

Short communication

Solvent Extraction of Microamounts of Calcium into Nitrobenzene Using Hydrogen Dicarbolylcobaltate and 2,3-Naphtho-15-crown-5

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Abstract

Extraction of microamounts of calcium by a nitrobenzene solution of hydrogen dicarbolylcobaltate (H^+B^-) in the presence of 2,3-naphtho-15-crown-5 (N15C5, L) has been investigated. The equilibrium data have been explained assuming that the complexes HL^+ , HL_2^+ , CaL^{2+} and CaL_2^{2+} are extracted into the organic phase. The values of extraction and stability constants of the species in nitrobenzene saturated with water have been determined.

Keywords: Calcium, hydrogen dicarbolylcobaltate, 2,3-naphtho-15-crown-5, extraction and stability constants, water – nitrobenzene system

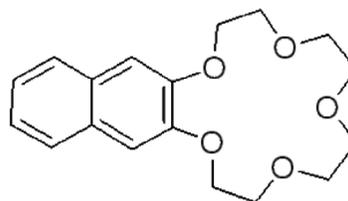
1. Introduction

In 1967, Pedersen¹ published his first paper dealing with cyclic polyether compounds with oxyethylene groups $-\text{CH}_2-\text{CH}_2-\text{O}-$ that are called crowns owing to their structure. These electroneutral crown compounds form relatively stable complexes in nonaqueous solvents, especially with alkali and alkaline-earth metal cations, the cations being placed in the ligand cavities. The ratio of the size of the crown cavity to the ion radius of the central cation is a decisive or at least an important factor in the stability of the complex formed. The complexing properties of the crowns are just due to the rapid development of the chemistry of these cyclic polyethers that we have witnessed in the recent decades.

Dicarbolylcobaltate anion and some of its halogen derivatives are very useful reagents for the extraction of alkali metal cations (especially Cs^+), and also in the presence of polyoxyethylene compounds – for the extraction of Sr^{2+} and Ba^{2+} from aqueous solution into an organic polar phase, both under laboratory conditions for purely theoretical or analytical purposes,² and on the technological scale for the separation of some high-activity isotopes

in the reprocessing of spent nuclear fuel and acidic radioactive waste.^{3–5}

Numerous naphtho-crown ethers have been synthesized and studied. The literature reports spectroscopic characteristics,^{6,7} X-ray structure analyses,⁸ complexation properties⁹ and studies of chiral naphtho-crowns.^{10–12} However, up to now, the protonation of these compounds has not been investigated. On the other hand, in the present work, the extraction of microamounts of calcium by a nitrobenzene solution of hydrogen dicarbolylcobaltate (H^+B^-)² in the presence of somewhat rigid 2,3-naphtho-15-crown-5 ligand (see Scheme 1) was studied. We intended to find the composition of the species in the nitroben-



Scheme 1. Structural formula of 2,3-naphtho-15-crown-5 (abbrev. N15C5 or L, respectively).

zene phase and to determine the corresponding equilibrium constants.

2. Experimental

2,3-Naphtho-15-crown-5 (N15C5, L) was supplied by Fluka, Buchs, Switzerland. Cesium dicarbollylcobaltate, Cs^+B^- , was synthesized in the Institute of Inorganic Chemistry, Řež, Czech Republic, using the method published by Hawthorne et al.¹³ A nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-)² was prepared from Cs^+B^- by the procedure described elsewhere.¹⁴ The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclide $^{45}\text{Ca}^{2+}$ (DuPont, Belgium) was of standard radiochemical purity.

The extraction experiments in the two-phase water–HCl– Ca^{2+} (microamounts)–nitrobenzene–N15C5– H^+B^- system were performed in 10 cm³ glass test-tubes covered with polyethylene stoppers, using 2 cm³ 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. 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).

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

3. Results and Discussion

The dependence of the logarithm of the calcium distribution ratios (log D) on the logarithm of the numerical

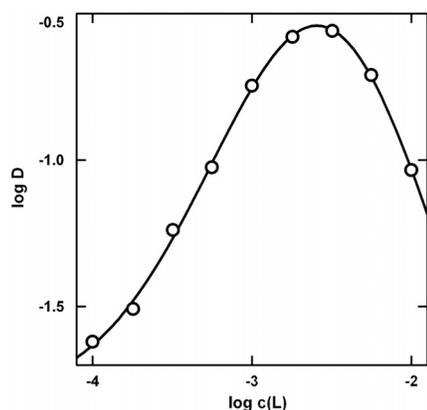
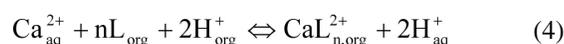
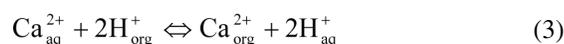
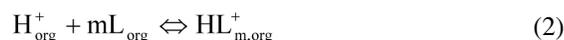


