

Short communication

Extraction of Calcium and Strontium into Phenyltrifluoromethyl Sulfone by Using Synergistic Mixture of Hydrogen Dicarbolylcobaltate and “Classical” CMPO

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Abstract

Solvent extraction of microamounts of calcium and strontium by a phenyltrifluoromethyl sulfone (FS 13) solution of hydrogen dicarbollycobaltate (H^+B^-) in the presence of octyl-phenyl-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (“classical” CMPO, L) has been investigated. The equilibrium data have been explained assuming that the species HL^+ , HL_2^+ , ML^{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 complex species in FS 13 saturated with water have been determined. In the considered FS 13 medium, it was found that the stability constants of the complex species CaL_n^{2+} , where $n = 1, 2, 3$ and L is “classical” CMPO, are higher than those of the corresponding complexes SrL_n^{2+} .

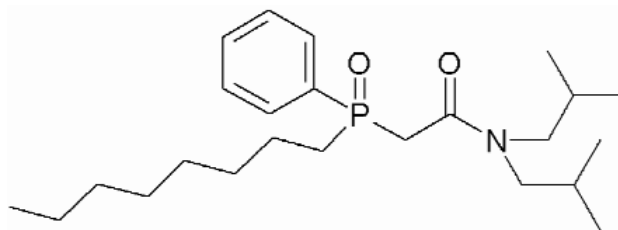
Keywords: Calcium, strontium, hydrogen dicarbollycobaltate, “classical” CMPO, phenyltrifluoromethyl sulfone, extraction and stability constants

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 whereas malonic diamides ($RR'NCO)_2CHR''$ (DIAMEX) were proposed in France.² Furthermore, a process involving chlorinated cobalt dicarbollide, polyethylene glycol (PEG 400), 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} In this context it is necessary to emphasize 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.

Recently, extractive properties of synergistic mixture of hydrogen dicarbollycobaltate (H^+B^-)⁶ and “classical” CMPO (see Scheme 1) toward Eu^{3+} and Am^{3+} has been investigated in the water-nitrobenzene system.⁷ On the other hand, in the current work, the solvent extraction of microamounts of calcium and strontium by a FS 13 solution of the mentioned 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 octyl-phenyl-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (abbrev. “classical” CMPO or L, respectively).

2. Experimental

Phenyltrifluoromethyl sulfone (FS 13) was kindly supplied by Khlopin Radium Institute, St. Petersburg, Russia. Octyl-phenyl-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (“classical” CMPO) was purchased from Alpha – Ventron. Cesium dicarbollylcobaltate, Cs^+B^- , was synthesized in the Institute of Inorganic Chemistry, Rež, Czech Republic, using the method published by Hawthorne et al.⁸ A FS 13 solution of hydrogen dicarbollylcobaltate (H^+B^-)⁶ was prepared from Cs^+B^- by the procedure described elsewhere.⁹ 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; $\text{M}^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+}$)–FS 13–“classical” CMPO– H^+B^- systems were performed in 10 cm³ glass test-tubes with polyethylene stoppers, using 2 cm³ of each phase. The test-tubes filled with the solutions were shaken for 2 hours at 25 ± 1 °C, using a laboratory shaker. Under these conditions, the equilibria in the systems under study were established after 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 cm³) 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 cm³ 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/A (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 FS 13 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) concentra-

tion of the “classical” CMPO ligand in the initial FS 13 phase, log *c*(L), are given in Figures 1 and 2, respectively. The initial concentration of hydrogen dicarbollylcobaltate in the organic phase, $c_{\text{B}} = 0.001 \text{ mol dm}^{-3}$, as well as the initial concentrations of HCl in the aqueous phase, $c(\text{HCl}) = 0.005$ and 0.01 mol dm^{-3} , are always related to the volume of one phase.

