

Extraction of Barium with Bis[Undecahydro-7,8-dicarbaundecaborato(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-dicarbaundecaborato(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_2^+ , BaL^{2+} , and BaL_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.

In our previous works [1–4], we have studied the extraction of Sr^{2+} and Ba^{2+} ions using a nitrobenzene solution of hydrogen bis[undecahydro-7,8-dicarbaundecaborato(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 $\text{ML}_{n,\text{org}}^{2+}$ complexes. The occurrence of maxima on the plot of metal ion distribution ratio (D) vs. the total polyoxonium compound concentration, $c(\text{L})$, has been explained in terms of competition between the charged $\text{ML}_{n,\text{org}}^{2+}$ complexes and protonated PEG (HL_{org}^+) 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_2^+ 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_2^+ , and SrL_2^{2+} in the organic phase. The complex SrL_2^{2+} , 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 ^{133}Ba (Polatom, Poland) was of standard radiochemical purity.

The extraction experiments in the system water— CsCl — Ba^{2+} (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 $25 \pm 2^\circ\text{C}$ 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^-
 $c(CsCl) = 0.05 \text{ mol dm}^{-3}$, $c_B = 0.01 \text{ mol dm}^{-3}$
 $-3.252 -1.919$; $-3.000 -1.702$; $-2.699 -1.350$; $-2.495 -1.188$; $-2.252 -0.998$; $-2.000 -2.464$; $-1.699 -3.279$.

 $c(CsCl) = 0.05 \text{ mol dm}^{-3}$, $c_B = 0.03 \text{ mol dm}^{-3}$
 $-3.252 -1.289$; $-3.000 -1.076$; $-2.699 -0.652$; $-2.495 -0.448$; $-2.252 -0.170$; $-2.000 -0.021$; $-1.699 -0.039$; $-1.495 -2.030$; $-1.252 -3.228$.

 $c(CsCl) = 0.05 \text{ mol dm}^{-3}$, $c_B = 0.05 \text{ mol dm}^{-3}$
 $-2.495 -0.207$; $-2.252 0.102$; $-2.000 0.308$; $-1.699 0.479$; $-1.495 0.507$; $-1.252 -1.763$; $-1.000 -2.931$.

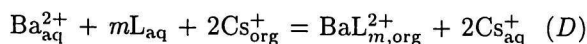
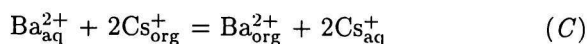
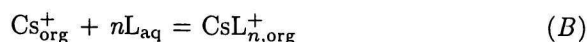
NK 350 (Gamma, Budapest, Hungary).

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 ($c_B = 0.01 \text{ mol dm}^{-3}$, 0.03 mol dm^{-3} , and 0.05 mol dm^{-3}) in the presence of 18C6 ($c(L) = 5.6 \times 10^{-4} - 0.10 \text{ mol dm}^{-3}$); 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_B , 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



to which the following equilibrium constants

$$K_D = \frac{[L_{org}]}{[L_{aq}]} \quad (1)$$

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

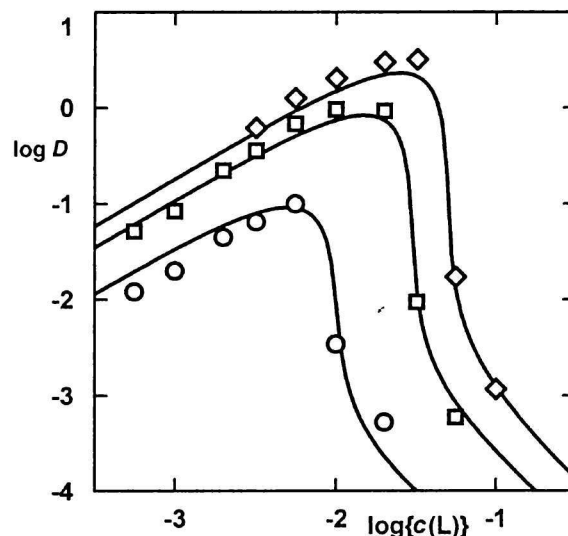


Fig. 1. Log D as a function of $\log \{c(L)\}$ for the system water—CsCl— Ba^{2+} (microamounts)—18C6—nitrobenzene— Cs^+B^- . \circ $c(CsCl) = 0.05 \text{ mol dm}^{-3}$, $c(CsB) = 0.01 \text{ mol dm}^{-3}$; \square $c(CsCl) = 0.05 \text{ mol dm}^{-3}$, $c(CsB) = 0.03 \text{ mol dm}^{-3}$; \diamond $c(CsCl) = 0.05 \text{ mol dm}^{-3}$, $c(CsB) = 0.05 \text{ mol dm}^{-3}$. The curves were calculated using the constants given in Table 3.

