Solvent Extraction of Barium into Nitrobenzene by Using Hydrogen Dicarbollylcobaltate in the Presence of Slovafol 909

Emanuel Makrlík,1,* Petr Vaňura2 and Pavel Selucký3

1 Faculty of Applied Sciences, University of West Bohemia, Husova 11, 306 14 Pilsen, Czech Republic
2 Institute of Chemical Technology, Prague, Faculty of Chemical Engineering, Department of Analytical Chemistry, Technická 5, 166 28 Prague 6, 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 barium by a nitrobenzene solution of hydrogen dicarbollylcobaltate (H+B–) in the presence of Slovafol 909 (L) has been investigated. The equilibrium data have been explained assuming that the species HL+, HL2+, BaL2+ and BaL2+2 are extracted into the organic phase. The values of extraction and stability constants of the complex species in nitrobenzene saturated with water have been determined.

Keywords: Barium, Slovafol 909, hydrogen dicarbollylcobaltate, extraction and stability constants, water – nitrobenzene system

1. Introduction

Dicarbollylcobaltate anion1 and some of its halogen derivatives are very useful reagents for the extraction of various metal cations (especially Cs+, Sr2+, Ba2+, Eu3+ and Am3+) from aqueous solutions into a polar organic phase, both under laboratory conditions for purely theoretical or analytical purposes,2–30 and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.31–33

In the current work, the extraction of microamounts of barium by a synergistic mixture of hydrogen dicarbollylcobaltate (H+B–)1 and Slovafol 909 (L) in nitrobenzene was studied. We intended to find the composition of the species in the organic phase and to determine the corresponding equilibrium constants.

2. Experimental

Slovafol 909 (p-nonylphenylnonaethylene glycol) was supplied by Chemical Works, Nováky, Slovakia. Cesium dicarbollylcobaltate, CsB–, was synthesized in the Institute of Inorganic Chemistry, Řež, Czech Republic, by applying the method published by Hawthorne et al.35 A nitrobenzene solution of hydrogen dicarbollylcobaltate (H+B–)1 was prepared from CsB– by the procedure described elsewhere.36 The other chemicals used (Lachema,
Brno, Czech Republic) were of reagent grade purity. The radionuclide $^{133}\text{Ba}^{2+}$ (Polatom, Poland) was of standard radiochemical purity.

The extraction experiments in the two-phase water–HCl–Ba$^{2+}$ (microamounts)–Slovafol 909–nitrobenzene–H$^+\text{B}^-$ system were performed in 10 cm$^3$ glass test-tubes with polyethylene stoppers, using 2 cm$^3$ 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 equilibrium in the system under study was established after approximately 20 min of shaking. Then the phases were separated by centrifugation. Afterwards, 1 cm$^3$ samples were taken from each phase and their $\gamma$-activities were measured using a well-type NaI(T1) scintillation detector connected to a $\gamma$-analyzer NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratios of barium, D, were determined as the ratios of the corresponding measured radioactivities of $^{133}\text{Ba}^{2+}$ in the nitrobenzene and aqueous samples.

### 3. Results and Discussion

The dependence of the logarithm of the barium distribution ratio (log D) on the logarithm of the numerical value of the total (analytical) concentration of the ligand Slovafol 909 in the aqueous phase, log $c(L)$, is given in Figure 1. The initial concentration of HCl in the aqueous phase, $c(\text{HCl}) = 0.10$ mol dm$^{-3}$, and the initial concentration of hydrogen dicarbollylcobaltate in the organic phase, $c_B = 0.001$ mol dm$^{-3}$, are related to the volume of one phase.

With respect to the results of previous previous,1,3,20,34,37 the considered water–HCl–Ba$^{2+}$ (microamounts)–Slovafol 909 (L)–nitrobenzene–H$^+\text{B}^-$ system can be described by the set of reactions

\begin{align}
\text{L}_{\text{aq}} &\rightleftharpoons \text{L}_{\text{org}} \tag{1} \\
\text{H}_{\text{org}}^+ + \text{L}_{\text{org}} &\rightleftharpoons \text{HL}_{\text{org}}^+ \tag{2} \\
\text{H}_{\text{org}}^+ + 2\text{L}_{\text{org}} &\rightleftharpoons \text{HL}_{2,\text{org}}^+ \tag{3} \\
\text{Ba}_{\text{aq}}^{2+} + 2\text{H}_{\text{aq}}^+ &\rightleftharpoons \text{Ba}_{\text{org}}^{2+} + 2\text{H}_{\text{org}}^+ \tag{4} \\
\text{Ba}_{\text{aq}}^{2+} + n\text{L}_{\text{org}} + 2\text{H}_{\text{aq}}^+ &\rightleftharpoons \text{BaL}_{\text{org}}^{2+} + 2\text{H}_{\text{org}}^+ \tag{5}
\end{align}