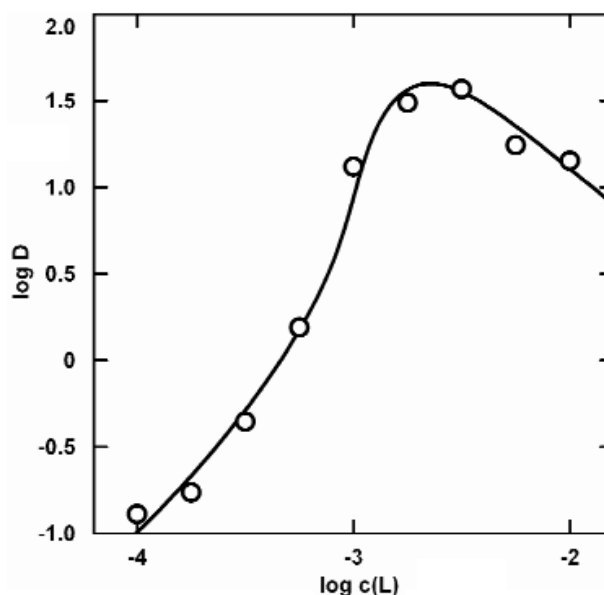


Figure 1: Log *D* as a function of log *c*(L), where L is “classical” CMPO, for the water–HCl– Ca^{2+} (microamounts)–FS 13–“classical” CMPO– H^+B^- system; $c(\text{HCl}) = 0.01 \text{ mol dm}^{-3}$, $c_{\text{B}} = 0.001 \text{ mol dm}^{-3}$. The curve was calculated using the constants given in Table 3.

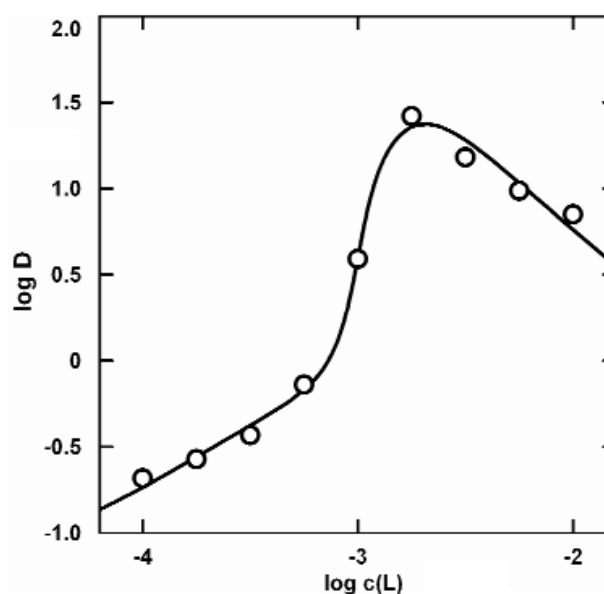
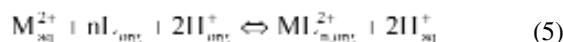
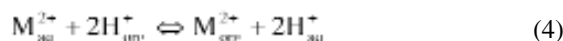


Figure 2: Log *D* as a function of log *c*(L), where L is “classical” CMPO, for the water–HCl– Sr^{2+} (microamounts)–FS 13–“classical” CMPO– H^+B^- system; $c(\text{HCl}) = 0.005 \text{ mol dm}^{-3}$, $c_{\text{B}} = 0.001 \text{ mol dm}^{-3}$. The curve was calculated using the constants given in Table 4.

Regarding the results of previous papers,^{6,10–14} the considered water–HCl–M²⁺ (microamounts; M²⁺ = Ca²⁺, Sr²⁺)–FS 13–“classical” CMPO (L)–H⁺B[–] systems can be described by the set of reactions:



to which the following equilibrium constants correspond:

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

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

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

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

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

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 “classical” CMPO ligand and the electroneutrality conditions in both phases of the system under consideration, was formulated^{15,16} and introduced into a more general least-squares minimizing program LETAGROP¹⁷ used for determination of the “best” values of the extraction constants $K_{\text{ex}}(ML_{n,\text{org}}^{2+})$ (M²⁺ = Ca²⁺, Sr²⁺; L = “classical” CMPO). 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.

Table 1: Comparison of various models of calcium extraction from aqueous solutions of HCl by FS 13 solution of H⁺B[–] in the presence of “classical” CMPO.

Calcium complexes in the organic phase	log K _{ex} ^a	U ^b
CaL ²⁺	10.13 (10.97)	53.50
CaL ₂ ²⁺	14.40 (14.91)	7.73
CaL ₃ ²⁺	18.46 (18.91)	3.52
CaL ²⁺ , CaL ₂ ²⁺	Transformed to CaL ₂ ²⁺	
CaL ₂ ²⁺ , CaL ₃ ²⁺	13.52 ± 0.25, 18.01 ± 0.22	0.16
CaL ²⁺ , CaL ₂ ²⁺ , CaL ₃ ²⁺	7.35 (7.87), 14.01 (14.30), 18.45 ± 0.23	0.02

^a The values of the extraction constants are given for each complex. The reliability interval of the constants is given as 3(K), where (K) is the standard deviation of the constant K.¹⁷ 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 $\log K(\log[K + 3\sigma(K)])$.¹⁷

^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 solutions of HCl by FS 13 solution of H⁺B[–] in the presence of “classical” CMPO.