$$K_{ex}(Ba_{org}^{2+}) = \frac{[Ba_{org}^{2+}][Cs_{aq}^+]^2}{[Ba_{aq}^{2+}][Cs_{org}^+]^2} \quad (3)$$

$$K_{ex}(BaL_{m,org}^{2+}) = \frac{[BaL_{m,org}^{2+}][Cs_{aq}^+]^2}{[Ba_{aq}^{2+}][L_{aq}]^m [Cs_{org}^+]^2} \quad (4)$$

$$\beta(CsL_{aq}^+) = \frac{[CsL_{aq}^+]}{[Cs_{aq}^+][L_{aq}]} \quad (5)$$

$$\beta(BaL_{aq}^{2+}) = \frac{[BaL_{aq}^{2+}]}{[Ba_{aq}^{2+}][L_{aq}]} \quad (6)$$

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

Cesium and barium complexes in the organic phase	log {K _{ex} } ^a	U ^b
CsL ⁺ , BaL ²⁺	3.78 ± 0.11, 4.93 ± 0.13	1.43
CsL ₂ ⁺ , BaL ₂ ²⁺	6.98 ± 1.69, 7.98 ± 0.94	14.89
CsL ⁺ , BaL ₂ ²⁺	3.69 ± 0.60, 8.67(9.16)	24.63
CsL ₂ ⁺ , BaL ₂ ²⁺	6.99 ± 0.99, 4.17 ± 0.23	7.14
CsL ⁺ , BaL ²⁺ , BaL ₂ ²⁺	5.13 ± 1.13, 6.10 ± 1.13, 9.65(10.30)	0.69
CsL ₂ ⁺ , BaL ²⁺ , BaL ₂ ²⁺	transforms to CsL ₂ ⁺ , BaL ²⁺	
CsL ⁺ , CsL ₂ ⁺ , BaL ₂ ²⁺	transforms to CsL ⁺ , BaL ²⁺	
CsL ⁺ , CsL ₂ ⁺ , BaL ₂ ²⁺	transforms to CsL ₂ ⁺ , BaL ₂ ²⁺	
CsL ⁺ , CsL ₂ ⁺ , BaL ₂ ²⁺	5.31 ± 0.62, 6.41 ± 1.13, 6.28 ± 0.60	0.63
BaL ₂ ²⁺	10.04(10.58)	

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 $\log \{K\} \pm (\log \{[K + 0.5\sigma(K)]\} - \log \{[K - 0.5\sigma(K)]\})$. For $\sigma(K) > 2K$, the previous relation is not valid and then only the upper limit is given in the parenthesis in the form $\log \{K\}(\log \{K + \sigma(K)\})$.

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

determination of the “best” values of the constants $K_{\text{ex}}(\text{CsL}_{n,\text{org}}^+)$ and $K_{\text{ex}}(\text{BaL}_{m,\text{org}}^{2+})$. The minimum of the sum of errors in $\log D$, *i.e.* the minimum of the expression

$$U = \sum (\log D_{\text{calc}} - \log D_{\text{exp}})^2 \quad (7)$$

was sought.

The values $K_{\text{D}} = 0.10$ [10], $\log K_{\text{ex}}(\text{BaL}_{\text{org}}^{2+}) = -5.1$ (inferred from Refs. [11] and [12]), $\log \{\beta(\text{CsL}_{\text{aq}}^+)\} = 0.99$ [13], and $\log \{\beta(\text{BaL}_{\text{aq}}^{2+})\} = 3.87$ [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⁺, CsL₂⁺, BaL²⁺, and BaL₂²⁺ to be extracted into the nitrobenzene phase.

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

Knowing the values $K_{\text{D}} = 0.10$ [10], $\log K_{\text{ex}}(\text{BaL}_{\text{org}}^{2+}) = -5.1$ (inferred from Refs. [11] and [12]) and the extraction constants $\log \{K_{\text{ex}}(\text{CsL}_{\text{org}}^+)\} = 5.31$, $\log \{K_{\text{ex}}(\text{CsL}_{2,\text{org}}^+)\} = 6.41$, $\log \{K_{\text{ex}}(\text{BaL}_{\text{org}}^{2+})\} = 6.28$, and $\log \{K_{\text{ex}}(\text{BaL}_{2,\text{org}}^{2+})\} = 10.04$ determined here, the stability constants of the complexes CsL⁺, CsL₂⁺, BaL²⁺, and BaL₂²⁺ in the nitrobenzene phase defined as

$$\beta(\text{CsL}_{\text{org}}^+) = \frac{[\text{CsL}_{\text{org}}^+]}{[\text{Cs}_{\text{org}}^+][\text{L}_{\text{org}}]} \quad (8)$$