Figure 1. Log D as a function of log c(L), where L is N15C5, for the water–HCl– Ca^{2+} (microamounts) – nitrobenzene –N15C5– H^+B^- system. $c(\text{HCl}) = 0.01 \text{ mol dm}^{-3}$, $c_{\text{B}} = 0.001 \text{ mol dm}^{-3}$. The curve was calculated using the constants given in Table 2.

value of the total (analytical) concentration of the ligand N15C5 in the initial nitrobenzene phase, log c(L), is given in Figure 1. The initial concentration of hydrogen dicarbollylcobaltate in the organic phase, $c_{\text{B}} = 0.001 \text{ mol dm}^{-3}$, as well as the initial concentration of HCl in the aqueous phase, $c(\text{HCl}) = 0.01 \text{ mol dm}^{-3}$, are always related to the volume of one phase.

With respect to previous results,^{2,15–17} the considered water–HCl– Ca^{2+} (microamounts)–nitrobenzene–N15C5(L)– H^+B^- system can be described by the set of reactions



to which the following equilibrium constants correspond:

$$K_{\text{D}} = \frac{[\text{L}_{\text{org}}]}{[\text{L}_{\text{aq}}]}, \quad (5)$$

$$\beta(\text{HL}_{\text{m,org}}^+) = \frac{[\text{HL}_{\text{m,org}}^+]}{[\text{H}_{\text{org}}^+][\text{L}_{\text{org}}]^m}, \quad (6)$$

$$K_{\text{ex}}(\text{Ca}_{\text{org}}^{2+}) = \frac{[\text{Ca}_{\text{org}}^{2+}][\text{H}_{\text{aq}}^+]^2}{[\text{Ca}_{\text{aq}}^{2+}][\text{H}_{\text{org}}^+]^2}, \quad (7)$$

$$K_{\text{ex}}(\text{CaL}_{\text{n,org}}^{2+}) = \frac{[\text{CaL}_{\text{n,org}}^{2+}][\text{H}_{\text{aq}}^+]^2}{[\text{Ca}_{\text{aq}}^{2+}][\text{L}_{\text{org}}^+]^n[\text{H}_{\text{org}}^+]^2}. \quad (8)$$

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 N15C5 ligand and the electroneutrality conditions in both phases of the system under study, was formulated¹⁹ and introduced into a more general least-squares minimizing program LETAGROP¹⁸ used for determination of the “best” values of the equilibrium constants $\beta(\text{HL}_{\text{m,org}}^+)$ and $K_{\text{ex}}(\text{CaL}_{\text{n,org}}^{2+})$ (L = N15C5). The minimum of the sum of errors in log D, i.e., the minimum of the expression

$$U = \sum(\log D_{\text{calc}} - \log D_{\text{exp}})^2 \quad (9)$$

was sought.

Table 1. Comparison of various models of calcium extraction from aqueous solutions of HCl by nitrobenzene solution of H⁺B⁻ in the presence of N15C5.

Hydrogen and calcium complexes in the organic phase	log β log K _{ex} ^a	U ^b
HL ⁺ , CaL ²⁺	2.54 (2.81), 4.43 (4.68)	0.15
HL ⁺ , CaL ₂ ²⁺	5.46 (6.25), 12.29 (13.36)	0.39
HL ₂ ⁺ , CaL ²⁺	4.58 ± 0.02, 4.02 ± 0.12	0.04
HL ₂ ⁺ , CaL ₂ ²⁺	5.48 ± 0.22, 7.65 ± 0.03	0.07
HL ⁺ , HL ₂ ⁺ , CaL ₂ ²⁺	transformed to HL ₂ ⁺ , CaL ₂ ²⁺	
HL ⁺ , HL ₂ ⁺ , CaL ₂ ²⁺	3.03 (3.59), 5.67 (5.95), 8.31 (8.88)	0.06
HL ⁺ , HL ₂ ⁺ , CaL ₂ ²⁺ , CaL ₂ ²⁺	3.13 (3.41), 5.53 ± 0.18, 4.29 ± 0.02, 8.22 (8.56)	0.002

^a The values of the protonation and extraction constants are given for each complex. The reliability interval of the constants is given as 3σ(K), where σ(K) is the standard deviation of the constant K.¹⁸ These values are given in the logarithmic scale using the approximate expression log K ± {log[K + 1.5σ(K)] – log[K – 1.5σ(K)]}. For σ(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 + 1.5σ(K)]).¹⁸

^b The error-square sum U = Σ(logD_{calc} – log D_{exp})².

