Distribution of Microamounts of Cesium in the Two–Phase Water–HCl–Nitrobenzene–2,3-Naphtho-15-crown-5–Hydrogen Dicarbollylcobaltate Extraction System

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Abstract

Extraction of microamounts of cesium 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^+, CsL^+ and CsL_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: Cesium, 2,3-naphtho-15-crown-5, hydrogen dicarbollylcobaltate, extraction and stability constants, water – nitrobenzene system

1. Introduction

The observation that macrocyclic polyethers form stable complexes with alkali and alkaline earth metal cations has stimulated a great deal of interest in these compounds for their possible applications in various branches of chemistry and biology.[1,2] Extensive thermodynamic data[3,4] suggest that the stability of macrocyclic complexes depends on the relative cation and ligand cavity size, the number and arrangements of the ligand bonding sites, the substitution on the macrocyclic ring and the solvent effects.

Dicarbollylcobaltate anion[5] 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,[6–31] and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.[32–34]

Numerous naphtho-crown ethers have been synthesized and studied. The literature reports spectroscopic characteristics,[35,36] X-ray structure analyses,[37] complexa-

tion properties[38] and studies of chiral naphtho-crowns.[39–41] On the other hand, in the present work, the extraction of microamounts of cesium by a nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-)[5] 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 nitrobenzene phase and to determine the corresponding equilibrium constants.
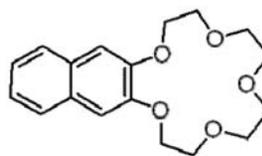
Scheme 1. Structural formula of 2,3-naphtho-15-crown-5 (abbrev. N15C5 or L, respectively).

2. Experimental

2,3-Naphtho-15-crown-5 (N15C5, L) was supplied by Fluka, Buchs, Switzerland. Cesium dicarbollylcobalta-

te, Cs^+B^-, was synthesized in the Institute of Inorganic Chemistry, Řež, Czech Republic, using the method published by Hawthorne et al.[42] A nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-)[5] was prepared from Cs^+B^- by the procedure described elsewhere.[43] The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclide $^{137}Cs^+$ (Techsnaveksport, Russia) was of standard radiochemical purity.

The extraction experiments in the two–phase water–HCl–Cs^+ (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. Afterwards, 1 cm³ samples were taken from each phase and their γ-activities were measured using a well-type NaI(T1) scintillation detector connected to a single-channel γ-analyzer NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratios of cesium, D, were determined as the ratios of the corresponding measured radioactivities of $^{137}Cs^+$ in the nitrobenzene and aqueous samples.

3. Results and Discussion

The dependences of the logarithm of the cesium 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), are given in Figure 1. The initial concentrations of hydrogen dicarbollylcobaltate in the organic phase, $c_B = 0.001$ and
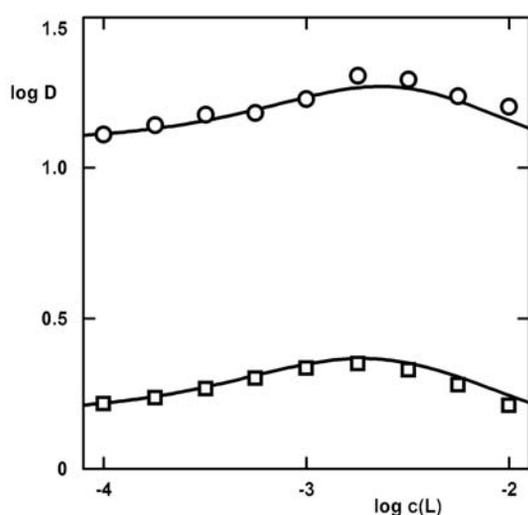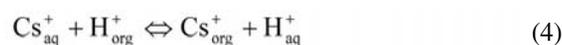

Figure 1. Log D as a function of log c(L), where L is N15C5, for the water–HCl–Cs^+ (microamounts) – nitrobenzene – N15C5–H^+B^- system. ○ c(HCl) = 0.10 mol dm⁻³, c_B = 0.001 mol dm⁻³. □ c(HCl) = 0.40 mol dm⁻³, c_B = 0.0005 mol dm⁻³. The curves were calculated using the constants given in Table 2.

0.0005 mol dm⁻³, as well as the initial concentrations of HCl in the aqueous phase, c(HCl) = 0.10 and 0.40 mol dm⁻³, are always related to the volume of one phase.

