Extraction of microamounts of strontium by a nitrobenzene solution of bis-1,2-dicarbollylcobaltate in the presence of 15-crown-5

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Extraction of ^{85}Sr by a nitrobenzene solution of bis-1,2-dicarbollylcobaltate in the presence of 15-crown-5 (15C5, L) has been investigated. The equilibrium data and the typical maxima concerning the dependencies of the Sr distribution ratios on the analytical concentration of 15C5 in the system under study can be explained assuming that the HL^+, HL_2^+ and SrL_2^{2+} species are extracted into the nitrobenzene phase. The values of the corresponding extraction and stability constants of the extracted species in nitrobenzene saturated with water have been determined.

Introduction

In our previous papers[1–4] we dealt with the extraction of Sr^{2+} and Ba^{2+} ions using a nitrobenzene solution of H^+ bis-1,2-dicarbollylcobaltate (abbrev. H^+B^-) in the presence of polyethylene glycols, polyethers and crowns. These ions (M^{2+}) have been found to be extracted in the form of the $ML_{n,\,org}^{2+}$ 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 $ML_{n,\,org}^{2+}$ complexes and protonated PEG (HL_{org}^+) during the balancing of the dicarbollylcobaltate electrostatic charge in the organic phase.

Quite different behavior has been found during the extraction of perchloric acid by the nitrobenzene solution of dibenzo-18-crown-6 in comparison with the extraction of this acid into nitrobenzene in the presence of 18-crown-6.[5,6] Extraction of cesium using a nitrobenzene solution of H^+B^- in the presence of dibenzo-18-crown-6 has been previously investigated.[7]

The aim of this paper is to study the extraction of microamounts of strontium by the nitrobenzene solution of H^+B^- in the presence of 15-crown-5 (15C5). We intended to find the composition of species in the organic phase and to determine the respective equilibrium constants.

Experimental

15-Crown-5 (Ventron, Karlsruhe, Germany) was used without additional purification. Cesium salt of bis-1,2-dicarbollylcobaltate, Cs^+B^-, was synthesized in the Institute of Inorganic Chemistry, Řež, Czech Republic. Hydrogen form of bis-1,2-dicarbollylcobaltate (H^+B^-) was prepared from the corresponding cesium salt (Cs^+B^-) by the procedure described in Reference 3. The other chemicals used (Lachema, Brno, Czech Republic) were of

reagent grade purity. The radionuclide ^{85}Sr (DuPont, Belgium) was of standard radiochemical purity.

The extraction experiments on a two–phase water–HNO_3–Sr^{2+} (microamounts) – 15C5–nitrobenzene–H^+B^- system were performed in 10 ml glass test – tubes with polyethylene stoppers using 2 ml of each phase. The test-tubes were shaken for two hours at a temperature of 25 ± 2 °C using a laboratory shaker. Under these conditions the equilibrium in the system under study has been established already after approximately 20 minutes of shaking. Then the phases were separated by centrifugation (5 min, 2500 rpm). After centrifugation, 1 ml 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 RFT Strahlungsmessgerät 20046 (RFT, Dresden, Germany).

The equilibrium distribution ratio of strontium (D) was determined as a ratio of the measured activities of the nitrobenzene and aqueous samples.

Results and discussion

The dependencies of the logarithm of the strontium distribution ratios (log D) on the logarithm of the total (analytical) concentration of the 15C5 ligand in the initial aqueous phase (log c(L)) were experimentally measured for various concentrations of nitric acid in the aqueous phase [$c(HNO_3) \approx 0.10$–2.0 mol/l] and for various concentrations of bis-1,2-dicarbollylcobaltate in the nitrobenzene phase [$c(B) = 0.0002$–0.01 mol/l] in the presence of 15C5 [$c(L) = 3 \cdot 10^{-5}$–0.01 mol/l]. The corresponding results are given in Table 1 and Fig. 1.

