Short communication

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

Emanuel Makrlík,[1,]* Petr Vaňura[2] and Pavel Selucký[3]

[1] *Faculty of Applied Sciences, University of West Bohemia, Husova 11, 306 14 Pilsen, Czech Republic*

[2] *Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague, Czech Republic*

[3] *Nuclear Research Institute, 250 68 Řež, Czech Republic*

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

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Abstract

Extraction of microamounts of calcium by a nitrobenzene solution of hydrogen dicarbollylcobaltate (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.

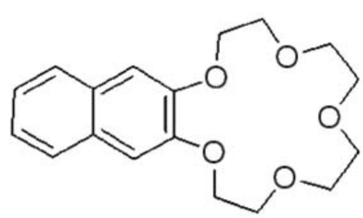
Keywords: Calcium, hydrogen dicarbollylcobaltate, 2,3-naphtho-15-crown-5, extraction and stability constants, water – nitrobenzene system

1. Introduction

In 1967, Pedersen[1] published his first paper dealing with cyclic polyether compounds with oxyethylene groups $–CH_2–CH_2–O–$ 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.

Dicarbollylcobaltate 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 properties [9] 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 dicarbollylcobaltate (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 $^{45}Ca^{2+}$ (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 cm^3 glass test-tubes covered with polyethylene stoppers, using 2 cm^3 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 cm^3) 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 $^{45}Ca^{2+}$ 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 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_B = 0.001 mol dm^{-3}, as well as the initial concentration of HCl in the aqueous phase, c(HCl) = 0.01 mol dm^{-3}, are always related to the volume of one phase.

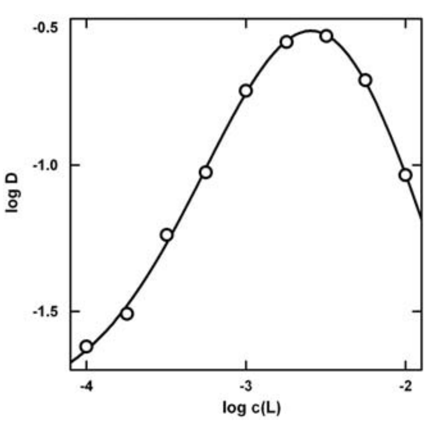


Figure 1. Log D as a function of log c(L), where L is N15C5, for the water–HCl–Ca^{2+} (microamounts) – nitrobenzene –N15C5 –H^+B^- system. c(HCl) = 0.01 mol dm^{-3}, c_B = 0.001 mol dm^{-3}. The curve was calculated using the constants given in Table 2.

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

$$L_{aq} \Leftrightarrow L_{org} \quad (1)$$

$$H^+_{org} + mL_{org} \Leftrightarrow HL^+_{m,org} \quad (2)$$

$$Ca^{2+}_{aq} + 2H^+_{org} \Leftrightarrow Ca^{2+}_{org} + 2H^+_{aq} \quad (3)$$

$$Ca^{2+}_{aq} + nL_{org} + 2H^+_{org} \Leftrightarrow CaL^{2+}_{n,org} + 2H^+_{aq} \quad (4)$$

to which the following equilibrium constants correspond:

$$K_D = \frac{[L_{org}]}{[L_{aq}]}, \quad (5)$$

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

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

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

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 formulated[19] and introduced into a more general least-squares minimizing program LETAGROP[18] used for determination of the "best" values of the equilibrium constants $\beta(HL^+_{m,org})$ and $K_{ex}(CaL^{2+}_{n.org})$ (L = N15C5). The minimum of the sum of errors in log D, i.e., the minimum of the expression

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

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+}	transformed to HL_2^+, CaL^{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+}, 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 $U = \sum(\log D_{cale} - \log D_{exp})^2$.

The values $\log K_D = 2.57$[15] and $\log K_{ex}(Ca^{2+}_{org}) = 0.2$[16] 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^+, HL_2^+, CaL^{2+} and CaL_2^{2+}(L = N15C5) to be extracted into the nitrobenzene phase.

Knowing the value $\log K_{ex}(Ca^{2+}_{org}) = 0.2$,[16] as well as the extraction constants $\log K_{ex}(CaL^{2+}_{org}) = 4.29$ and $\log K_{ex}(CaL^{2+}_{2,org}) = 8.22$ determined here (Table 1), the stability constants of the complexes CaL^{2+} and CaL_2^{2+} in the nitrobenzene phase defined as

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

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

can be evaluated applying the following simple relations:

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

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

The respective equilibrium constants are summarized in Table 2.

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

Table 2. Equilibrium constants in the water–HCl–Ca^{2+} (microamounts)–nitrobenzene–N15C5–H^+B^- system.