Strontium complexes in the organic phase	log K _{ex} ^a	U ^b
SrL ²⁺	9.73 (10.56)	50.60
SrL ₂ ²⁺	14.14 (14.60)	5.49
SrL ₃ ²⁺	17.86 (18.33)	3.28
SrL ²⁺ , SrL ₂ ²⁺	Transformed to SrL ₂ ²⁺	
SrL ₂ ²⁺ , SrL ₃ ²⁺	13.35 (13.64), 17.53 (17.79)	0.35
SrL ²⁺ , SrL ₂ ²⁺ , SrL ₃ ²⁺	7.17 (7.45), 12.89 (13.29), 17.58 0.19	0.03

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

The values $\log K_D = 3.2$ (see Table 3, footnote *a*), $\log \beta(\text{HL}_{\text{org}}^+) = 5.67$ (see Table 3, footnote *b*), $\log \beta(\text{HL}_{2,\text{org}}^+) = 8.64$ (see Table 3, footnote *b*), $\log K_{\text{ex}}(\text{Ca}^{2+}) = -0.1^{20}$ and $\log K_{\text{ex}}(\text{Sr}^{2+}) = 0.1^{20}$ 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+} , ML_2^{2+} and ML_3^{2+} ($\text{M}^{2+} = \text{Ca}^{2+}$, Sr^{2+} ; $\text{L} =$ “classical” CMPO) to be extracted into the FS 13 phase.

Table 3: Equilibrium constants in the water–HCl– Ca^{2+} (microamounts)–FS 13–“classical” CMPO– H^+B^- system.

Equilibrium	log K
$\text{L}_{\text{aq}} \rightleftharpoons \text{L}_{\text{org}}$	3.2 ^a
$\text{H}^+_{\text{org}} + \text{L}_{\text{org}} \rightleftharpoons \text{HL}^+_{\text{org}}$	5.67 ^b
$\text{H}^+_{\text{org}} + 2\text{L}_{\text{org}} \rightleftharpoons \text{HL}^+_{2,\text{org}}$	8.64 ^b
$\text{Ca}^{2+}_{\text{aq}} + 2\text{H}^+_{\text{org}} \rightleftharpoons \text{Ca}^{2+}_{\text{org}} + 2\text{HL}^+_{\text{aq}}$	-0.1 ^c
$\text{Ca}^{2+}_{\text{aq}} + \text{L}_{\text{org}} + 2\text{H}^+_{\text{org}} \rightleftharpoons \text{CaL}^{2+}_{\text{aq}} + 2\text{H}^+_{\text{aq}}$	7.35
$\text{Ca}^{2+}_{\text{aq}} + 2\text{L}_{\text{org}} + 2\text{H}^+_{\text{org}} \rightleftharpoons \text{CaL}^{2+}_{2,\text{org}} + 2\text{H}^+_{\text{aq}}$	14.01
$\text{Ca}^{2+}_{\text{aq}} + 3\text{L}_{\text{org}} + 2\text{H}^+_{\text{org}} \rightleftharpoons \text{CaL}^{2+}_{3,\text{org}} + 2\text{H}^+_{\text{aq}}$	18.45
$\text{Ca}^{2+}_{\text{org}} + \text{L}_{\text{org}} \rightleftharpoons \text{CaL}^{2+}_{\text{org}}$	7.45
$\text{Ca}^{2+}_{\text{org}} + 2\text{L}_{\text{org}} \rightleftharpoons \text{CaL}^{2+}_{2,\text{org}}$	14.11
$\text{Ca}^{2+}_{\text{org}} + 3\text{L}_{\text{org}} \rightleftharpoons \text{CaL}^{2+}_{3,\text{org}}$	18.55

^a Determined by the method of the concentration dependent distribution.¹⁸

^b Determined by the method described in detail in Ref. 19.

^c Ref. 20.