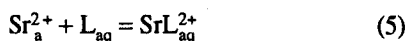With regard to the results of previous papers,[1–5] the two-phase water–HNO_3–Sr^{2+} (microamounts–15C5–nitrobenzene–H^+B^- system can be described by the following set of reactions

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

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Table 1. Log D as a function of log $c(L)$ (L = 15C5) for strontium extraction from an aqueous solution of nitric acid by a nitrobenzene solution of H^+B^-

$c(HNO_3) = 0.1073$ mol/l, $c_B = 0.000969$ mol/l

−4.300	0.195;	−4.000	0.814;	−3.699	1.611;	−3.523	1.829;
−3.398	1.932;	−3.301	2.381;	−3.155	2.746;	−3.000	2.477;
−2.699	3.204;	−2.398	3.081;	−2.301	3.264;	−2.222	3.038;
−2.099	2.968;	−2.046	3.004;	−2.000	2.932;	−1.824	2.711;
−1.523	2.342;						

$c(HNO_3) = 0.0981$ mol/l, $c_B = 0.0002$ mol/l

−4.495	−0.817;	−4.252	−0.476;	−4.000	0.047;	−3.745	0.487;
−3.495	0.827;	−3.252	1.020;	−3.000	1.214;	−2.745	1.173;
−2.495	1.173;	−2.252	1.014;	−2.000	0.818;	−1.745	0.534;
−1.495	0.312;	−1.252	−0.148;	−1.000	−0.555;		

$c(HNO_3) = 0.4617$ mol/l, $c_B = 0.001$ mol/l

−4.495	−1.819;	−4.252	−1.219;	−4.000	−0.756;	−3.745	−0.181;
−3.495	0.236;	−3.252	0.682;	−3.000	1.175;	−2.745	1.355;
−2.495	1.336;	−2.252	1.345;	−2.000	1.281;	−1.745	1.043;
−1.495	0.802;	−1.252	0.445;	−1.000	−0.038;		

$c(HNO_3) = 2.055$ mol/l, $c_B = 0.00485$ mol/l

−4.301	−2.307;	−4.000	−1.792;	−3.602	−1.085;	−3.301	−0.433;
−3.000	0.142;	−2.602	0.886;	−2.301	1.297;	−2.000	1.380;
−1.602	1.421;	−1.456	1.271;	−1.301	0.921;		

$c(HNO_3) = 1.026$ mol/l, $c_B = 0.001$ mol/l

−4.495	−2.105;	−4.252	−1.667;	−4.000	−1.170	−3.745	−0.570;
−3.495	−0.117;	−3.252	0.337;	−3.000	0.708;	−2.745	0.918;
−2.495	0.924;	−2.252	0.924;	−2.000	0.745;	−1.745	0.632;
−1.495	0.445;	−1.252	0.028;	−1.000	−0.401;		

$c(HNO_3) = 2.066$ mol/l, $c_B = 0.01$ mol/l

−4.495	−2.619;	−4.252	−2.150;	−4.000	−1.648;	−3.745	−1.231;
−3.495	−0.752;	−3.252	−0.258;	−3.000	0.215;	−2.745	0.701;
−2.495	1.207;	−2.252	1.683;	−2.000	2.020;	−1.745	2.104;
−1.495	1.943;	−1.252	1.700;	−1.000	1.312;		

$$H^+_{org} + nL_{aq} = HL^+_{n,org} \qquad (2)$$

$$Sr^{2+}_{aq} + nL_{aq} + 2H^+_{org} = SrL^{2+}_{n\,org} + 2H^+_{aq} \qquad (3)$$

$$H^+_{aq} + L_{aq} = HL^+_{aq} \qquad (4)$$

$$Sr^{2+}_a + L_{aq} = SrL^{2+}_{aq} \qquad (5)$$

to which the following equilibrium constants

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

$$K_{ex}(HL^+_{n,org}) = [HL^+_{n,org}]/[H^+_{org}]\,[L_{aq}]^n \qquad (7)$$

$$K_{ex}(SrL^{2+}_{n\,,org}) =$$

$$= [SrL^{2+}_{n\,,org}]\,[H^+_{aq}]^2/[Sr^{2+}_{a\,q}]\,[L_{aq}]^n\,[H^+_{org}]^2 \qquad (8)$$

