Extraction of Barium with 
Bis[Undeca­hydro-7,8-dicar­baundance­caborato(2–)]cobaltate(1–) 
in the Presence of 18-Crown-6

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Extraction of microamounts of barium with a nitrobenzene solution of cesium bis[undeca­hydro-7,8-dicar­baundance­caborato(2–)]cobaltate(1–) (abbr. Cs⁺B⁻) in the presence of 18-crown-6 (18C6, L) has been investigated. The equilibrium data have been explained assuming that the complexes CsL⁺, CsL⁺, BaL²⁺, and BaL²⁺ are extracted into the organic phase. The values of extraction and stability constants of the species in nitrobenzene saturated with water have been determined.

In our previous works [1—4], we have studied the extraction of Sr²⁺ and Ba²⁺ ions using a nitrobenzene solution of hydrogen bis[undeca­hydro-7,8-dicar­baundance­caborato(2–)]cobaltate(1–) (hydrogen dicarbollylcobaltate, abbr. H⁺B⁻) in the presence of poly(ethylene glycols), polyethers, and crown ethers. These ions (M⁺²) have been found to be extracted in the form of the ML²⁺ complexes. The occurrence of maxima on the plot of metal ion distribution ratio (D) vs. the total polyoxonium compound concentration, c(L), has been explained in terms of competition between the charged ML²⁺ complexes and protonated PEG (HL⁺) during the balancing of the dicarbollylcobaltate electrostatic charge in the organic phase.

During the extraction of perchloric acid with a nitrobenzene solution of 18-crown-6 (18C6) only the complex HL⁺ has been found in the organic phase [5]. The extraction of cesium using a nitrobenzene solution of H⁺B⁻ in the presence of dibenzo-18-crown-6 has been investigated; the complexes CsL⁺ and CsL⁺ have been found in the organic phase [6].

On the other hand, the extraction of strontium with a nitrobenzene solution of hydrogen dicarbollylcobaltate (H⁺B⁻) in the presence of 15-crown-5 (15C5) can be explained by a simple model involving the presence of the species HL⁺, HL⁺, and SrL²⁺ in the organic phase. The complex SrL²⁺, which exists in aqueous solution, has not been found in the nitrobenzene phase [7].

The aim of this paper is to study the extraction of microamounts of barium with the nitrobenzene solution of cesium dicarbollylcobaltate (Cs⁺B⁻) in the presence of 18-crown-6 (18C6, L). We intended to find the composition of species present in the organic phase and to determine the respective equilibrium constants.

EXPERIMENTAL

18-Crown-6 (Merck, Darmstadt, Germany) was used without any purification. Cesium salt of dicarbollylcobaltate, Cs⁺B⁻, was synthesized in the Institute of Inorganic Chemistry, Řež, Czech Republic, using the method published by Hawthorne et al. [8]. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclide ¹³³Ba (Polatom, Poland) was of standard radiochemical purity.

The extraction experiments in the system water—CsCl—Ba²⁺(microamounts)—18C6—nitrobenzene—Cs⁺B⁻ 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 h at 25 ± 2°C using a laboratory shaker. Under these conditions an equilibrium in the system under study has established after approximately 30 min shaking. Then the phases were separated by centrifugation (5 min, 2500 min⁻¹). After centrifugation, 1 cm³ samples were taken from each phase and their γ-activities were measured using a well-type NaI(Tl) scintillation detector connected with a single-channel γ-analyzer.
Table 1. Log D as a Function of log \( \{c(L)\} \) (L = 18C6) for Barium Extraction from the Aqueous Solution of Cesium Chloride by the Nitrobenzene Solutions of Cs\(^{+}\)B\(^{-}\)

<table>
<thead>
<tr>
<th>( c(CsCl) )</th>
<th>( c(CsB) )</th>
<th>Log D</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 mol dm(^{-3})</td>
<td>0.01 mol dm(^{-3})</td>
<td>-3.252 -1.919; -3.000 -1.170; -2.699 -1.350; -2.495 -1.188; -2.252 -0.998; -2.000 -2.464; -1.699 -3.279.</td>
</tr>
<tr>
<td>0.05 mol dm(^{-3})</td>
<td>0.03 mol dm(^{-3})</td>
<td>-3.252 -1.289; -3.000 -1.076; -2.699 -0.652; -2.495 -0.448; -2.252 -0.170; -2.000 -0.021; -1.699 -0.039; -1.495 -2.030; -1.252 -3.228.</td>
</tr>
<tr>
<td>0.05 mol dm(^{-3})</td>
<td>0.05 mol dm(^{-3})</td>
<td>-2.495 -0.207; -2.252 0.102; -2.000 0.308; -1.699 0.479; -1.495 0.507; -1.252 -1.763; -1.000 -2.931.</td>
</tr>
</tbody>
</table>

NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratio of barium, \( D \), was determined as a ratio of the measured radioactivities of nitrobenzene and aqueous samples.

