

Short communication

Solvent Extraction of Calcium and Strontium into Nitrobenzene by Using a Synergistic Mixture of Hydrogen Dicarbollylcobaltate and Bis(Diphenylphosphino)Methane Dioxide

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Abstract

Extraction of microamounts of calcium and strontium by a nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-) in the presence of bis(diphenylphosphino)methane dioxide (DPPMDO, L) has been investigated. The equilibrium data have been explained assuming that the species HL^+ , HL_2^+ , ML_2^{2+} , ML_3^{2+} and ML_4^{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+} , CaL_3^{2+} and CaL_4^{2+} , where L is DPPMDO, are somewhat higher than those of the corresponding complex species SrL_2^{2+} , SrL_3^{2+} and SrL_4^{2+} with the same ligand L.

Keywords: Calcium, strontium, bis(diphenylphosphino)methane dioxide, hydrogen dicarbollylcobaltate, complexation, extraction and stability constants, water-nitrobenzene system

1. Introduction

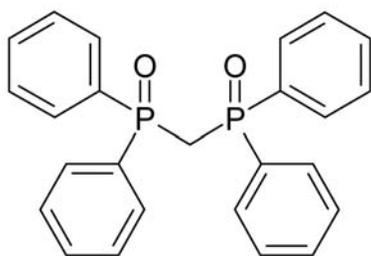
Bidentate phosphonates, phosphine oxides and malonamides have been intensively studied for the extraction of trivalent lanthanides and actinides from acidic media.^{1–3} A process using octyl-phenyl-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (i.e. “classical” CMPO) and called TRUEX was apparently used in the United States,¹ while malonic diamides (RR'NCO)₂CHR'' (DIAMEX) were proposed in France.² Furthermore, a process involving chlorinated cobalt dicarbollide, polyethylene glycol (PEG 400) and diphenyl-*N,N*-dibutylcarbamoylmethyl phosphine oxide (DPDBCMPPO), also called UNEX, has been reported for the simultaneous recovery of cesium,

strontium, lanthanides and actinides from highly acidic media into phenyltrifluoromethyl sulfone (abbrev. FS 13).^{4,5} At this point it should be noted that the mentioned FS 13 diluent was developed for the UNEX process as an alternative organic diluent to the highly polar nitrobenzene. Besides this, FS 13 has the advantage of low viscosity and very good solubility of the UNEX extractants and metal solvates.⁵ On the other hand, nitrobenzene derivatives have been successfully utilized as diluents for cobalt dicarbollide processes in Russia, however, they are deemed unsuitable for use in the United States due to the perceived hazards associated with nitrobenzene.

The dicarbollylcobaltate anion⁶ and some of its halogen derivatives are very useful reagents for the extrac-

tion 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,^{7–27} and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.^{4,5}

Recently, extractive properties of a synergistic mixture of hydrogen dicarbollylcobaltate (H^+B^-)⁶ and bis(diphenylphosphino)methane dioxide (DPPMDO, L; see Scheme 1) toward Eu^{3+} and Am^{3+} have been investigated in the water-nitrobenzene system.²⁸ 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 bis(diphenylphosphino)methane dioxide (abbrev. DPPMDO or L, respectively).

2. Experimental

Bis(diphenylphosphino)methane dioxide (DPPMDO) was synthesized similarly as 1,2-bis(diphenylphosphino)ethane dioxide (DPPEtDO) by the method presented in Ref. 29. Cesium dicarbollylcobaltate, Cs^+B^- , was produced by means of the method published by Hawthorne et al.³⁰ A nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-)⁶ was prepared from Cs^+B^- by the procedure described elsewhere.³¹ The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclides $^{45}\text{Ca}^{2+}$ and $^{85}\text{Sr}^{2+}$ were supplied by DuPont, Belgium.