Knowing the values $\log K_{\text{ex}}(\text{Ca}^{2+}) = -0.1^{20}$ and $\log K_{\text{ex}}(\text{Sr}^{2+}) = 0.1^{20}$ as well as the extraction constants $\log K_{\text{ex}}(\text{CaL}^{2+}_{\text{org}}) = 7.35$, $\log K_{\text{ex}}(\text{CaL}^{2+}_{2,\text{org}}) = 14.01$, $\log K_{\text{ex}}(\text{CaL}^{2+}_{3,\text{org}}) = 18.45$, $\log K_{\text{ex}}(\text{SrL}^{2+}_{\text{org}}) = 7.17$, $\log K_{\text{ex}}(\text{SrL}^{2+}_{2,\text{org}}) = 12.89$ and $\log K_{\text{ex}}(\text{SrL}^{2+}_{3,\text{org}}) = 17.58$ determined here (see Tables 1 and 2), the stability constants of the complexes ML^{2+} , ML_2^{2+} and ML_3^{2+} ($\text{M}^{2+} = \text{Ca}^{2+}$, Sr^{2+} ; $\text{L} =$ “classical” CMPO) in the organic phase defined as

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

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

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

can be evaluated applying the following simple relations:

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

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

$$\log \beta(\text{ML}^{2+}_{3,\text{org}}) - \log K_{\text{ex}}(\text{ML}^{2+}_{3,\text{org}}) - \log K_{\text{ex}}(\text{M}^{2+}_{\text{org}}) \quad (17)$$

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

Table 4: Equilibrium constants in the water–HCl– Sr^{2+} (microamounts)–FS 13–“classical” CMPO– H^+B^- system.

Equilibrium	log K
$\text{L}_{\text{aq}} \rightleftharpoons \text{L}_{\text{org}}$	3.2 ^a
$\text{H}^+_{\text{org}} + \text{L}_{\text{org}} \rightleftharpoons \text{HL}^+_{\text{org}}$	5.67 ^b
$\text{H}^+_{\text{org}} + 2\text{L}_{\text{org}} \rightleftharpoons \text{HL}^+_{2,\text{org}}$	8.64 ^b
$\text{Sr}^{2+}_{\text{aq}} + 2\text{H}^+_{\text{org}} \rightleftharpoons \text{Sr}^{2+}_{\text{org}} + 2\text{HL}^+_{\text{aq}}$	0.1 ^c
$\text{Sr}^{2+}_{\text{aq}} + \text{L}_{\text{org}} + 2\text{H}^+_{\text{org}} \rightleftharpoons \text{SrL}^{2+}_{\text{aq}} + 2\text{H}^+_{\text{aq}}$	7.17
$\text{Sr}^{2+}_{\text{aq}} + 2\text{L}_{\text{org}} + 2\text{H}^+_{\text{org}} \rightleftharpoons \text{SrL}^{2+}_{2,\text{org}} + 2\text{H}^+_{\text{aq}}$	12.89
$\text{Sr}^{2+}_{\text{aq}} + 3\text{L}_{\text{org}} + 2\text{H}^+_{\text{org}} \rightleftharpoons \text{SrL}^{2+}_{3,\text{org}} + 2\text{H}^+_{\text{aq}}$	17.58
$\text{Sr}^{2+}_{\text{org}} + \text{L}_{\text{org}} \rightleftharpoons \text{SrL}^{2+}_{\text{org}}$	7.07
$\text{Sr}^{2+}_{\text{org}} + 2\text{L}_{\text{org}} \rightleftharpoons \text{SrL}^{2+}_{2,\text{org}}$	12.79
$\text{Sr}^{2+}_{\text{org}} + 3\text{L}_{\text{org}} \rightleftharpoons \text{SrL}^{2+}_{3,\text{org}}$	17.48

^a Determined by the method of the concentration dependent distribution.¹⁸

^b Determined by the method described in detail in Ref. 19.

^c Ref. 20.

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 FS 13 phase, whereas Figure

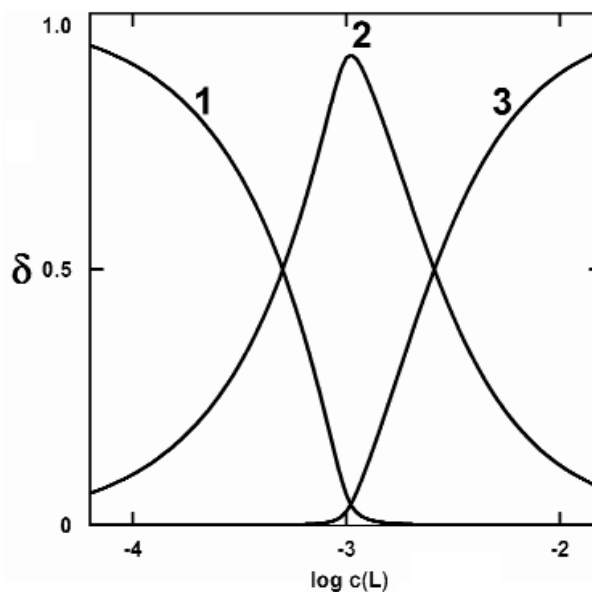


Figure 3: Distribution diagram of hydrogen cation in the equilibrium organic phase of the water–HCl– Ca^{2+} (microamounts)–FS 13–“classical” CMPO– H^+B^- extraction system in the forms of H^+ , HL^+ and HL_2^+ ; $c(\text{HCl}) = 0.01 \text{ mol dm}^{-3}$, $c_B = 0.001 \text{ mol dm}^{-3}$.