**RESULTS AND DISCUSSION**

The dependences of the logarithm of the barium distribution ratios (log \( D \)) on the logarithm of the numerical value of total (analytical) concentration of the ligand 18C6 in the initial aqueous phase, log \( \{c(L)\} \), were measured for three concentrations of cesium dicarbollylcobaltate in the nitrobenzene phase (\( c(CsB) = 0.01 \) mol dm\(^{-3}\), 0.03 mol dm\(^{-3}\), and 0.05 mol dm\(^{-3}\)) in the presence of 18C6 (\( c(L) = 5.6 \times 10^{-4} -0.10 \) mol dm\(^{-3}\)); the initial concentration of cesium chloride in the aqueous phase, \( c(CsCl) \), was 0.05 mol dm\(^{-3}\). The mentioned initial concentrations \( c(CsCl) \), \( c(CsB) \), and \( c(L) \) are always related to the volume of one phase. The results are given in Table 1 and Fig. 1.

With regard to the results of previous papers [1—7, 10—13], the system water—CsCl—Ba\(^{2+}\) (microamounts)—18C6—nitrobenzene—Cs\(^{+}\)B\(^{-}\) can be described by the set of reactions

\[
L_{aq} = L_{org} \tag{A}
\]
\[
Cs_{aq}^{+} + nL_{aq} = CsL_{n,org}^{+} \tag{B}
\]
\[
Ba_{aq}^{2+} + 2Cs_{aq}^{+} = Ba_{aq}^{2+} + 2Cs_{aq}^{+} \tag{C}
\]
\[
Ba_{aq}^{2+} + mL_{aq} + 2Cs_{aq}^{+} = BaL_{m,org}^{2+} + 2Cs_{aq}^{+} \tag{D}
\]
\[
Cs_{aq}^{+} + L_{aq} = CsL_{aq}^{+} \tag{E}
\]
\[
Ba_{aq}^{2+} + L_{aq} = BaL_{aq}^{2+} \tag{F}
\]

with the following equilibrium constants

\[
K_D = \frac{[L_{org}]}{[L_{aq}]} \tag{1}
\]
\[
K_{ex}(CsL_{n,org}^{+}) = \frac{[CsL_{n,org}^{+}]}{[Cs_{org}^{+}][L_{aq}]} \tag{2}
\]

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

\[
K_{ex}(Ba_{aq}^{2+}) = \frac{[Ba_{org}^{2+}][Cs_{aq}^{+}][L_{aq}]}{[Ba_{aq}^{2+}][Cs_{org}^{+}]} \tag{3}
\]
\[
K_{ex}(Ba_{aq}^{2+}) = \frac{[BaL_{m,org}^{2+}][Cs_{aq}^{+}][L_{aq}]}{[Ba_{aq}^{2+}][Cs_{org}^{+}][L_{aq}]} \tag{4}
\]
\[
\beta(Cs_{aq}^{+}) = \frac{[CsL_{aq}^{+}]}{[Cs_{aq}^{+}][L_{aq}]} \tag{5}
\]
\[
\beta(BaL_{aq}^{2+}) = \frac{[BaL_{aq}^{2+}]}{[Ba_{aq}^{2+}][L_{aq}]} \tag{6}
\]
correspond; subscripts \( aq \) and \( org \) denote the aqueous and organic phases, respectively.