The extraction experiments in the two-phase water-HCl- M^{2+} (microamounts; $\text{M}^{2+} = \text{Ca}^{2+}$, Sr^{2+})-nitrobenzene-DPPMDO- 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 appa-

ratus NRB-213 (Tesla P?emyšlení, 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 DPPMDO ligand in the initial nitrobenzene phase, $\log c(\text{L})$, are given in Figures 1 and 2, respectively. The initial concentration of hydrogen dicarbollylcobaltate in the organic phase, $c_{\text{B}} = 0.001$ mol/L, as well as the initial concentration of HCl in the aqueous phase, $c(\text{HCl}) = 0.05$ mol/L, are always related to the volume of one phase.

With respect to the results of previous papers,^{8,10,19,26,27} the considered water-HCl- M^{2+} (microamounts; $\text{M}^{2+} = \text{Ca}^{2+}$, Sr^{2+})-nitrobenzene-DPPMDO(L)- H^+B^- systems can be described by the set of reactions:

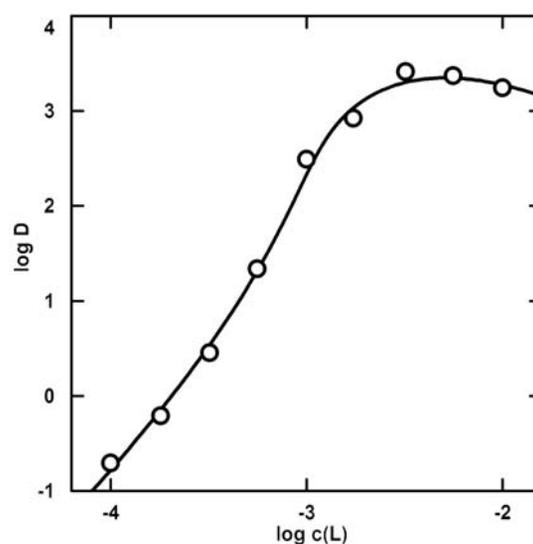


Figure 1. Log D as a function of $\log c(\text{L})$, where L = DPPMDO, for the system water-HCl- Ca^{2+} (microamounts)-nitrobenzene-DPPMDO- H^+B^- ; $c(\text{HCl}) = 0.05$ mol/L, $c_{\text{B}} = 0.001$ mol/L. The curve was calculated using the constants given in Table 3.

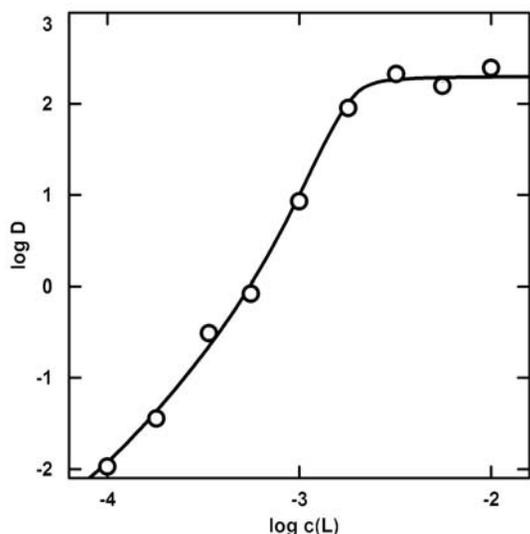
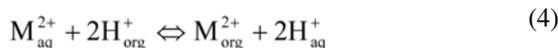


Figure 2. Log D as a function of log c(L), where L = DPPMDO, for the system water–HCl–Sr²⁺ (microamounts)–nitrobenzene–DPPMDO–H⁺B⁻; c(HCl) = 0.05 mol/L, c_B = 0.001 mol/L. The curve was calculated using the constants given in Table 4.



to which the following equilibrium constants correspond:

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

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

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

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

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

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 DPPMDO ligand 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 LETAGROP³⁴ used for determination of the “best” values of the extraction constants $K_{\text{ex}}(\text{ML}_{n,\text{org}}^{2+})$ ($M^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+}$; L = DPPMDO). 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 $\log K_{\text{D}} = 2.01$,²⁸ $\log \beta(\text{HL}_{\text{org}}^{+}) = 6.56$,²⁸ $\log \beta(\text{HL}_{2,\text{org}}^{+}) = 9.48$,²⁸ $\log K_{\text{ex}}(\text{Ca}_{\text{org}}^{2+}) = 0.2$,³⁵ and $\log K_{\text{ex}}(\text{Sr}_{\text{org}}^{2+}) = 0.7$,³² 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+} , ML_3^{2+} and ML_4^{2+} ($M^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+}$; L = DPPMDO) to be extracted into the nitrobenzene phase.

