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

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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^+, HL_2^+, BaL^{2+} and BaL_2^{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 anion[1] 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,[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]

Extraction of microamounts of Sr^{2+} and Ba^{2+} by a nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-)[1] in the presence of polyethylene glycols PEG 200, PEG 300 and PEG 400 has been studied. It has been found that the extraction of the protonated polyethylene glycol molecule HL^+ and the extraction of the complex ML^{2+} ($M^{2+} = Sr^{2+}$, Ba^{2+}; L = PEG 200, PEG 300, PEG 400) are predominant reactions in this water – nitrobenzene system. The respective equilibrium constants have been determined. The hydration numbers of the HL^+ and ML^{2+} complex cations in the organic phase have been obtained.

The extraction and stability constants in the nitrobenzene phase increase in the order $H^+ < Sr^{2+} < Ba^{2+}$ and PEG 200 < PEG 300 < PEG 400, whereas the hydration numbers decrease in the same sequence.[34]

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, Cs^+B^-, 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 Cs^+B^- by the procedure described elsewhere.[36] The other chemicals used (Lachema,

Brno, Czech Republic) were of reagent grade purity. The radionuclide $^{133}Ba^{2+}$ (Polatom, Poland) was of standard radiochemical purity.

The extraction experiments in the two–phase water–HCl–Ba^{2+} (microamounts)– Slovafol 909–nitrobenzene–H$^+$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 γ-activities were measured using a well-type NaI(T1) scintillation detector connected to a γ-analyzer NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratios of barium, D, were determined as the ratios of the corresponding measured radioactivities of $^{133}Ba^{2+}$ 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(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$^+$B$^-$ system
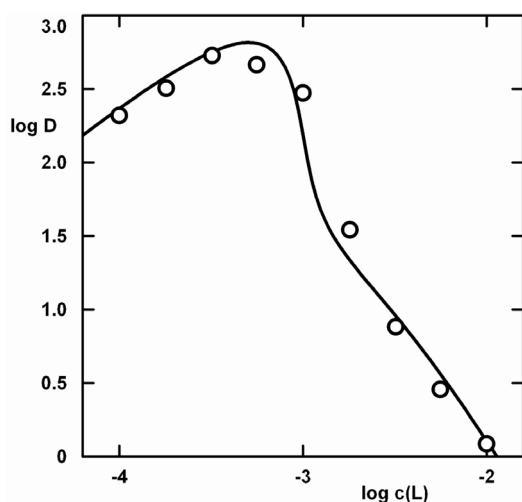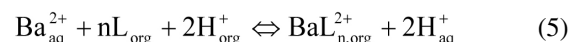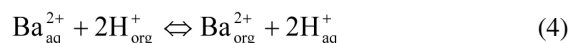

Figure 1: Log D as a function of log c(L), where L is Slovafol 909, for the system water–HCl–Ba^{2+} (microamounts) – Slovafol 909 – nitrobenzene–H$^+$B$^-$; c(HCl = 0.10 mol dm^{-3}, c$_B$ = 0.001 mol dm^{-3}. The curve was calculated using the constants given in Table 2.

can be described by the set of reactions

$$L_{aq} \Leftrightarrow L_{org} \tag{1}$$

$$H^+_{org} + L_{org} \Leftrightarrow HL^+_{org} \tag{2}$$

$$H^+_{org} + 2L_{org} \Leftrightarrow HL^+_{2,org} \tag{3}$$

$$Ba^{2+}_{aq} + 2H^+_{org} \Leftrightarrow Ba^{2+}_{org} + 2H^+_{aq} \tag{4}$$

$$Ba^{2+}_{aq} + nL_{org} + 2H^+_{org} \Leftrightarrow BaL^{2+}_{n,org} + 2H^+_{aq} \tag{5}$$

to which the following equilibrium constants correspond:

$$K_D = \frac{[L_{org}]}{[L_{aq}]} \tag{6}$$

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

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

$$K_{ex}(Ba^{2+}_{org}) = \frac{[Ba^{2+}_{org}][H^+_{aq}]^2}{[Ba^{2+}_{aq}][H^+_{org}]^2} \tag{9}$$

$$K_{ex}(BaL^{2+}_{n,org}) = \frac{[BaL^{2+}_{n,org}][H^+_{aq}]^2}{[Ba^{2+}_{aq}][L_{org}]^n[H^+_{org}]^2} \tag{10}$$

The subscripts "aq" and "nb" denote the aqueous and organic phases, respectively.

A subroutine UBBE, based on the relations given above, the mass balance of the Slovafol 909 ligand and the electroneutrality conditions in both phases of the system under study, was formulated[34,38] and introduced into a more general least-squares minimizing program LETAGROP[39] used for determination of the "best" values of the extraction constants K$_{ex}$(BaL$^{2+}_{n,org}$). The minimum of the sum of errors in log D, i.e., the minimum of the expression

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

was sought.