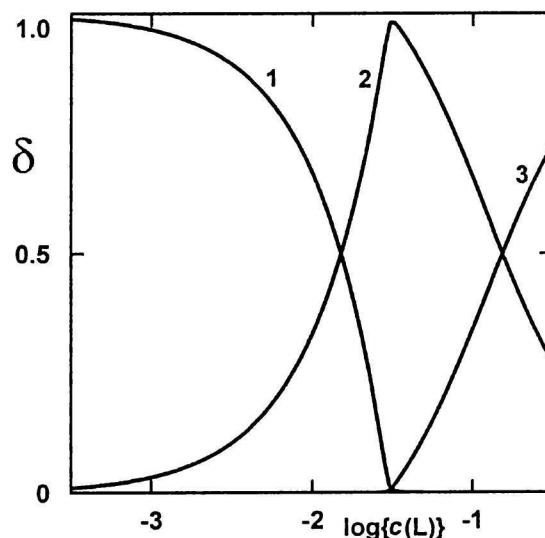


Fig. 2. Distribution diagram of cesium present in the equilibrium nitrobenzene phase of the system water—CsCl—Ba²⁺ (microamounts)—18C6—nitrobenzene—Cs⁺B⁻ in the forms of Cs⁺, CsL⁺, and CsL₂⁺. $c(\text{CsCl}) = 0.05 \text{ mol dm}^{-3}$, $c_{\text{B}} = 0.03 \text{ mol dm}^{-3}$, 1δ (Cs⁺), 2δ (CsL⁺), 3δ (CsL₂⁺). The distribution curves were calculated using the constants $\log K_{\text{D}} = -1.0$, $\log \{\beta(\text{CsL}_{\text{aq}}^+)\} = 0.99$, $\log \{K_{\text{ex}}(\text{CsL}_{\text{org}}^+)\} = 5.31$, and $\log \{K_{\text{ex}}(\text{CsL}_{2,\text{org}}^+)\} = 6.41$.

$$\beta(\text{CsL}_{2,\text{org}}^+) = \frac{[\text{CsL}_{2,\text{org}}^+]}{[\text{Cs}_{\text{org}}^+][\text{L}_{\text{org}}]^2} \quad (9)$$

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

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

can be evaluated using the simple relations

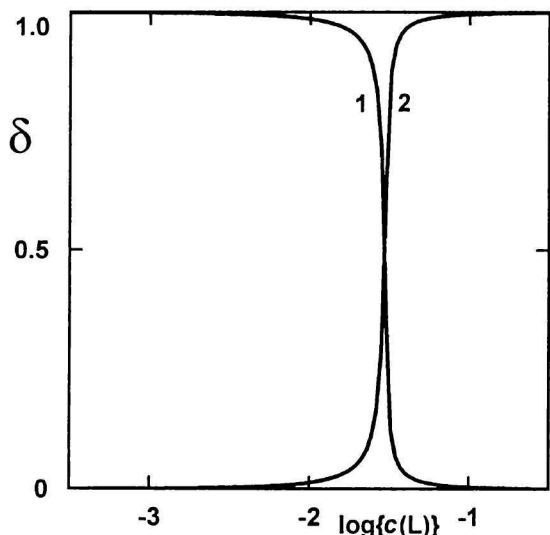


Fig. 3. Distribution diagram of barium present in the equilibrium nitrobenzene phase of the system water—CsCl—Ba²⁺ (microamounts)—18C6—nitrobenzene—Cs⁺B⁻ in the forms of BaL²⁺ and BaL_{2,2}²⁺. $c(\text{CsCl}) = 0.05 \text{ mol dm}^{-3}$, $c_{\text{B}} = 0.03 \text{ mol dm}^{-3}$; 1δ (BaL²⁺), 2δ (BaL_{2,2}²⁺). The distribution curves were calculated using the constants given in Table 3.

$$\log \{\beta(\text{CsL}_{\text{org}}^+)\} = \log \{K_{\text{ex}}(\text{CsL}_{\text{org}}^+)\} - \log K_{\text{D}} \quad (12)$$