Table 1. Comparison of various models of calcium extraction from aqueous solution of HCl by nitrobenzene solution of H⁺B⁻ in the presence of DPPMDO.

| Calcium complexes in the organic phase | log K _{ex} ^a | U ^b |
|--|---|----------------|
| CaL ₂ ²⁺ | 19.33 (19.97) | 17.60 |
| CaL ₂ ²⁺ | 24.16 (24.64) | 5.51 |
| CaL ₃ ²⁺ | 27.73 (28.73) | 55.90 |
| CaL ₂ ²⁺ , CaL ₃ ²⁺ | 17.81 (18.23), 23.33 (23.66) | 0.61 |
| CaL ₃ ²⁺ , CaL ₄ ²⁺ | Transformed to CaL ₃ ²⁺ | |
| CaL ₂ ²⁺ , CaL ₃ ²⁺ , CaL ₄ ²⁺ | 17.81 (18.15), 23.22 (23.45), 25.17 (25.42) | 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.³⁴ 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 parentheses in the form of log K (log [K + 3σ(K)]).³⁴

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

Table 2. Comparison of various models of strontium extraction from aqueous solution of HCl by nitrobenzene solution of H⁺B⁻ in the presence of DPPMDO.

| Strontium complexes in the organic phase | log K _{ex} ^a | U ^b |
|--|---|----------------|
| SrL ₂ ²⁺ | 18.18 (18.85) | 20.60 |
| SrL ₃ ²⁺ | 22.87 (23.32) | 3.83 |
| SrL ₄ ²⁺ | 25.58 (26.41) | 24.40 |
| SrL ₂ ²⁺ , SrL ₃ ²⁺ | 16.73 (17.04), 22.40 (22.67) | 0.53 |
| SrL ₃ ²⁺ , SrL ₄ ²⁺ | Transformed to CaL ₃ ²⁺ | |
| SrL ₂ ²⁺ , SrL ₃ ²⁺ , SrL ₄ ²⁺ | 16.75 (17.01), 22.12 (22.40), 24.69 (25.02) | 0.03 |

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

Knowing the values $\log K_{\text{ex}}(\text{Ca}_{\text{org}}^{2+}) = 0.2$,³⁵ and $\log K_{\text{ex}}(\text{Sr}_{\text{org}}^{2+}) = 0.7$,³² as well as the extraction constants $\log K_{\text{ex}}(\text{CaL}_{2,\text{org}}^{2+}) = 17.81$, $\log K_{\text{ex}}(\text{CaL}_{3,\text{org}}^{2+}) = 23.22$, $\log K_{\text{ex}}(\text{CaL}_{4,\text{org}}^{2+}) = 25.17$, $\log K_{\text{ex}}(\text{SrL}_{2,\text{org}}^{2+}) = 16.75$, $\log K_{\text{ex}}(\text{SrL}_{3,\text{org}}^{2+}) = 22.12$ and $\log K_{\text{ex}}(\text{SrL}_{4,\text{org}}^{2+}) = 24.69$ de-

terminated here (see Tables 1 and 2), the stability constants of the complexes $ML_{2,org}^{2+}$, $ML_{3,org}^{2+}$ and $ML_{4,org}^{2+}$ ($M^{2+} = Ca^{2+}$, Sr^{2+} ; $L = DPPMDO$) in the organic phase defined as

$$\beta(ML_{2,org}^{2+}) = \frac{[ML_{2,org}^{2+}]}{[M_{org}^{2+}][L_{org}]^2} \quad (12)$$

$$\beta(ML_{3,org}^{2+}) = \frac{[ML_{3,org}^{2+}]}{[M_{org}^{2+}][L_{org}]^3} \quad (13)$$

$$\beta(ML_{4,org}^{2+}) = \frac{[ML_{4,org}^{2+}]}{[M_{org}^{2+}][L_{org}]^4} \quad (14)$$

can be evaluated applying the following simple relations:

$$\log \beta(ML_{2,org}^{2+}) = \log K_{ex}(ML_{2,org}^{2+}) - \log K_{ex}(M_{org}^{2+}) \quad (15)$$