A subroutine UBBE, based on the relations given above, mass balance of the crown ligand, and the electroneutrality conditions in both phases, was formulated [1, 4] and introduced into a more general least-squares minimizing program LETAGROP [9] used for
Table 2. Comparison of Different Models of Barium Extraction from the Aqueous Solution of Cesium Chloride by the Nitrobenzene Solutions of Cs\(^+\)B\(^-\) in the Presence of 18-Crown-6

<table>
<thead>
<tr>
<th>Cesium and barium complexes in the organic phase</th>
<th>(\log {K_{ex}})</th>
<th>(u^6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsL(^+), BaL(^2+)</td>
<td>3.78 ± 0.11, 4.93 ± 0.13</td>
<td>1.43</td>
</tr>
<tr>
<td>CsL(^+), BaL(^2+)</td>
<td>6.98 ± 1.69, 7.98 ± 0.94</td>
<td>14.89</td>
</tr>
<tr>
<td>CsL(^+), BaL(^2+)</td>
<td>3.69 ± 0.60, 8.67(9.16)</td>
<td>24.63</td>
</tr>
<tr>
<td>CsL(^+), BaL(^2+)</td>
<td>6.99 ± 0.99, 4.17 ± 0.23</td>
<td>7.14</td>
</tr>
<tr>
<td>CsL(^+), BaL(^2+), BaL(^2+)</td>
<td>5.31 ± 1.13, 6.10 ± 1.13, 9.65(10.30)</td>
<td>0.69</td>
</tr>
<tr>
<td>CsL(^+), CsL(^+), BaL(^2+)</td>
<td>transforms to CsL(^+), BaL(^2+)</td>
<td></td>
</tr>
<tr>
<td>CsL(^+), CsL(^+), BaL(^2+)</td>
<td>transforms to CsL(^+), BaL(^2+)</td>
<td></td>
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<td>CsL(^+), CsL(^+), BaL(^2+)</td>
<td>transforms to CsL(^+), BaL(^2+)</td>
<td></td>
</tr>
<tr>
<td>CsL(^+), CsL(^+), BaL(^2+)</td>
<td>5.31 ± 0.62, 6.41 ± 1.13, 6.28 ± 0.60</td>
<td>0.63</td>
</tr>
<tr>
<td>BaL(^2+)</td>
<td>10.04(10.58)</td>
<td></td>
</tr>
</tbody>
</table>

a) The values of the extraction constants are given for each complex. The reliability interval of the constants is given as \(\sigma(K)\), which is the standard deviation of the constant \(K\). These values are expressed in the logarithmic scale using the approximate relation \(\log \{K\} ± \left(\log \left\{K + 0.5\sigma(K)\right\} - \log \left\{K - 0.5\sigma(K)\right\}\right)\).

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

The values \(K_D = 0.10\) [10], \(\log K_{ex}(BaL_{org}^{2+}) = -5.1\) (inferred from Refs. [11] and [12]), \(\log \{\beta(CsL_{aq}^+)\} = 0.99\) [13], and \(\log \{\beta(BaL_{aq}^{2+})\} = 3.87\) [13] were used for the respective calculations. The results are listed in Table 2. From here it is evident that the extraction data can be explained assuming the complex species CsL\(^+\), CsL\(^2+\), BaL\(^2+\), and BaL\(^2+\) to be extracted into the nitrobenzene phase.

Fig. 2 presents the contributions of the species Cs\(^+\), CsL\(^+\), and CsL\(^2+\) to the total cesium concentration in the equilibrium nitrobenzene phase while Fig. 3 depicts the contributions of the particles BaL\(^2+\) and BaL\(^2+\) to the total barium concentration in the equilibrium organic phase. From both these figures it follows that the “sandwich” type complexes CsL\(^+\), CsL\(^2+\), BaL\(^2+\), and BaL\(^2+\) are present in significant concentrations only at relatively high amounts of the 18C6 ligand in the system under study.

Knowing the values \(K_D = 0.10\) [10], \(\log K_{ex}(BaL_{org}^{2+}) = -5.1\) (inferred from Refs. [11] and [12]) and the extraction constants \(\log K_{ex}(CsL_{org}^+) = 5.31\), \(\log K_{ex}(BaL_{org}^{2+}) = 6.28\), and \(\log K_{ex}(BaL_{org}^{2+}) = 10.04\) determined here, the stability constants of the complexes CsL\(^+\), CsL\(^2+\), BaL\(^2+\), and BaL\(^2+\) in the nitrobenzene phase defined as

\[\beta(CsL_{org}^+) = \frac{[CsL_{org}^+]}{[Cs^+][L_{org}]} \quad \beta(CsL_{org}^{2+}) = \frac{[CsL_{org}^{2+}]}{[Cs_{org}^+][L_{org}]} \quad \beta(BaL_{org}^{2+}) = \frac{[BaL_{org}^{2+}]}{[Ba_{org}^{2+}][L_{org}]} \]

can be evaluated using the simple relations
The respective equilibrium constants are summarized in Table 3.