The values log K$_D$ = 1.38,[37] log β(HL$^+_{org}$)= 5.64,[37] log β(HL$^+_{2,org}$) = 8.27[37] and log K$_{ex}$(Ba$^{2+}_{org}$) = 0.9[34] were used for the respective calculations. The results are listed in Table 1. From this table it is evident that the extraction data can be best explained assuming the barium complex species BaL^{2+} and BaL$^{2+}_2$ to be extracted into the nitrobenzene phase.

Knowing the value lok K$_{ex}$(Ba$^{2+}_{org}$) = 0.9,[34] as well as the extraction constants log K$_{ex}$(BaL$^{2+}_{org}$) = 13.05 and log K$_{ex}$(BaL$^{2+}_{2,org}$) = 16.65 determined here (Table 1), the stability constants of the complexes BaL$^{2+}_{org}$ and BaL$^{2+}_{2,org}$ in the nitrobenzene phase defined as

Table 1: Comparison of three different models of barium extraction from aqueous solution of HCl by nitrobenzene solution of H^+B^- in the presence of Slovafol 909.

Barium complexes in the organic phase	$\log K_{ex}$ [a]	U [b]
BaL^{2+}	13.52 (14.09)	2.83
BaL_2^{2+}	17.89 (18.48)	12.00
BaL^{2+}, 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.[39] 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 $\log K$ ($\log[K + 3\sigma(K)]$).[39]
[b] The error-square sum $U = \Sigma(\log D_{calc} - \log D_{exp})^2$.

$$\beta(BaL^{2+}_{org}) = \frac{[BaL^{2+}_{org}]}{[Ba^{2+}_{org}][L_{org}]} \quad (12)$$

$$\beta(BaL^{2+}_{2,org}) = \frac{[BaL^{2+}_{2,org}]}{[Ba^{2+}_{org}][L_{org}]^2} \quad (13)$$

can be evaluated applying the following simple relations:

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

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

The respective equilibrium constants are summarized in Table 2.

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

Equilibrium	$\log K$
$L_{aq} \Leftrightarrow L_{org}$	1.38 [a]
$H^+_{org} + L_{org} \Leftrightarrow HL^+_{org}$	5.64 [a]
$H^+_{org} + 2L_{org} \Leftrightarrow HL^+_{2,org}$	8.27 [a]
$Ba^{2+}_{aq} + 2H^+_{org} \Leftrightarrow Ba^{2+}_{org} + 2H^+_{aq}$	0.9 [b]
$Ba^{2+}_{aq} + L_{org} + 2H^+_{org} \Leftrightarrow BaL^{2+}_{org} + 2H^+_{aq}$	13.05
$Ba^{2+}_{aq} + 2L_{org} + 2H^+_{org} \Leftrightarrow BaL^{2+}_{2,org} + 2H^+_{aq}$	16.65
$Ba^{2+}_{org} + L_{org} \Leftrightarrow BaL^{2+}_{org}$	12.15
$Ba^{2+}_{org} + 2L_{org} \Leftrightarrow BaL^{2+}_{2,org}$	15.75

[a] Ref. 37. [b] Ref. 34.

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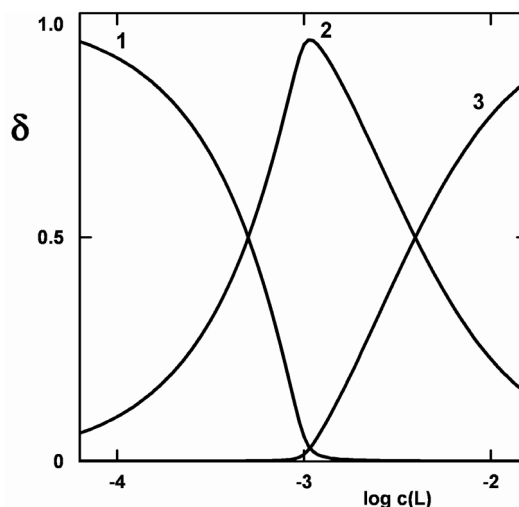

Figure 2: Distribution diagram of hydrogen cation in the equilibrium nitrobenzene phase of the system water–HCl–Ba^{2+} (microamounts) –Slovafol 909–nitrobenzene–H^+B^- in the forms of H^+, HL^+ and HL^+_2;
$c(HCl) = 0.10$ mol dm^{-3}, $c_B = 0.001$ mol dm^{-3}
1 $\delta[H^+] = [H^+_{org}]/c(H^+)_{org}$,
2 $\delta[HL^+] = [HL^+_{org}]/c(H^+)_{org}$,
3 $\delta[HL^+_2] = [HL^+_{2,org}]/c(H^+)_{org}$,
where $c(H^+)_{org} = [H^+_{org}] + [HL^+_{org}] + [HL^+_{2,org}]$.
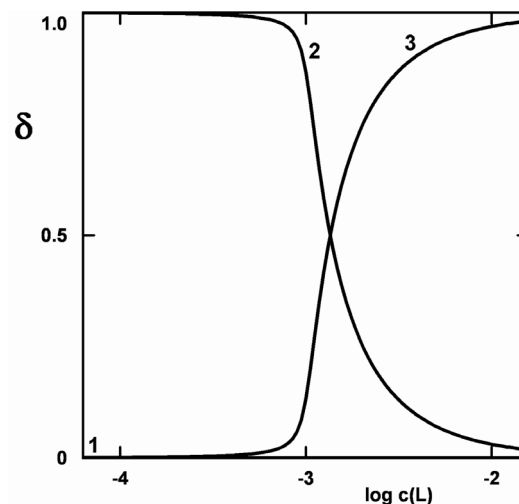The distribution curves were calculated using the constants given in Table 2.