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

$$\log \beta(ML_{4,org}^{2+}) = \log K_{ex}(ML_{4,org}^{2+}) - \log K_{ex}(M_{org}^{2+}) \quad (17)$$

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

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

| Equilibrium | log K |
|--|-------------------|
| $L_{aq} \rightleftharpoons L_{org}$ | 2.01 ^a |
| $H_{org}^+ + L_{org} \rightleftharpoons H_{org}^+$ | 6.56 ^a |
| $H_{org}^+ + 2L_{org} \rightleftharpoons H_{2,org}^+$ | 9.48 ^a |
| $Ca_{aq}^{2+} + 2H_{org}^+ \rightleftharpoons Ca_{org}^{2+} + 2H_{aq}^+$ | 0.2 ^b |
| $Ca_{aq}^{2+} + 2L_{org} + 2H_{org}^+ \rightleftharpoons CaL_{2,org}^{2+} + 2H_{aq}^+$ | 17.81 |
| $Ca_{aq}^{2+} + 3L_{org} + 2H_{org}^+ \rightleftharpoons CaL_{3,org}^{2+} + 2H_{aq}^+$ | 23.22 |
| $Ca_{aq}^{2+} + 4L_{org} + 2H_{org}^+ \rightleftharpoons CaL_{4,org}^{2+} + 2H_{aq}^+$ | 25.17 |
| $Ca_{org}^{2+} + 2L_{org} \rightleftharpoons CaL_{2,org}^{2+}$ | 17.61 |
| $Ca_{org}^{2+} + 3L_{org} \rightleftharpoons CaL_{3,org}^{2+}$ | 23.02 |
| $Ca_{org}^{2+} + 4L_{org} \rightleftharpoons CaL_{4,org}^{2+}$ | 24.97 |

^a Ref. 28. ^b Ref. 32.

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

| Equilibrium | log K |
|--|-------------------|
| $L_{aq} \rightleftharpoons L_{org}$ | 2.01 ^a |
| $H_{org}^+ + L_{org} \rightleftharpoons H_{org}^+$ | 6.56 ^a |
| $H_{org}^+ + 2L_{org} \rightleftharpoons H_{2,org}^+$ | 9.48 ^a |
| $Sr_{aq}^{2+} + 2H_{org}^+ \rightleftharpoons Sr_{org}^{2+} + 2H_{aq}^+$ | 0.2 ^b |
| $Sr_{aq}^{2+} + 2L_{org} + 2H_{org}^+ \rightleftharpoons SrL_{2,org}^{2+} + 2H_{aq}^+$ | 16.75 |
| $Sr_{aq}^{2+} + 3L_{org} + 2H_{org}^+ \rightleftharpoons SrL_{3,org}^{2+} + 2H_{aq}^+$ | 22.12 |
| $Sr_{aq}^{2+} + 4L_{org} + 2H_{org}^+ \rightleftharpoons SrL_{4,org}^{2+} + 2H_{aq}^+$ | 24.69 |
| $Sr_{org}^{2+} + 2L_{org} \rightleftharpoons SrL_{2,org}^{2+}$ | 16.05 |
| $Sr_{org}^{2+} + 3L_{org} \rightleftharpoons SrL_{3,org}^{2+}$ | 21.42 |
| $Sr_{org}^{2+} + 4L_{org} \rightleftharpoons SrL_{4,org}^{2+}$ | 23.99 |

^a Ref. 28. ^b Ref. 32.