With regard to previous results,[5,44–48] the considered water–HCl–Cs^+(microamounts)–nitrobenzene–N15C5 (L)–H^+B^- systems can be described by the set of reactions

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

$$H^+_{org} + L_{org} \Leftrightarrow HL^+_{org} \qquad (2)$$

$$H^+_{org} + 2L_{org} \Leftrightarrow HL^+_{2,org} \qquad (3)$$

$$Cs^+_{aq} + H^+_{org} \Leftrightarrow Cs^+_{org} + H^+_{aq} \qquad (4)$$

$$Cs^+_{aq} + nL_{org} + H^+_{org} \Leftrightarrow CsL^+_{n,org} + H^+_{aq} \qquad (5)$$

to which the following equilibrium constants correspond:

$$K_D = \frac{[L_{org}]}{[L_{aq}]}, \qquad (6)$$

$$\beta(HL^+_{org}) = \frac{[HL^+_{org}]}{[H^+_{org}][L_{org}]}, \qquad (7)$$

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

$$K_{ex}(Cs^+_{org}) = \frac{[Cs^+_{org}][H^+_{aq}]}{[Cs^+_{aq}][H^+_{org}]}, \qquad (9)$$

$$K_{ex}(CsL^+_{n,org}) = \frac{[CsL^+_{n,org}][H^+_{aq}]}{[Cs^+_{aq}][L_{org}]^n[H^+_{org}]}. \qquad (10)$$

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 N15C5 ligand and the electroneutrality conditions in both phases of the system under study, was formulated[47,48] and introduced into a more general least-squares minimizing program LETAGROP[49] used for determination of the "best" values of the extraction constants $K_{ex}(CsL^+_{n,org})$ (L = N15C5). The minimum of the sum of errors in log D, i.e., the minimum of the expression

$$U = \sum (\log D_{calc} - \log D_{exp})^2 \qquad (11)$$

was sought.

The values log K_D = 2.57 (see Table 2, footnote a), log $\beta(HL^+_{org})$ = 3.13,[45] log $\beta(HL^+_{2,org})$ = 5.53[45] and log $K_{ex}(Cs^+_{org})$ = 3.09[46] were used for the respective calculations. The results are summarized in Table 1, from which it is evident that the extraction data can be best explained

assuming the complexes CsL^+ and CsL_2^+ (L = N15C5) to be extracted into the nitrobenzene phase.

Knowing the value $\log K_{ex}(Cs_{org}^+) = 3.09$,[46] as well as the extraction constants $\log K_{ex}(CsL_{org}^+) = 6.55$ and $\log K_{ex}(CsL_{2,org}^+) = 8.56$ determined here (Table 1), the stability constants of the complexes CsL^+ and CsL_2^+ in the nitrobenzene phase defined as

$$\beta(CsL_{org}^+) = \frac{[CsL_{org}^+]}{[Cs_{org}^+][L_{org}]}, \qquad (12)$$

$$\beta(CsL_{2,org}^+) = \frac{[CsL_{2,org}^+]}{[Cs_{org}^+][L_{org}]^2}, \qquad (13)$$

can be evaluated applying the following simple relations:

$$\log \beta(CsL_{org}^+) = \log K_{ex}(CsL_{org}^+) - \log K_{ex}(Cs_{org}^+), \quad (14)$$

$$\log \beta(CsL_{2,org}^+) = \log K_{ex}(CsL_{2,org}^+) - \log K_{ex}(Cs_{org}^+). \quad (15)$$

Table 1. Comparison of three different models of cesium extraction from aqueous solutions of HCl by nitrobenzene solution of H^+B^- in the presence of N15C5.

Cesium complexes in the organic phase	$\log K_{ex}$ [a]	U [b]
CsL^+	6.67 (7.03)	0.04
CsL_2^+	9.17 (10.11)	0.33
CsL^+, CsL_2^+	6.55 (6.69), 8.56 (9.08)	0.01

[a] The values of the extraction constants are given for each complex. The reliability interval of the constants is given as $3\sigma(K)$, where $\sigma(K)$ is the standard deviation of the constant K. [49] 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 $\sigma(K) > 0.2K$, the previous expression is not valid and then only the upper limit is given in the parentheses in the form of $\log K(\log[K + 3\sigma(K)])$. [49]
[b] The error-square sum $U = \Sigma(\log D_{calc} - \log D_{exp})^2$.

The respective equilibrium constants are listed in Table 2.

Table 2. Equilibrium constants in the water–HCl–Cs^+ (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 [b]
$H_{org}^+ + 2L_{org} \Leftrightarrow HL_{2,org}^+$	5.53 [b]
$Cs_{aq}^+ + H_{org}^+ \Leftrightarrow Cs_{org}^+ + H_{aq}^+$	3.09 [c]
$Cs_{aq}^+ + L_{org} + H_{org}^+ \Leftrightarrow CsL_{org}^+ + H_{aq}^+$	6.55
$Cs_{aq}^+ + 2L_{org} + H_{org}^+ \Leftrightarrow CsL_{2,org}^+ + H_{aq}^+$	8.56
$Cs_{org}^+ + L_{org} \Leftrightarrow CsL_{org}^+$	3.46
$Cs_{org}^+ + 2L_{org} \Leftrightarrow CsL_{2,org}^+$	5.47

[a] Determined by the concentration dependent distribution method. [44]
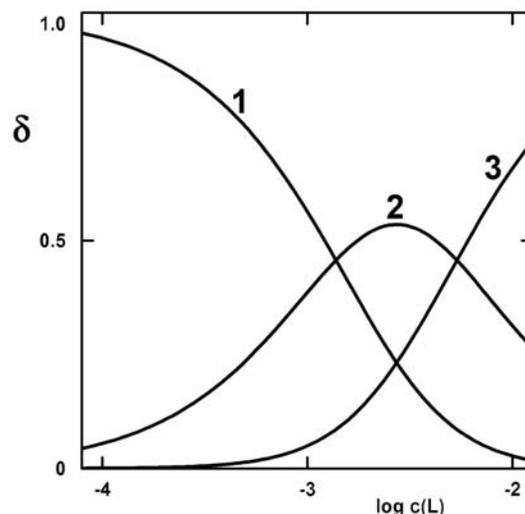[b] Ref. 45. [c] Ref. 46.