Figure 3: Distribution diagram of barium in the equilibrium nitrobenzene phase of the system water–HCl–Ba^{2+} (microamounts) –Slovafol 909 –nitrobenzene–H^+B^- in the forms of Ba^{2+}, BaL^{2+} and BaL^{2+}_2;
$c(HCl) = 0.01$ mol dm^{-3}, $c_B = 0.001$ mol dm^{-3}
1 $\delta[Ba^{2+}] = [Ba^{2+}_{org}]/c(Ba^{2+})_{org}$,
2 $\delta[BaL^{2+}] = [BaL^{2+}_{org}]/c(Ba^{2+})_{org}$,
3 $\delta[BaL^{2+}_2] = [BaL^{2+}_{2,org}]/c(Ba^{2+})_{org}$,
where $c(Ba^{2+})_{org} = [Ba^{2+}_{org}] + [BaL^{2+}_{org}] + [BaL^{2+}_{2,org}]$.
The distribution curves were calculated using the constants given in Table 2.

Finally, it should be noted that the stability constants of the complex species ML^{2+}_{org} and $ML^{2+}_{2,org}$, 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.

M^{2+}	$\log \beta(ML^{2+}_{org})$	$\log \beta(ML^{2+}_{2,org})$
Ca^{2+}	9. 01 [a]	12.79 [a]
Sr^{2+}	10.22 [b]	14.52 [b]
Ba^{2+}	12.15 [c]	15.75 [c]

[a] Ref. 40.   [b] Ref. 3.   [c] This work.

turated with water are given in Table 3. Thus, in this medium, the stability of the considered complexes ML^{2+}_{org} and $ML^{2+}_{2,org}$ increases in the series of $Ca^{2+} < Sr^{2+} < Ba^{2+}$.

In conclusion, Table 4 summarizes stability constants of the complexes BaL^{2+}_{org} and $BaL^{2+}_{2,org}$ with fourteen oxyethylene ligands L, denoted by the symbols diglyme, triglyme, tetraglyme, PEG 200, PEG 300, PEG 400, Slovafol 909, 15C5, B15C5, 18C6, B18C6, DB18C6, DCH18C6 and DB21C7, in nitrobenzene saturated with water at 25 °C. From the data reviewed in this table it follows that in the mentioned nitrobenzene medium, the stability constants of the complexes BaL^{2+}_{org} increase in the order diglyme < triglyme < tetraglyme < DB18C6 < DB21C7 < B18C6 < PEG 200 < DCH18C6 < Slovafol 909 < PEG 300 < 18C6 < PEG 400, whereas the stability of the cationic complex species $BaL^{2+}_{2,org}$ increases in the following sequence: tetraglyme < triglyme < DB18C6 < DB21C7 < B15C5 < B18C6 < DCH18C6 < Slovafol 909 < 15C5 < 18C6.

Table 4: Stability constants of the complexes BaL^{2+}_{org} and $BaL^{2+}_{2,org}$ [L = diglyme, triglyme, tetraglyme, PEG 200, PEG 300, PEG 400, Slovafol 909, 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), benzo-18-crown-6 (B18C6), dibenzo-18-crown-6 (DB18C6), dicyclohexano-18-crown-6 (DCH18C6), dibenzo-21-crown-7 (DB21C7)] in nitrobenzene saturated with water at 25 °C.

L	$\log \beta(BaL^{2+}_{org})$	$\log \beta(BaL^{2+}_{2,org})$	Ref.
Diglyme	3.37	–	41
Triglyme	5.18	8.03	41
Tetraglyme	6.23	7.35	41
PEG 200	10.93	–	34
PEG 300	12.17	–	34
PEG 400	12.80	–	34
Slovafol 909	12.15	15.75	This work
15C5	–	16.15	42
B15C5	–	13.3	43
18C6	12.47	17.78	38
B18C6	10.09	14.86	20
DB18C6	7.57	10.21	44
DCH18C6	11.75	15.43	45
DB21C7	8.86	12.26	46

4. Acknowledgements

5. References

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Povzetek

Proučevali smo ekstrakcijo mikrokoličin barija z raztopino hidrogen dikarbolilkobaltata (H^+B^-) v nitrobenzenu v prisotnosti Slovafol 909 (L). Predpostavljamo, da so v ravnotežju v organski fazi prisotni kompleksi HL^+, HL_2^+, BaL^{2+} in BaL_2^{2+}, za katere smo določili konstante ekstrakcije in konstante stabilnosti.