Moreover, Figure 3 depicts 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 Figures 4 and 5 show the contributions of the cations Ca_{org}^{2+} , $CaL_{2,org}^{2+}$, $CaL_{3,org}^{2+}$, $CaL_{4,org}^{2+}$ and Sr_{org}^{2+} , $SrL_{2,org}^{2+}$, $SrL_{3,org}^{2+}$, $SrL_{4,org}^{2+}$, 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 $HL_{2,org}^+$, $CaL_{4,org}^{2+}$ and $SrL_{4,org}^{2+}$ are present in significant concentrations only at relatively high amounts of the DPPMDO ligand in the systems under consideration.

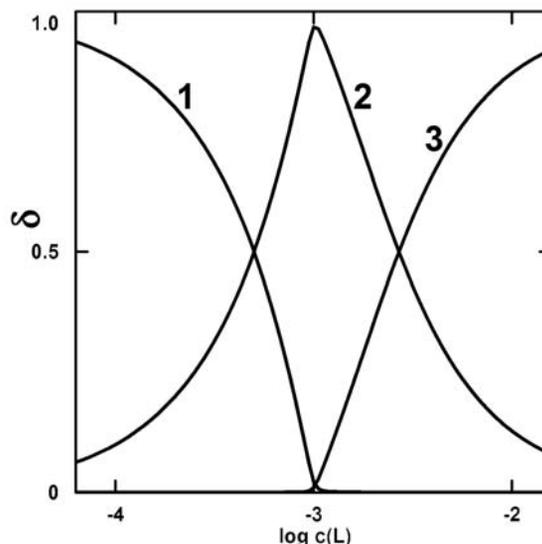


Figure 3. Distribution diagram of hydrogen cation in the equilibrium nitrobenzene phase of the water–HCl– Ca^{2+} (microamounts)–nitrobenzene–DPPMDO– H^+B^- extraction system in the forms of HL^+ , HL^+ and HL_2^+ ; $c(HCl) = 0.05$ mol/L, $c_B = 0.001$ mol/L.

$$1 \delta(H^+) = [H_{org}^+]/c(H^+)_{org}, \quad 2 \delta(HL^+) = [HL_{org}^+]/c(H^+)_{org},$$

$$3 \delta(HL_2^+) = [HL_{2,org}^+]/c(H^+)_{org}, \quad \text{where } c(H^+)_{org} = [H_{org}^+] + [HL_{org}^+] + [HL_{2,org}^+].$$

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 $ML_{2,org}^{2+}$, $ML_{3,org}^{2+}$ and $ML_{4,org}^{2+}$ ($M^{2+} = Ca^{2+}$, Sr^{2+} ; $L = DPPMDO$) in nitrobenzene saturated with water are $\log \beta(CaL_{2,org}^{2+}) = 17.61$, $\log \beta(SrL_{2,org}^{2+}) = 16.05$, $\log \beta(CaL_{3,org}^{2+}) = 23.02$, $\log \beta(SrL_{3,org}^{2+}) = 21.42$, $\log \beta(CaL_{4,org}^{2+}) = 24.97$ and $\log \beta(SrL_{4,org}^{2+}) = 23.99$, as given in Tables 3 and 4. Thus, in the considered nitrobenzene medium, the stability constants of the complexes $CaL_{2,org}^{2+}$, $CaL_{3,org}^{2+}$ and $CaL_{4,org}^{2+}$, where L is DPPMDO, are somewhat higher than those of the corresponding complex species $SrL_{2,org}^{2+}$, $SrL_{3,org}^{2+}$ and $SrL_{4,org}^{2+}$ with the same ligand L .