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

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

$$3 \delta(\text{HL}_2^+) = [\text{HL}_2^+_{\text{org}}]/c(\text{H}^+)_{\text{org}},$$

$$\text{where } c(\text{H}^+)_{\text{org}} = [\text{H}^+_{\text{org}}] + [\text{HL}^+_{\text{org}}] + [\text{HL}_2^+_{\text{org}}].$$

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

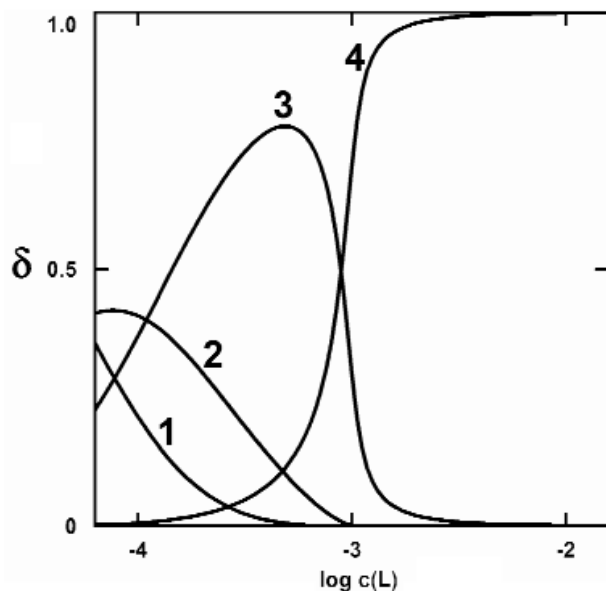


Figure 4: Distribution diagram of calcium in the equilibrium organic phase of the water–HCl–Ca²⁺ (microamounts) –FS 13–“classical” CMPO – H⁺B⁻ extraction system in the forms of Ca²⁺, CaL²⁺, CaL₂²⁺ and CaL₃²⁺. c(HCl) = 0.01 mol dm⁻³, c_B = 0.001 mol dm⁻³.

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

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

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

$$4 \delta(\text{CaL}_{3,\text{org}}^{2+}) = [\text{CaL}_{3,\text{org}}^{2+}] / c(\text{Ca}^{2+})_{\text{org}},$$

where

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

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

4 and 5 show the contributions of the cations M²⁺, ML_{org}²⁺, ML_{2,org}²⁺ and ML_{3,org}²⁺ (M²⁺ = Ca²⁺, Sr²⁺; L = “classical” CMPO) to the total divalent metal cation concentrations in the corresponding equilibrium organic phase. From Figures 3, 4 and 5 it follows that the cationic complex species HL_{2,org}⁺, CaL_{3,org}²⁺ and SrL_{3,org}²⁺ are present in significant concentrations only at relatively high amounts of the “classical” CMPO ligand in the systems under consideration.

Moreover, it should be noted that the stability constants of the complex species ML_{org}²⁺, ML_{2,org}²⁺ and ML_{3,org}²⁺ (M²⁺ = Ca²⁺, Sr²⁺; L = “classical” CMPO) in FS 13 saturated with water are log β (CaL_{org}²⁺) = 7.45, log β (SrL_{org}²⁺) = 7.07, log β (CaL_{2,org}²⁺) = 14.11, log β (SrL_{2,org}²⁺) = 12.79, log β (CaL_{3,org}²⁺) = 18.55 and log β (SrL_{3,org}²⁺) = 17.48 as given in