In conclusion it should be noted that the stability constants of the complexes $\text{CsL}^+$, $\text{CsL}_2^+$, and $\text{BaLa}^+$ ($L = 18$-crown-6) in water-saturated nitrobenzene, evaluated in the systems water—HNO$_3$—CsCl—$\text{Ba}^{2+}$ ([14] and water—HClO$_4$—$\text{Ba}^{2+}$ (microamounts)—18C6—nitrobenzene—$\text{H}^+\text{B}^-$ [4], are log $\beta(\text{CsL}_2^+)$ = 6.54 [14], log $\beta(\text{CsLa}^+_2)$ = 8.64 [14], and log $\beta(\text{BaLa}^+) = 12.47$ [4] which are in good agreement with the values log $\beta(\text{CsLa}^+)$ = 6.31, log $\beta(\text{CsLa}^+_2)$ = 8.41, and log $\beta(\text{BaLa}^+)$ = 12.38 determined in this work (see Table 3). Somewhat higher difference between the values log $\beta(\text{BaLa}^+)$ = 17.78 [4] and log $\beta(\text{BaLa}^+_2)$ = 17.14 calculated here (see also Table 3) is apparently due to different ionic powers of the aqueous phases of the systems under consideration.

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REFERENCES


![Fig. 3. Distribution diagram of barium present in the equilibrium nitrobenzene phase of the system water—CsCl—$\text{Ba}^{2+}$ (microamounts)—18C6—nitrobenzene—$\text{Cs}^+$ $\text{B}^-$ in the forms of $\text{BaL}^+$ and $\text{BaL}_2^+$, log $\beta(\text{CsLa})$ = 0.99 [13], log $\beta(\text{BaLa})$ = 3.87 [13], and log $\beta(\text{BaLa}_2)$ = -2.7 [11]. The respective equilibrium constants are summarized in Table 3.](image-url)

![Table 3. Equilibrium Constants for the Water—CsCl—$\text{Ba}^{2+}$ (Microamounts)—18C6—Nitrobenzene—$\text{Cs}^+$ $\text{B}^-$ System](table-url)

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>log ${K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{La}^+ = \text{org}$</td>
<td>-1.0$^a$</td>
</tr>
<tr>
<td>$\text{CsLa}^+ + \text{aq} = \text{CsLa}^+^+$</td>
<td>0.99$^b$</td>
</tr>
<tr>
<td>$\text{BaLa}^+ + \text{aq} = \text{BaLa}^+^+$</td>
<td>3.87$^b$</td>
</tr>
<tr>
<td>$\text{CsLa}^+ + \text{aq} = \text{CsLa}^+^+$</td>
<td>5.31</td>
</tr>
<tr>
<td>$\text{CsLa}^+ + \text{aq} = \text{CsLa}^+^+$</td>
<td>6.41</td>
</tr>
<tr>
<td>$\text{BaLa}^+ + \text{aq} + 2\text{CsLa}^+^+$</td>
<td>-5.1$^c$</td>
</tr>
<tr>
<td>$\text{BaLa}^+ + 2\text{CsLa}^+ + 2\text{CsLa}^+^+$</td>
<td>6.28</td>
</tr>
<tr>
<td>$\text{BaLa}^+ + 2\text{CsLa}^+ + 2\text{CsLa}^+^+$</td>
<td>10.04</td>
</tr>
<tr>
<td>$\text{CsLa}^+ + \text{org} = \text{org}$</td>
<td>6.31</td>
</tr>
<tr>
<td>$\text{CsLa}^+ + 2\text{org} = \text{org}$</td>
<td>8.41</td>
</tr>
<tr>
<td>$\text{BaLa}^+ + \text{org} = \text{org}$</td>
<td>12.38</td>
</tr>
<tr>
<td>$\text{BaLa}^+ + 2\text{org} = \text{org}$</td>
<td>17.14</td>
</tr>
<tr>
<td>$\text{CsLa}^+ + \text{org}$</td>
<td>1.6</td>
</tr>
<tr>
<td>$\text{BaLa}^+ + \text{org}$</td>
<td>-3.0</td>
</tr>
</tbody>
</table>

$^a$ Ref. [10], $^b$ Ref. [13], $^c$ inferred from Refs. [11] and [12].