In conclusion, Table 5 summarizes the stability constants of the complexes HL^+ , HL_2^+ , $ML_{2,org}^{2+}$, $ML_{3,org}^{2+}$ and $ML_{4,org}^{2+}$ ($M^{2+} = Ca^{2+}$, Sr^{2+}) with two electroneutral ligands L , denoted by the symbols DPPeDO and DPPMDO (see

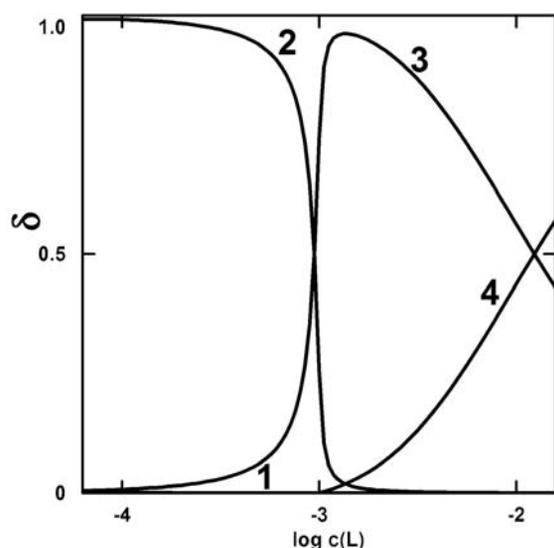


Figure 4. Distribution diagram of calcium in the equilibrium nitrobenzene phase of the water–HCl–Ca²⁺ (microamounts)–nitrobenzene – DPPMDO – H⁺B⁻ extraction system in the forms of Ca²⁺, CaL₂²⁺, CaL₃²⁺ and CaL₄²⁺; c(HCl) = 0.05 mol/L, c_B = 0.001 mol/L. 1 $\delta(\text{Ca}^{2+}) = [\text{Ca}_{\text{org}}^{2+}]/c(\text{Ca}^{2+})_{\text{org}}$, 2 $\delta(\text{CaL}_2^{2+}) = [\text{CaL}_{2,\text{org}}^{2+}]/c(\text{Ca}^{2+})_{\text{org}}$, 3 $\delta(\text{CaL}_3^{2+}) = [\text{CaL}_{3,\text{org}}^{2+}]/c(\text{Ca}^{2+})_{\text{org}}$, 4 $\delta(\text{CaL}_4^{2+}) = [\text{CaL}_{4,\text{org}}^{2+}]/c(\text{Ca}^{2+})_{\text{org}}$, where $c(\text{Ca}^{2+})_{\text{org}} = [\text{Ca}_{\text{org}}^{2+}] + [\text{CaL}_{2,\text{org}}^{2+}] + [\text{CaL}_{3,\text{org}}^{2+}] + [\text{CaL}_{4,\text{org}}^{2+}]$. The distribution curves were calculated using the constants given in Table 3.