The values log K_D = 2.57¹⁵ and log K_{ex}(Ca²⁺_{org}) = 0.2¹⁶ were used for the respective calculations. The results are listed in Table 1, from which it is evident that the extraction data can be best explained assuming the complexes HL⁺, HL₂⁺, CaL²⁺ and CaL₂²⁺ (L = N15C5) to be extracted into the nitrobenzene phase.

Knowing the value log K_{ex}(Ca²⁺_{org}) = 0.2,¹⁶ as well as the extraction constants log K_{ex}(CaL₂²⁺_{org}) = 4.29 and log K_{ex}(CaL₂²⁺_{org}) = 8.22 determined here (Table 1), the stability constants of the complexes CaL²⁺ and CaL₂²⁺ in the nitrobenzene phase defined as

$$\beta(\text{CaL}_{\text{org}}^{2+}) = \frac{[\text{CaL}_{\text{org}}^{2+}]}{[\text{Ca}_{\text{org}}^{2+}][\text{L}_{\text{org}}]}, \quad (10)$$

$$\beta(\text{CaL}_{2,\text{org}}^{2+}) = \frac{[\text{CaL}_{2,\text{org}}^{2+}]}{[\text{Ca}_{\text{org}}^{2+}][\text{L}_{\text{org}}]^2}, \quad (11)$$

can be evaluated applying the following simple relations:

Table 2. Equilibrium constants in the water–HCl–Ca²⁺ (microamounts)–nitrobenzene–N15C5–H⁺B⁻ system.

Equilibrium	log K
L _{aq} ⇌ L _{org}	2.57 ^a
H ⁺ _{org} + L _{org} ⇌ HL ⁺ _{org}	3.13
H ⁺ _{org} + 2L _{org} ⇌ HL ₂ ⁺ _{org}	5.53
Ca ²⁺ _{aq} + 2H ⁺ _{org} ⇌ Ca ²⁺ _{org} + 2H ⁺ _{aq}	0.2 ^b
Ca ²⁺ _{aq} + L _{org} + 2H ⁺ _{org} ⇌ CaL ₂ ²⁺ _{org} + 2H ⁺ _{aq}	4.29
Ca ²⁺ _{aq} + 2L _{org} + 2H ⁺ _{org} ⇌ CaL ₂ ²⁺ _{org} + 2H ⁺ _{aq}	8.22
Ca ²⁺ _{org} + L _{org} ⇌ CaL ₂ ²⁺ _{org}	4.09
Ca ²⁺ _{org} + 2L _{org} ⇌ CaL ₂ ²⁺ _{org}	8.02

^a Determined by the method of the concentration dependent distribution.¹⁵

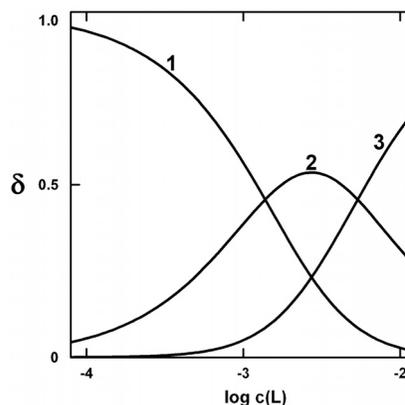
^b Ref. 16.

$$\log \beta(\text{CaL}_{\text{org}}^{2+}) = \log K_{\text{ex}}(\text{CaL}_{\text{org}}^{2+}) - \log K_{\text{ex}}(\text{Ca}_{\text{org}}^{2+}), \quad (12)$$

$$\log \beta(\text{CaL}_{2,\text{org}}^{2+}) = \log K_{\text{ex}}(\text{CaL}_{2,\text{org}}^{2+}) - \log K_{\text{ex}}(\text{Ca}_{\text{org}}^{2+}). \quad (13)$$

The respective equilibrium constants are summarized in Table 2.

Furthermore, Figure 2 depicts the contributions of the species H⁺_{org}, HL⁺_{org} and HL₂⁺_{org} to the total hydrogen cation concentration in the equilibrium nitrobenzene phase, whereas Figure 3 shows the contributions of the cations Ca²⁺_{org}, CaL²⁺_{org} and CaL₂²⁺_{org} to the total calcium concentration in the equilibrium organic phase. From Figures

**Figure 2.** Distribution diagram of hydrogen cation in the equilibrium nitrobenzene phase of the water–HCl–Ca²⁺ (microamounts)–nitrobenzene–N15C5–H⁺B⁻ extraction system in the forms of H⁺, HL⁺ and HL₂⁺.

c(HCl) = 0.01 mol dm⁻³, c_B = 0.001 mol dm⁻³.