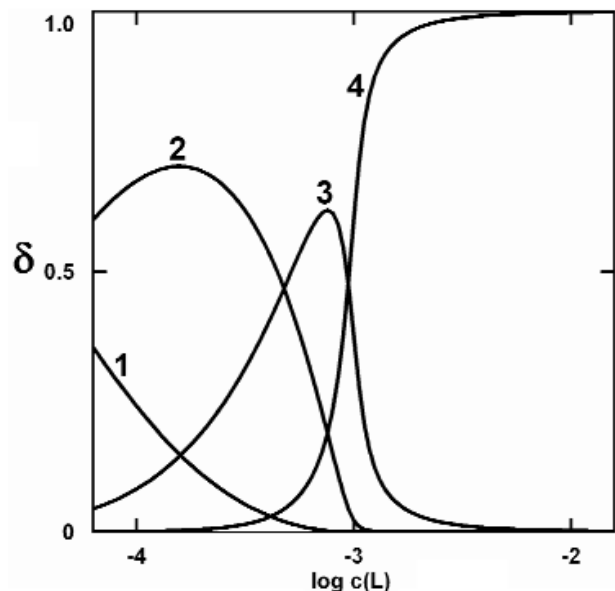


Figure 5: Distribution diagram of strontium in the equilibrium organic phase of the water–HCl–Sr²⁺ (microamounts) –FS 13–“classical” CMPO – H⁺B⁻ extraction system in the forms of Sr²⁺, SrL²⁺, SrL₂²⁺ and SrL₃²⁺. c(HCl) = 0.005 mol dm⁻³, c_B = 0.001 mol dm⁻³.

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

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

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

$$4 \delta(\text{SrL}_{3,\text{org}}^{2+}) = [\text{SrL}_{3,\text{org}}^{2+}] / c(\text{Sr}^{2+})_{\text{org}},$$

where

$$c(\text{Sr}^{2+})_{\text{org}} = [\text{Sr}_{\text{org}}^{2+}] + [\text{SrL}_{\text{org}}^{2+}] + [\text{SrL}_{2,\text{org}}^{2+}] + [\text{SrL}_{3,\text{org}}^{2+}].$$

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

Tables 3 and 4. Thus, in the considered FS 13 medium, the stability constants of the complex species CaL_n²⁺, where n = 1, 2, 3 and L is “classical” CMPO, are higher than those of the corresponding complexes SrL_n²⁺.

Finally, the stability constants of the complexes EuL_{3,org}³⁺ and AmL_{3,org}³⁺ in FS 13 saturated with water are log β (EuL_{3,org}³⁺) = 23.35²¹ and log β (AmL_{3,org}³⁺) = 23.69.²¹ It means that the stability of the complex cations CaL₃²⁺, SrL₃²⁺, EuL₃³⁺ and AmL₃³⁺, where L is “classical” CMPO, in the mentioned medium increases in the series of Sr²⁺ < Ca²⁺ << Eu³⁺ ≈ Am³⁺.

In conclusion, Table 5 summarizes stability constants of the cationic complexes ML_n²⁺ (M²⁺ = Ca²⁺, Sr²⁺; L = “classical” CMPO; n = 2, 3) in water-saturated nitro-

Table 5: Stability constants of the complexes ML_n²⁺ (M²⁺ = Ca²⁺, Sr²⁺; L = “classical” CMPO; n = 2, 3) in nitrobenzene saturated with water (I) and in FS 13 saturated with water (II) at 25 °C.

Medium	log β (CaL _{2,org} ²⁺)	log β (CaL _{3,org} ²⁺)	log β (SrL _{2,org} ²⁺)	log β (SrL _{3,org} ²⁺)
I ^a	14.46	19.52	13.09	17.31
I ^b	14.11	18.55	12.79	17.48

^a Ref. 14.

^b This work.

benzene and in FS 13 saturated with water. From the data reviewed in this table it follows that the stabilities of considered complexes ML_n^{2+} in both media are comparable.

4. Acknowledgements

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5. References

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Povzetek

Proučevali smo ekstrakcijo mikrokoličin kalcijevih in stroncijevih ionov z raztopino hydrogendikarbolilkobaltata (H^+B^-) v prisotnosti oktil-fenil-*N,N*-diisobutilkarbamoilmetil karbamoilmetilfosfin oksida (CMPO, L) v feniltrifluorometilsulfonu (FS 13). Dobljene podatke za ravnotežja smo razložili s predpostavko ekstrakcije kompleksov HL^+ , HL_2^+ , ML^{2+} , ML_2^{2+} in ML_3^{2+} ($M^{2+} = Ca^{2+}, Sr^{2+}$) v organsko fazo. Določili smo konstante nastanka kompleksov v FS13 nasičenem z vodo. Ugotovili smo, da so konstante stabilnosti kompleksov CaL_n^{2+} ($n = 1, 2, 3$) višje od konstant kompleksov s stroncijem.