$$K(HL^+_{aq}) = [HL^+_{aq}]/[H^+_{aq}]\,[L_{aq}] \qquad (9)$$

$$K(SrL^{2+}_{aq}) = [SrL^{2+}_{aq}]/[Sr^{2+}_{aq}]\,[L_{aq}] \qquad (10)$$

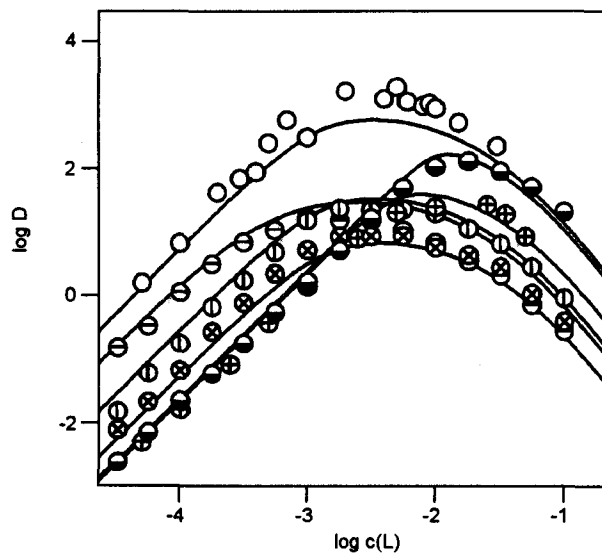correspond; aq and org denote the presence of the particles in the aqueous and organic phases, respectively.

Fig. 1. Log D as a function of log $c(L)$ in the system water–HNO_3–Sr^{2+} (microamounts)–15C5–nitrobenzene–H^+B^-; O $c_B = 0.000969$ mol/l, $c(HNO_3) = 0.1073$ mol/l; ⊖ $c_B = 0.0002$ mol/l, $c(HNO_3) =$ = 0.0981 mol/l; ⊕ $c_B = 0.0010$ mol/l, $c(HNO_3) = 0.4617$ mol/l; ⊕ $c_B =$ = 0.00485 mol/l, $c(HNO_3) = 2.055$ mol/l; ⊗ $c_B = 0.001$ mol/l, $c(HNO_3) = 1.026$ mol/l; ⊝ $c_B = 0.01$ mol/l, $c(HNO_3) = 2.066$ mol/l. The solid curves were calculated for the constants given in Table 3

Table 2. Comparison of various models of strontium extraction from the aqueous solution of nitric acid by nitrobenzene solutions of H^+B^- in the presence of 15-crown-5

Model	log K_{ex}*	U**
HL^+, SrL^{2+}	1.87(2.18), 9.16(9.40)	42.8975
HL^+, SrL_2^{2+}	3.99(4.28), 14.82(15.27)	8.0092
HL_2^+, SrL^{2+}	3.22(3.54), 9.03 ± 0.25	42.7801
HL_2^+, SrL_2^{2+}	4.71(4.93), 12.63(12.84)	30.6198
HL^+, HL_2^+, SrL^{2+}	1.54(2.17), 2.98(3.56), 9.10(9.35)	42.2881
HL^+, HL_2^+, SrL_2^{2+}	3.61(3.83), 5.00(5.21), 14.27(14.60)	4.7016
HL^+, HL_2^+, SrL^{2+}, SrL_2^{2+}	transforms to HL^+, HL_2^+, SrL_2^{2+}	

*The values of the extraction constants are given for each complex. The following values were used for the computations: $K_D = 0.22$,[9] log $K_{ex}(Sr_{org}^{2+}) = 0.70$,[1] log $K(SrL_{aq}^{2+}) = 1.95$,[11] and log $K(HL_{aq}^+) = -0.57$.[10] The reliability interval of the constants are given – in agreement with Reference 8 – as $3s(K)$, where $s(K)$ is the standard deviation of the constant K. These values are expressed in the logarithmic scale using the approximate relation log $K ± \{[\log K + 1.5s(K)] - [\log K - 1.5s(K)]\}$. For $s(K) > 0.2K$, the previous relation is not valid and then only the upper limit is given in the parenthesis in the form log $K(\log (K + 3s(K))$.