Figure 2. Distribution diagram of hydrogen cation in the equilibrium nitrobenzene phase of the water–HCl–Cs^+ (microamounts)–nitrobenzene–N15C5–H^+B^- extraction system in the forms of H^+, HL^+ and HL_2^+. $c(HCl) = 0.10$ 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.

Moreover, 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, whe-
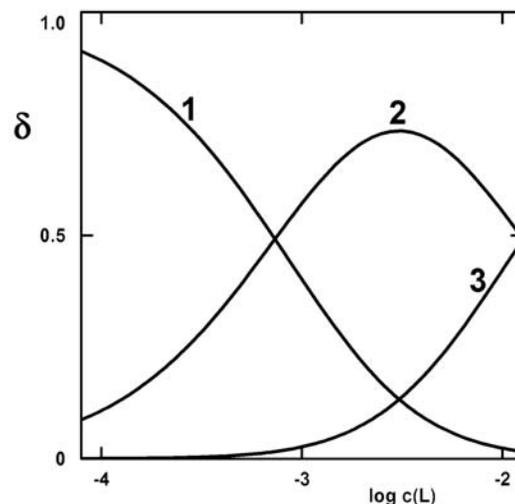

Figure 3. Distribution diagram of cesium in the equilibrium nitrobenzene phase of the water–HCl–Cs^+ (microamounts)–nitrobenzene–N15C5–H^+B^- extraction system in the forms of Cs^+, CsL^+ and CsL_2^+. $c(HCl) = 0.10$ mol dm^{-3}, $c_B = 0.001$ mol dm^{-3}.
  1 $\delta(Cs^+) = [Cs_{org}^+]/c(Cs^+)_{org}$,
  2 $\delta(CsL^+) = [CsL_{org}^+]/c(Cs^+)_{org}$,
  3 $\delta(CsL_2^+) = [CsL_{2,org}^+]/c(Cs^+)_{org}$,
where $c(Cs^+)_{org} = [Cs_{org}^+] + [CsL_{org}^+] + [CsL_{2,org}^+]$.
The distribution curves were calculated using the constants given in Table 2.

Table 3. Stability constants of the complexes HL^+, HL_2^+, CsL^+ and CsL_2^+, where L = 15-crown-5 (15C5), 2,3-naphtho-15-crown-5 (N15C5), in nitrobenzene saturated with water at 25 °C.

L	$\log \beta (HL^+_{org})$	$\log \beta (HL^+_{2,org})$	$\log \beta (CsL^+_{org})$	$\log \beta (CsL^+_{2,org})$
15C5	4.27 [a]	6.32 [a]	4.24 [b]	6.72 [b]
N15C5	3.13 [c]	5.53 [c]	3.46 [d]	5.47 [d]

[a] Ref. 50. [b] Ref. 51. [c] Ref. 45. [d] This work.

reas Figure 3 shows the contributions of the cations Cs^+_{org}, CsL^+_{org} and $CsL^+_{2,org}$ to the total cesium concentration in the equilibrium organic phase. From Figures 2 and 3 it follows that the complexes $HL^+_{2,org}$ and $CsL^+_{2,org}$ are present in significant concentrations only at relatively high amounts of the N15C5 ligand in the system under consideration.

In conclusion, the stability constants of the complexes HL^+, HL_2^+, CsL^+ and CsL_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}, $HL^+_{2,org}$ CsL^+_{org}, and $CsL^+_{2,org}$, where L = 15C5, in water saturated nitrobenzene in comparison with the stability of the respective complexes of H^+ and Cs^+ with N15C5 ligand in the mentioned medium (see Table 3) can be obviously explained on the basis of the higher flexibility of the ligand 15C5 compared with the relatively rigid structure of N15C5.

4. Acknowledgements

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Povzetek

Proučevali smo ekstrakcijo mikrokoličin cezija z raztopino vodikovega dikarbolilkobaltata (H$^+$B$^-$) v nitrobenzenu ob prisotnosti 2,3-nafto-15-crown-5 (N15C5, L). Dobljena ravnotežja smo pojasnili s predpostavko, da se kompleksi HL$^+$, HL$_2^+$, CsL$^+$ in CsL$_2^+$ ekstrahirajo v organsko fazo. Določili smo konstante ekstrakcije in stabilnosti kompleksov v nitrobenzenu nasičenem z vodo.