![Figure 1: Log D as a function of log c(L), where L is Slovafol 909, for the system water–HCl–Ba$^{2+}$ (microamounts)–Slovafol 909–nitrobenzene–H$^+\text{B}^-$ system.](image)

The equilibrium distribution ratios of barium, D, were determined as the ratios of the corresponding measured radioactivities of $^{133}\text{Ba}^{2+}$ in the nitrobenzene and aqueous samples. The equilibrium distribution ratios of barium, D, were determined as the ratios of the corresponding measured radioactivities of $^{133}\text{Ba}^{2+}$ in the nitrobenzene and aqueous samples. The equilibrium distribution ratios of barium, D, were determined as the ratios of the corresponding measured radioactivities of $^{133}\text{Ba}^{2+}$ in the nitrobenzene and aqueous samples. The equilibrium distribution ratios of barium, D, were determined as the ratios of the corresponding measured radioactivities of $^{133}\text{Ba}^{2+}$ in the nitrobenzene and aqueous samples. The equilibrium distribution ratios of barium, D, were determined as the ratios of the corresponding measured radioactivities of $^{133}\text{Ba}^{2+}$ in the nitrobenzene and aqueous samples.
Barium complexes in the organic phase & log $K_{ex}$ & $U$ 
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$\text{BaL}^{2+}$ & 13.52 (14.09) & 2.83 
$\text{BaL}_2^{2+}$ & 17.89 (18.48) & 12.00 
$\text{BaL}^{2+}, \text{BaL}_2^{2+}$ & 13.05 ± 0.22, 16.65 (16.87) & 0.02 

$^a$ 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 $K$. 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 $\log K (\log[K + 3\sigma(K)])$. $^b$ The error-square sum $U = \sum (\log D_{calc} - \log D_{exp})^2$.

$\beta(\text{BaL}_2^{2+})_{\text{org}} = \frac{[\text{BaL}_2^{2+}]_{\text{org}}}{[\text{Ba}^{2+}]_{\text{org}}[\text{L}]_{\text{org}}}$ (12)

$\beta(\text{BaL}_2^{2+})_{\text{org}} = \frac{[\text{BaL}_2^{2+}]_{\text{org}}}{[\text{Ba}^{2+}]_{\text{org}}[\text{L}]_{\text{org}}^2}$ (13)

can be evaluated applying the following simple relations:

$\log \beta(\text{BaL}_2^{2+})_{\text{org}} = \log K_{ex}(\text{BaL}_2^{2+})_{\text{org}} - \log K_{ex}(\text{Ba}^{2+})_{\text{org}}$ (14)

$\log \beta(\text{BaL}_2^{2+})_{\text{org}} = \log K_{ex}(\text{BaL}_2^{2+})_{\text{org}} - \log K_{ex}(\text{Ba}^{2+})_{\text{org}}$ (15)

The respective equilibrium constants are summarized in Table 2.

Table 2: Equilibrium constants in the water–HCl–Ba$^{2+}$ (microamounts)–Slovafol 909–nitrobenzene – H$^+$ extraction system.

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>log $K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_{aq} \rightleftharpoons L_{org}$</td>
<td>1.38 $^a$</td>
</tr>
<tr>
<td>$H^+<em>{aq} + L</em>{org} \rightleftharpoons HL_{org}$</td>
<td>5.64 $^a$</td>
</tr>
<tr>
<td>$H^+<em>{aq} + 2L</em>{org} \rightleftharpoons HL_{org}^2_{aq}$</td>
<td>8.27 $^a$</td>
</tr>
<tr>
<td>$\text{Ba}^{2+}<em>{aq} + 2H^+</em>{aq} \rightleftharpoons \text{BaL}^{2+}<em>{aq} + 2H^+</em>{aq}$</td>
<td>0.9 $^b$</td>
</tr>
<tr>
<td>$\text{Ba}^{2+}<em>{aq} + 2L</em>{org} + 2H^+<em>{aq} \rightleftharpoons \text{BaL}^{2+}</em>{aq} + 2H^+_{aq}$</td>
<td>13.05</td>
</tr>
<tr>
<td>$\text{Ba}^{2+}<em>{aq} + 2L</em>{org} + 2H^+<em>{aq} \rightleftharpoons \text{BaL}^{2+}</em>{aq} + 2H^+_{aq}$</td>
<td>16.65</td>
</tr>
<tr>
<td>$\text{Ba}^{2+}<em>{aq} + L</em>{org} \rightleftharpoons \text{BaL}_{aq}$</td>
<td>12.15</td>
</tr>
<tr>
<td>$\text{Ba}^{2+}<em>{aq} + 2L</em>{org} \rightleftharpoons \text{BaL}_{aq}^2$</td>
<td>15.75</td>
</tr>
</tbody>
</table>

$^a$ Ref. 37. $^b$ Ref. 34.