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

A subroutine UBBE, based on the relations given above, the mass balances of the crown ligand and the electroneutrality conditions of both phases, was formulated[1,4] and inserted into the more general least-squares minimizing program LETAGROP[8] was used for the evaluation of the "best" values of the constants $K_{ex}(HL_{n,org}^+)$ and $K_{ex}(SrL_{n,org}^{2+})$. The minimum of sum of errors of log D, i.e., the minimum of the expression

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

was sought.

The following values log $K_{ex}(Sr_{org}^{2+}) = 0.70$,[1] $K_D = 0.22$,[9] log $K(HL_{aq}^+) = -0.57$[10] and log $K(SrL_{aq}^{2+}) = 1.95$,[11] were used for the respective calculations. The results are presented in Table 2.

From Table 2 it is evident that the extraction data can be explained assuming that the species HL^+, HL_2^+ and SrL_2^{2+} are extracted into the nitrobenzene phase. In this respect it is necessary to note that the SrL^{2+} complex was not proven in the organic phase since the minimum of the function U was found for the zero value of the corresponding extraction constant.

Furthermore, Fig. 2 presents the dependence of the H_{org}^+, HL_{org}^+ and $HL_{2,org}^+$ particles on the total acidity of the organic phase. From Fig. 2 it follows that the HL_2^+ complex in the nitrobenzene phase is present in significant concentrations only at relatively high concentrations of the 15C5 ligand in the system under study. On the other hand, in the nitrobenzene phase strontium is present almost completely in the form of SrL_2^{2+} so the concentration of the cation Sr^{2+} in this phase is practically negligible.

Knowing the values log $K_{ex}(Sr_{org}^{2+}) = 0.70$,[1] $K_D = 0.22$,[9] and the extraction constants log $K_{ex}(HL_{org}^+) = 3.61$, log $K_{ex}(HL_{2,org}^+) = 5.00$ and log $K_{ex}(SrL_{2,org}^{2+}) = 14.27$, determined in this paper, then the stability constants of the
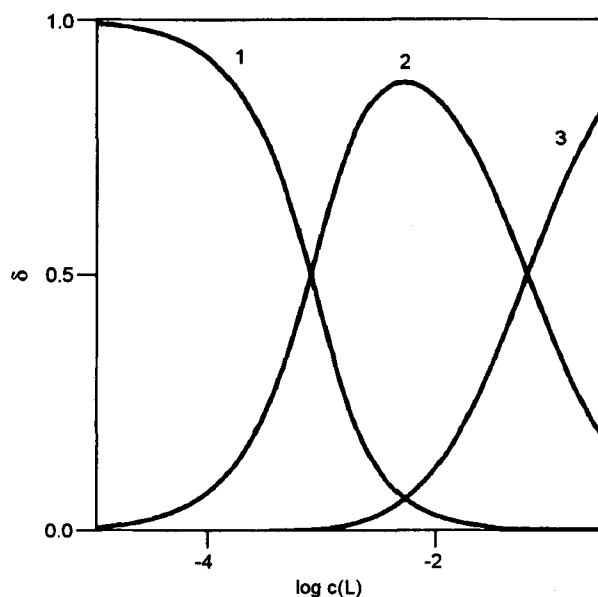

