zaitsev, *Solvent Extr. Ion Exch.* **2001**, *19*, 23–36.
16. W. W. Schulz, E. P. Horwitz, *Separ. Sci. Technol.* **1988**, *23*, 1191–1210.
17. C. Cuillerdier, C. Musikas, P. Hoel, L. Nigond, X. Vitart, *Separ. Sci. Technol.* **1991**, *26*, 1229–1244.
18. G. R. Mahajan, D. R. Prabhu, V. K. Manchanda, L. P. Badheka, *Waste Management* **1998**, *18*, 125–133.
19. T. Matsumura, K. Takeshita, *J. Nucl. Sci. Technol. (Japan)* **2006**, *43*, 824–827.
20. S. A. Ansari, P. N. Pathak, V. K. Manchanda, M. Husain, A. K. Prasad, V. S. Parmar, *Solvent Extr. Ion Exch.* **2005**, *23*, 463–479.
21. S. A. Ansari, P. N. Pathak, M. Husain, A. K. Prasad, V. S. Parmar, V. K. Manchanda, *Radiochim. Acta* **2006**, *94*, 307–312.
22. K. van Hecke, G. Modolo, *J. Radioanal. Nucl. Chem.* **2004**, *261*, 269–275.
23. H. H. Dam, D. N. Reinhoudt, W. Verboom, *Chem. Soc. Rev.* **2007**, *36*, 367–377.
24. M. Y. Alyapyshev, V. A. Babain, I. V. Smirnov, *Radiochemistry (Radiokhimiya), Engl. Ed.* **2004**, *46*, 270–271.
25. M. Y. Alyapyshev, V. A. Babain, I. V. Smirnov, A. Y. Shadrin, *Radiochemistry (Radiokhimiya), Engl. Ed.* **2006**, *48*, 369–373.
26. V. A. Babain, M. Y. Alyapyshev, R. N. Kiseleva, *Radiochim. Acta* **2007**, *95*, 217–223.
27. M. Alyapyshev, V. Babain, N. Borisova, I. Eliseev, D. Kirsanov, A. Kostin, A. Legin, M. Reshetova, Z. Smirnova, *Polyhedron* **2010**, *29*, 1998–2005.
28. V. Smirnov, A. V. Chirkov, V. A. Babain, E. Y. Pokrovskaya, T. A. Artamonova, *Radiochim. Acta* **2009**, *97*, 593–601.
29. Y. Sasaki, Y. Morita, Y. Kitatsuji, T. Kimura, *Chem. Lett.* **2010**, *39*, 898–899.
30. E. Makrlík, P. Vaňura, P. Selucký, Z. Spíchal, *J. Radioanal. Nucl. Chem.* **2011**, *289*, 13–18.
31. Z. Spíchal, M. Nečas, J. Pinkas, *Inorg. Chem.* **2005**, *44*, 2074–2080.
32. M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, P. A. Wegner, *J. Am. Chem. Soc.* **1968**, *90*, 879–896.
33. E. Makrlík, *Collect. Czech. Chem. Commun.* **1992**, *57*, 289–295.
34. E. Makrlík, P. Vaňura, P. Selucký, *J. Radioanal. Nucl. Chem.* **2010**, *284*, 87–92.
35. E. Makrlík, P. Vaňura, P. Selucký, *J. Radioanal. Nucl. Chem.* **2010**, *285*, 383–387.
36. P. Vaňura, E. Makrlík, J. Rais, M. Kyrš, *Collect. Czech. Chem. Commun.* **1982**, *47*, 1444–1464.
37. P. Vaňura, E. Makrlík, *Collect. Czech. Chem. Commun.* **1993**, *58*, 1324–1336.
38. L. G. Sillén, B. Warnqvist, *Arkiv Kemi* **1969**, *31*, 315–339.
39. P. Vaňura, *Czech. J. Phys.* **1999**, *49 (Suppl. S1)*, 761–767

Povzetek

Raziskovali smo ekstrakcijo mikrokoličin kalcija in stroncija z raztopino hidrogendikarbolilkoblatata (H^+B^-) v prisotnosti 1,2-(difenilfosfino)etan dioksida (DPPEtDO, L). Ravnotežja smo razložili s pomočjo predpostavke, da se kompleksi HL^+ , HL_2^+ , ML_2^+ in ML_3^{2+} ($M^{2+} = Ca^{2+}, Sr^{2+}$) ekstrahirajo v organsko fazo. Določili smo konstante porazdelitve ter konstante stabilnosti kompleksov v nitrobenzenu, nasičenem z vodo. Ugotovili smo, da so v preiskovanih medijih konstante stabilnosti kompleksov CaL_2^{2+} in CaL_3^{2+} (L pomeni DPPEtDO) višje kot pri kompleksih SrL_2^{2+} in SrL_3^{2+} .