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

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

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

Finally, the individual extraction constants of the cations CsL⁺ and BaL²⁺, denoted $K_i(\text{CsL}^+)$ and $K_i(\text{BaL}^{2+})$, respectively, in the water—nitrobenzene system corresponding to the transfer of these complex cations from the aqueous into the nitrobenzene phase [11]

$$\text{CsL}_{\text{aq}}^+ = \text{CsL}_{\text{org}}^+ \quad (G)$$

$$\text{BaL}_{\text{aq}}^{2+} = \text{BaL}_{\text{org}}^{2+} \quad (H)$$

were evaluated using the following relationships

$$\log K_i(\text{CsL}^+) = \log \{K_{\text{ex}}(\text{CsL}_{\text{org}}^+)\} - \log \{\beta(\text{CsL}_{\text{aq}}^+)\} + \log K_i(\text{Cs}^+) \quad (16)$$

$$\log K_i(\text{BaL}^{2+}) = \log \{K_{\text{ex}}(\text{BaL}_{\text{org}}^{2+})\} - \log \{\beta(\text{BaL}_{\text{aq}}^{2+})\} + 2 \log K_i(\text{Cs}^+) \quad (17)$$

where $\log \{\beta(\text{CsL}_{\text{aq}}^+)\} = 0.99$ [13], $\log \{\beta(\text{BaL}_{\text{aq}}^{2+})\} = 3.87$ [13], and $\log K_i(\text{Cs}^+) = -2.7$ [11]. The respective

Table 3. Equilibrium Constants for the Water—CsCl—Ba²⁺ (Microamounts)—18C6—Nitrobenzene—Cs⁺B⁻ System

Equilibrium	log {K}
$\text{L}_{\text{aq}} = \text{L}_{\text{org}}$	-1.0 ^a
$\text{Cs}_{\text{aq}}^+ + \text{L}_{\text{aq}} = \text{CsL}_{\text{aq}}^+$	0.99 ^b
$\text{Ba}_{\text{aq}}^{2+} + \text{L}_{\text{aq}} = \text{BaL}_{\text{aq}}^{2+}$	3.87 ^b
$\text{Cs}_{\text{org}}^+ + \text{L}_{\text{aq}} = \text{CsL}_{\text{org}}^+$	5.31
$\text{Cs}_{\text{org}}^+ + 2\text{L}_{\text{aq}} = \text{CsL}_{2,\text{org}}^+$	6.41
$\text{Ba}_{\text{aq}}^{2+} + 2\text{Cs}_{\text{org}}^+ = \text{Ba}_{\text{org}}^{2+} + 2\text{Cs}_{\text{aq}}^+$	-5.1 ^c
$\text{Ba}_{\text{aq}}^{2+} + \text{L}_{\text{aq}} + 2\text{Cs}_{\text{org}}^+ = \text{BaL}_{\text{org}}^{2+} + 2\text{Cs}_{\text{aq}}^+$	6.28
$\text{Ba}_{\text{aq}}^{2+} + 2\text{L}_{\text{aq}} + 2\text{Cs}_{\text{org}}^+ = \text{BaL}_{2,\text{org}}^{2+} + 2\text{Cs}_{\text{aq}}^+$	10.04
$\text{Cs}_{\text{org}}^+ + \text{L}_{\text{org}} = \text{CsL}_{\text{org}}^+$	6.31
$\text{Cs}_{\text{org}}^+ + 2\text{L}_{\text{org}} = \text{CsL}_{2,\text{org}}^+$	8.41
$\text{Ba}_{\text{org}}^{2+} + \text{L}_{\text{org}} = \text{BaL}_{\text{org}}^{2+}$	12.38
$\text{Ba}_{\text{org}}^{2+} + 2\text{L}_{\text{org}} = \text{BaL}_{2,\text{org}}^{2+}$	17.14
$\text{CsL}_{\text{aq}}^+ = \text{CsL}_{\text{org}}^+$	1.6
$\text{BaL}_{\text{aq}}^{2+} = \text{BaL}_{\text{org}}^{2+}$	-3.0

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

equilibrium constants are summarized in Table 3.

In conclusion it should be noted that the stability constants of the complexes CsL⁺, CsL₂⁺, and BaL²⁺ (L = 18-crown-6) in water-saturated nitrobenzene, evaluated in the systems water—HNO₃—Cs⁺ (microamounts)—18C6—nitrobenzene—H⁺B⁻ [14] and water—HClO₄—Ba²⁺ (microamounts)—18C6—nitrobenzene—H⁺B⁻ [4], are $\log \{\beta(\text{CsL}_{\text{org}}^+)\} = 6.54$ [14], $\log \{\beta(\text{CsL}_{2,\text{org}}^+)\} = 8.64$ [14], and $\log \{\beta(\text{BaL}_{\text{org}}^{2+})\} = 12.47$ [4] which are in good agreement with the values $\log \{\beta(\text{CsL}_{\text{org}}^+)\} = 6.31$, $\log \{\beta(\text{CsL}_{2,\text{org}}^+)\} = 8.41$, and $\log \{\beta(\text{BaL}_{\text{org}}^{2+})\} = 12.38$ determined in this work (see Table 3). Somewhat higher difference between the values $\log \{\beta(\text{BaL}_{2,\text{org}}^{2+})\} = 17.78$ [4] and $\log \{\beta(\text{BaL}_{2,\text{org}}^{2+})\} = 17.14$ 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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