Fig. 2. The fractions of the species containing H^+ (δ) present in the organic phase of the system water–HNO_3–Sr^{2+} (microamounts)–15C5–nitrobenzene–H^+B^- as functions of log $c(L)$: $c(HNO_3) = 1.026$ mol/l, $c_B = 0.001$ mol/l. $1\delta(H^+)$, $2\delta(HL^+)$, $3\delta(HL_2^+)$. The solid curves were calculated for the constants log $K_D = -0.66$, log $K_{ex}(HL^+) = 3.61$ and log $K_{ex}(HL_2^+) = 5.00$

complexes HL^+, HL_2^+ and SrL_2^{2+} in the nitrobenzene phase defined as

$$K(HL_{org}^+) = [HL_{org}^+]/[H_{org}^+] [L_{org}] \qquad (12)$$

$$\beta(HL_{2,org}^+) = [HL_{2,org}^+]/[H_{org}^+] [L_{org}]^2 \qquad (13)$$

$$\beta(SrL_{2,org}^{2+}) = [SrL_{2,org}^{2+}]/[Sr_{org}^{2+}] [L_{org}]^2 \qquad (14)$$

can be evaluated on the basis of the simple relations:

$$\log K(HL_{org}^+) = \log K_{ex}(HL_{org}^+) - \log K_D \qquad (15)$$

$$\log \beta(HL_{2,org}^+) = \log K_{ex}(HL_{2,org}^+) - 2 \log K_D \qquad (16)$$

$$\log \beta(SrL_{2,org}^{2+}) = \\ = \log K_{ex}(SrL_{2,org}^{2+}) - \log K_{ex}(Sr_{org}^{2+}) - 2 \log K_D \qquad (17)$$

Finally, the individual extraction constant of the HL^+ cation, denoted $K_i(HL^+)$, in the water–nitrobenzene system and the standard Gibbs energy corresponding to the transfer of that complex cation from the aqueous phase into the nitrobenzene one, $\Delta G_{tr}^0(HL^+)$,[12] were evaluated by using the following equations

$$\log K_i(HL^+) = \\ = \log K_{ex}(HL_{org}^+) - \log K(HL_{aq}^+) + \log K_i(H^+) \qquad (18)$$

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$$\Delta G^0_{tr}(HL^+) = -2.303\ RT \log K_i(HL^+) \qquad (19)$$

where $\log K(HL^+_{aq}) = -0.57^{10}$ and $\log K_i(H^+) = -5.7.^{12}$ The corresponding equilibrium constants are summarized in Table 3.

Table 3. The equilibrium constants on the water–HNO$_3$–Sr^{2+} (microamounts)–15C5–nitrobenzene–H$^+$B$^-$ system

Reaction	$\log K$
$L_{aq} = L_{org}$	-0.66^a
$H^+_{aq} + L_{aq} = HL^+_{aq}$	-0.57^b
$Sr^{2+}_{aq} + L_{aq} = SrL^{2+}_{aq}$	1.95^c
$Sr^{2+}_{aq} + 2H^+_{org} = Sr^{2+}_{org} + 2H^+_{aq}$	0.70^d
$H^+_{org} + L_{aq} = HL^+_{org}$	3.61
$H^+_{org} + 2L_{aq} = HL^+_{2,org}$	5.00
$Sr^{2+}_{aq} + 2L_{aq} + 2H^+_{org} = SrL^{2+}_{2,org} + 2H^+_{aq}$	14.27
$H^+_{org} + L_{org} + HL^+_{org}$	4.27
$H^+_{org} + 2L_{org} = HL^+_{2,org}$	6.32
$Sr^{2+}_{org} + 2L_{org} = SrL^{2+}_{2,org}$	14.89
$\log K_i(HL^+)$	-1.5
$\Delta G^0_{tr}(HL^+)$, kJ/mol	8.6

^{a}Ref.[9]
^{b}Ref.[10]

In conclusion it should be noted that IWACHIDO et al. have proven (on the basis of conductometric measurements) only the SrL$^{2+}_2$ (L = 15C5) complex forming in the organic phase of the water–nitrobenzene extraction system.[9] This fact confirms our results quite unambiguously.

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