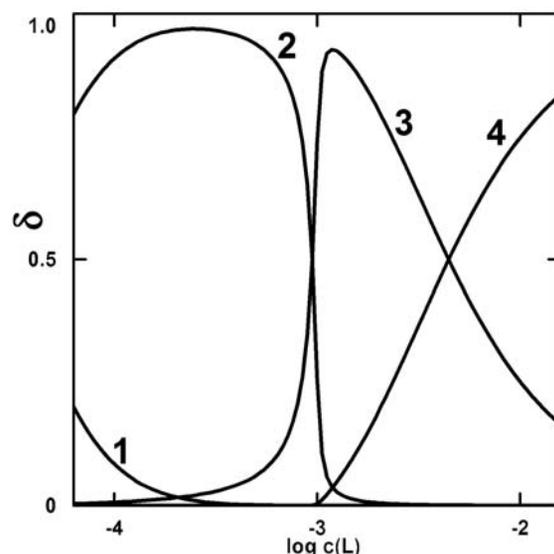


Figure 5. Distribution diagram of strontium in the equilibrium nitrobenzene phase of the water–HCl–Sr²⁺ (microamounts)–nitrobenzene – DPPMDO – H⁺B⁻ extraction system in the forms of Sr²⁺, SrL₂²⁺, SrL₃²⁺ and SrL₄²⁺; c(HCl) = 0.05 mol/L, c_B = 0.001 mol/L. 1 $\delta(\text{Sr}^{2+}) = [\text{Sr}_{\text{org}}^{2+}]/c(\text{Sr}^{2+})_{\text{org}}$, 2 $\delta(\text{SrL}_2^{2+}) = [\text{SrL}_{2,\text{org}}^{2+}]/c(\text{Sr}^{2+})_{\text{org}}$, 3 $\delta(\text{SrL}_3^{2+}) = [\text{SrL}_{3,\text{org}}^{2+}]/c(\text{Sr}^{2+})_{\text{org}}$, 4 $\delta(\text{SrL}_4^{2+}) = [\text{SrL}_{4,\text{org}}^{2+}]/c(\text{Sr}^{2+})_{\text{org}}$, where $c(\text{Sr}^{2+})_{\text{org}} = [\text{Sr}_{\text{org}}^{2+}] + [\text{SrL}_{2,\text{org}}^{2+}] + [\text{SrL}_{3,\text{org}}^{2+}] + [\text{SrL}_{4,\text{org}}^{2+}]$. The distribution curves were calculated using the constants given in Table 4.

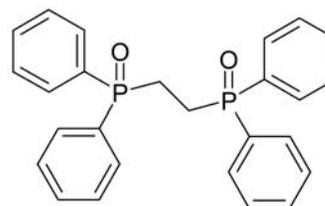
Schemes 1 and 2), in nitrobenzene saturated with water. From the data reviewed in this table it follows that in the mentioned medium, the stability constants of the cationic species HL⁺, HL₂⁺, ML₂²⁺ and ML₃²⁺ (M²⁺ = Ca²⁺, Sr²⁺),

where L = DPPMDO, are substantially higher than those of the corresponding complex species HL⁺, HL₂⁺, ML₂²⁺ and ML₃²⁺ (M²⁺ = Ca²⁺, Sr²⁺) involving the DPPEtDO ligand.

Table 5. Stability constants of the complex species HL⁺, HL₂⁺ and ML_n²⁺ [n = 2, 3, 4; M²⁺ = Ca²⁺, Sr²⁺; L = 1,2-bis(diphenylphosphino)ethane dioxide (abbrev. DPPEtDO), bis(diphenylphosphino)methane dioxide (DPPMDO)] in nitrobenzene saturated with water at 25 °C.

| Quantity | L | |
|---|----------------------|---------------------|
| | DPPEtDO ^a | DPPMDO ^b |
| log β (HL _{org} ⁺) | 4.88 | 6.56 ^c |
| log β (HL _{2,org} ⁺) | 7.33 | 9.48 ^c |
| log β (CaL _{2,org} ²⁺) | 12.34 | 17.61 |
| log β (CaL _{3,org} ²⁺) | 17.03 | 23.02 |
| log β (CaL _{4,org} ²⁺) | – | 24.97 |
| log β (SrL _{2,org} ²⁺) | 10.29 | 16.05 |
| log β (SrL _{3,org} ²⁺) | 14.12 | 21.42 |
| log β (SrL _{4,org} ²⁺) | – | 23.99 |

^a Ref. 36. ^b This work. ^c Ref. 28.



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

4. Acknowledgements

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Povzetek

Proučevali smo ekstrakcijo mikrokoličin kalcija in stroncija z raztopino hidrogendikarbolilkobaltata (H^+B^-) v nitrobenzenu v prisotnosti bis(difenilfosfino)metan dioksida (DPPMDO, L). Dobljena ravnotežja smo razložili s pomočjo predpostavke, da se kompleksi HL^+ , HL_2^+ , ML_2^{2+} , ML_3^{2+} in ML_4^{2+} ($M^{2+} = Ca^{2+}, Sr^{2+}$) ekstrahirajo v organsko fazo. Določili smo konstante porazdelitve in konstante stabilnosti kationskih kompleksov v nitrobenzenu, nasičenem z vodo. Izkazalo se je, da so konstante stabilnosti kompleksov CaL_2^{2+} , CaL_3^{2+} in CaL_4^{2+} (L je DPPMDO) višje kot pa so vrednosti konstant kompleksov SrL_2^{2+} , SrL_3^{2+} in SrL_4^{2+} .