Equilibrium	log K
$L_{aq} \Leftrightarrow L_{org}$	2.57 [a]
$H^+_{org} + L_{org} \Leftrightarrow HL^+_{org}$	3.13
$H^+_{org} + 2L_{org} \Leftrightarrow HL^+_{2,org}$	5.53
$Ca^{2+}_{aq} + 2H^+_{org} \Leftrightarrow Ca^{2+}_{org} + 2H^+_{aq}$	0.2 [b]
$Ca^{2+}_{aq} + L_{org} + 2H^+_{org} \Leftrightarrow CaL^{2+}_{org} + 2H^+_{aq}$	4.29
$Ca^{2+}_{aq} + 2L_{org} + 2H^+_{org} \Leftrightarrow CaL^{2+}_{2,org} + 2H^+_{aq}$	8.22
$Ca^{2+}_{org} + L_{org} \Leftrightarrow CaL^{2+}_{org}$	4.09
$Ca^{2+}_{org} + 2L_{org} \Leftrightarrow CaL^{2+}_{2,org}$	8.02

[a] Determined by the method of the concentration dependent distribution.[15]
[b] Ref. 16.

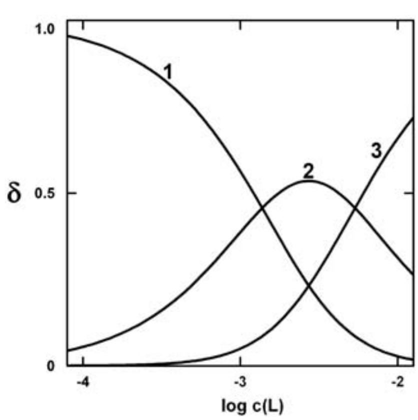


Figure 2. Distribution diagram of hydrogen cation in the equilibrium nitrobenzene phase of the water–HCl–Ca^{2+} (microamounts) -nitrobenzene–N15C5–H^+B^- extraction system in the forms of H^+, HL^+ and HL_2^+.
c(HCl) = 0.01 mol dm^{-3}, c_B = 0.001 mol dm^{-3}.
1 $\delta(H^+) = [H^+_{org}] / c(H^+)_{org}$,
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 2.

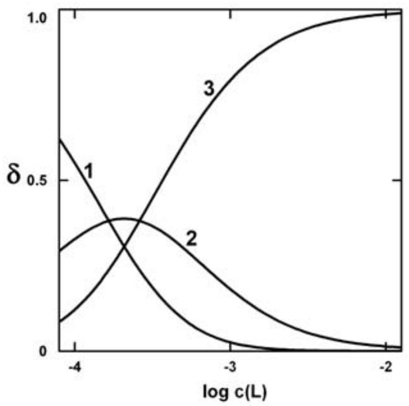


Figure 3. Distribution diagram of calcium in the equilibrium nitrobenzene phase of the water–HCl–Ca^{2+} (microamounts) -nitrobenzene–N15C5–H^+B^- extraction system in the forms of Ca^{2+}, CaL^{2+} and CaL_2^{2+}.
c(HCl) = 0.01 mol dm^{-3}, c_B = 0.001 mol dm^{-3}.
1 $\delta(Ca^{2+}) = [Ca^{2+}_{org}] / c(Ca^{2+})_{org}$,
2 $\delta(CaL^{2+}) = [CaL^{2+}_{org}] / c(Ca^{2+})_{org}$,
3 $\delta(CaL_2^{2+}) = (CaL^{2+}_{2,org}) / c(Ca^{2+})_{org}$,
where $c(Ca^{2+})_{org} = [Ca^{2+}_{org}] + [CaL^{2+}_{org}] + [CaL^{2+}_{2,org}]$.
The distribution curves were calculated using the constants given in Table 2.

2 and 3 it follows that the complexes $HL^+_{2,org}$ and $CaL^{2+}_{2,org}$ 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^+, HL_2^+, CaL^{2+} and CaL_2^{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^+_{org}, $HL^+_{2,org}$, CaL^{2+}_{org} and $CaL^{2+}_{2,org}$, where L = 15C5, in water saturated nitrobenzene (see Table 3) in comparison with the stability of the respective complexes of H^+ and Ca^{2+} with N15C5 in the mentioned medium determined here [$\log \beta (HL^+_{org}) = 3.13$, $\log \beta (HL^+_{2,org}) = 5.53$, $\log \beta (CaL^{2+}_{org}) = 4.09$ and $\log \beta (CaL^{2+}_{2,org}) = 8.02$] 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^+, HL_2^+, CaL^{2+} and CaL_2^{2+}, where L = 15-crown-5 (15C5), 2,3-naphtho-15-crown-5 (N15C5), in nitrobenzene saturated with water at 25 °C

L	$\log \beta (HL^+_{org})$	$\log \beta (HL^+_{2,org})$	$\log \beta (CaL^{2+}_{org})$	$\log \beta (CaL^{2+}_{2,org})$
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.