Moreover, Figure 2 depicts the contributions of the species $H^+_{org}$, $HL_{org}^2$, and $HL_{org}^2$ to the total hydrogen cation concentration in the equilibrium nitrobenzene phase, while Figure 3 shows the contributions of the cations $\text{Ba}^{2+}_{org}$, $\text{BaL}_{org}^2$, and $\text{BaL}_{org}^2$ to the total barium concentration in the equilibrium organic phase. From both of these figures it follows that the complexes $HL_{org}^2$ and $HL_{org}^2$ are present in significant concentrations only at relatively high amounts of the Slovafol 909 ligand in the system under consideration.

Finally, it should be noted that the stability constants of the complex species $ML_{org}^2$ and $ML_{org}^2$, where $M^{2+} = Ca^{2+}, Sr^{2+}, Ba^{2+}$ and $L$ is Slovafol 909, in nitrobenzene sa-
Table 3: Stability constants of the complexes ML\(_2\)\(^+\) and ML\(_2\)\(^{2+}\) (M\(^{2+}\) = Ca\(^{2+}\), Sr\(^{2+}\), Ba\(^{2+}\); L = Slovafol 909) in nitrobenzene saturated with water at 25 °C.

<table>
<thead>
<tr>
<th>M(^{2+})</th>
<th>log β (ML(_2)(^{2+}))</th>
<th>log β (ML(_2)(^{2+}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(^{2+})</td>
<td>9.01 (^a)</td>
<td>12.79 (^a)</td>
</tr>
<tr>
<td>Sr(^{2+})</td>
<td>10.22 (^b)</td>
<td>14.52 (^b)</td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td>12.15 (^c)</td>
<td>15.75 (^c)</td>
</tr>
</tbody>
</table>

\(^a\)Ref. 40. \(^b\)Ref. 3. \(^c\)This work.

Table 4: Stability constants of the complexes Ba\(_2\)\(^{2+}\) and Ba\(_2\)\(^{4+}\) \(\log \beta(\text{Ba}_2\text{L}_{\text{org}})\) and \(\log \beta(\text{Ba}_2\text{L}_{\text{org}})\) in nitrobenzene saturated with water at 25 °C.

<table>
<thead>
<tr>
<th>L</th>
<th>(\log \beta(\text{Ba}<em>2\text{L}</em>{\text{org}}))</th>
<th>(\log \beta(\text{Ba}<em>2\text{L}</em>{\text{org}}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diglyme</td>
<td>3.37</td>
<td>-</td>
<td>41</td>
</tr>
<tr>
<td>Triglyme</td>
<td>5.18</td>
<td>8.03</td>
<td>41</td>
</tr>
<tr>
<td>Tetraglyme</td>
<td>6.23</td>
<td>7.35</td>
<td>41</td>
</tr>
<tr>
<td>PEG 200</td>
<td>10.93</td>
<td>-</td>
<td>34</td>
</tr>
<tr>
<td>PEG 300</td>
<td>12.17</td>
<td>-</td>
<td>34</td>
</tr>
<tr>
<td>PEG 400</td>
<td>12.80</td>
<td>-</td>
<td>34</td>
</tr>
<tr>
<td>Slovafol 909</td>
<td>12.15</td>
<td>15.75</td>
<td>This work</td>
</tr>
<tr>
<td>15C5</td>
<td>-</td>
<td>16.15</td>
<td>42</td>
</tr>
<tr>
<td>B15C5</td>
<td>-</td>
<td>13.3</td>
<td>43</td>
</tr>
<tr>
<td>18C6</td>
<td>12.47</td>
<td>17.78</td>
<td>38</td>
</tr>
<tr>
<td>B18C6</td>
<td>10.09</td>
<td>14.86</td>
<td>20</td>
</tr>
<tr>
<td>DB18C6</td>
<td>7.57</td>
<td>10.21</td>
<td>44</td>
</tr>
<tr>
<td>DCH18C6</td>
<td>11.75</td>
<td>15.43</td>
<td>45</td>
</tr>
<tr>
<td>DB21C7</td>
<td>8.86</td>
<td>12.26</td>
<td>46</td>
</tr>
</tbody>
</table>

5. References

29. E. Makrílk, P. Vaňura, P. Selucký, V. A. Babain, I. V. Smiri...
Povzetek

Proučevali smo ekstrakcijo mikrokoličin barija z raztopino hydrogen dikaarboličnokobaltata (H\(\text{++}\)) v nitrobenzenu v prisotnosti Slovafol 909 (L). Predpostavljamo, da so v ravnovesju v organski fazi prisotni kompleksi \(\text{HL}^{+}\), \(\text{HL}^{+2}\), \(\text{BaL}^{2+}\) in \(\text{BaL}^{2+2}\), za katere smo določili konstante ekstrakcije in konstante stabilnosti.