1 δ(H⁺) = [H⁺_{org}] / c(H⁺)_{org},

2 δ(HL⁺) = [HL⁺_{org}] / c(H⁺)_{org},

3 δ(HL₂⁺) = [HL₂⁺_{org}] / c(H⁺)_{org},

where c(H⁺)_{org} = [H⁺_{org}] + [HL⁺_{org}] + [HL₂⁺_{org}].

The distribution curves were calculated using the constants given in Table 2.

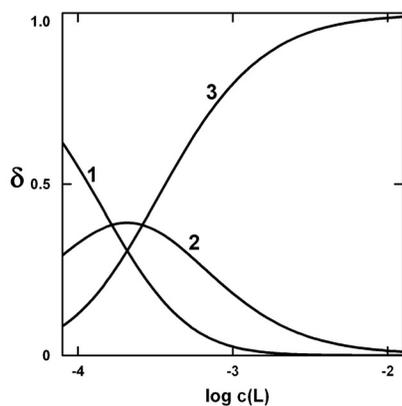


Figure 3. Distribution diagram of calcium in the equilibrium nitrobenzene phase of the water–HCl–Ca²⁺ (microamounts) –nitrobenzene–N15C5–H⁺B[–] extraction system in the forms of Ca²⁺, CaL²⁺ and CaL₂²⁺.

$c(\text{HCl}) = 0.01 \text{ mol dm}^{-3}$, $c_{\text{B}} = 0.001 \text{ mol dm}^{-3}$.

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

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

$$3 \delta(\text{CaL}_2^{2+}) = (\text{CaL}_{2,\text{org}}^{2+}) / c(\text{Ca}^{2+})_{\text{org}}$$

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

The distribution curves were calculated using the constants given in Table 2.

2 and 3 it follows that the complexes HL_{2,org}⁺ and CaL_{2,org}²⁺ are present in significant concentrations only at relatively high amounts of the N15C5 ligand in the system under consideration.

Finally, the stability constants of the complexes HL_{2,org}⁺, HL_{2,org}⁺, CaL_{2,org}²⁺ and CaL_{2,org}²⁺ (L = 15C5, N15C5) in nitrobenzene saturated with water at 25 °C are reviewed in Table 3. In this context it should be noted that somewhat higher stability of the cationic complex species HL_{2,org}⁺, HL_{2,org}⁺, CaL_{2,org}²⁺ and CaL_{2,org}²⁺, where L = 15C5, in water saturated nitrobenzene (see Table 3) in comparison with the stability of the respective complexes of H⁺ and Ca²⁺ with N15C5 in the mentioned medium determined here [$\log \beta(\text{HL}_{\text{org}}^+) = 3.13$, $\log \beta(\text{HL}_{2,\text{org}}^+) = 5.53$, $\log \beta(\text{CaL}_{\text{org}}^{2+}) = 4.09$ and $\log \beta(\text{CaL}_{2,\text{org}}^{2+}) = 8.02$] can be obviously explained on the basis of the higher flexibility of the 15C5 ligand compared with the relatively rigid structure of N15C5.

4. Acknowledgements

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Table 3. Stability constants of the complexes, HL_{2,org}⁺, HL_{2,org}⁺, CaL_{2,org}²⁺ and CaL_{2,org}²⁺, where L = 15-crown-5 (15C5), 2,3-naphtho-15-crown-5 (N15C5), in nitrobenzene saturated with water at 25 °C

L	$\log \beta(\text{HL}_{\text{org}}^+)$	$\log \beta(\text{HL}_{2,\text{org}}^+)$	$\log \beta(\text{CaL}_{\text{org}}^{2+})$	$\log \beta(\text{CaL}_{2,\text{org}}^{2+})$
15C5	4.27 ^a	6.32 ^a	7.63 ^b	11.57 ^b
N15C5	3.13 ^c	5.53 ^c	4.09 ^c	8.02 ^c

^a Ref. 20.

^b Ref. 21.

^c This work.

Povzetek

Raziskovali smo ekstrakcijo mikrokoličin kalcija z nitrobenzenovo raztopino vodikovega dikarbolilkobaltata (H^+B^-) ob prisotnosti crown etra 2,3-naftalen-15-crown-5 (N15C5, L). Dobljene eksperimentalne podatke smo obravnavali ob predpostavki, da so v organsko fazo ekstrahirani kompleksi HL^+ , HL_2^+ , CaL^{2+} in CaL_2^{2+} . Določili smo ravnotežne koncentracije ter konstante stabilnosti kompleksov v nitrobenzen, nasičenem z vodo.