Short communication

Solvent Extraction of Strontium into Nitrobenzene by Using a Synergistic Mixture of Hydrogen Dicarbollylcobaltate and Dibenzo-30-crown-10

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Abstract

Extraction of microamounts of strontium by a nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-) in the presence of dibenzo-30-crown-10 (DB30C10, L) has been investigated. The equilibrium data have been explained assuming that the species HL^+, SrL^{2+}, $SrHL^{3+}$ and $SrHL_2^{3+}$ are extracted into the organic phase. The values of extraction and stability constants of the cationic complexes in nitrobenzene saturated with water have been determined.

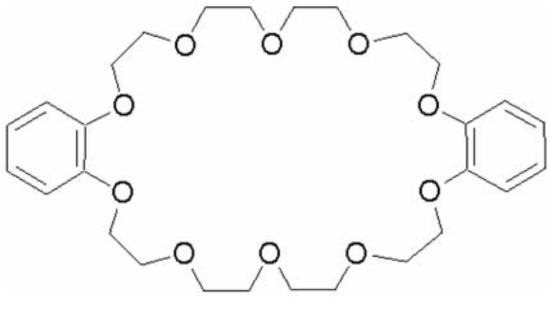
Keywords: Strontium, hydrogen dicarbollylcobaltate, dibenzo-30-crown-10, water-nitrobenzene system, extraction and stability constants, complexation

1. Introduction

In 1967, Pedersen published his first papers[1,2] dealing with cyclic polyether compounds with oxyethylene groups $–CH_2–CH_2–O–$, that are called crowns owing to their structure. These electroneutral crown compounds form relatively stable complexes in nonaqueous solvents, especially with alkali and alkaline-earth metal cations, the cations being placed in the ligand cavities. The ratio of the size of the crown ligand cavity to the ion radius of the central cation is a decisive or at least an important factor in the stability of the complex compounds formed.[3] It is the complexing properties of the crowns that are due to the rapid development of the chemistry of these cyclic polyethers that we have witnessed in the recent decades. At this point it should be noted that several reviews have covered many aspects of their chemistry.[3–6]

The dicarbollylcobaltate anion[7] 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,[8–29] and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.[30,31]

In the current work, the solvent extraction of microamounts of strontium by a nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-)[7] in the presence dibenzo-30-crown-10 (DB30C10, L) (see Scheme 1) was studied. We intended to find the composition of the species in the organic phase and to determine the corresponding equilibrium constants.



Scheme 1. Structural formula of dibenzo-30-crown-10 (abbrev. DB30C10 or L, respectively).

2. Experimental

Dibenzo-30-crown-10 (DB30C10, L) (see Scheme 1) was supplied by Aldrich. Cesium dicarbollylcobaltate, Cs^+B^-, was synthesized by means of the method published by Hawthorne et al.[32] A nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-)[7] was prepared from Cs^+B^- by the procedure described elsewhere.[33] The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclide $^{85}Sr^{2+}$ (DuPont, Belgium) was of standard radiochemical purity.

The extraction experiments in the two–phase water–HCl–Sr^{2+} (microamounts)–nitrobenzene–DB30C10 –H^+B^- system were performed in 10 mL glass test-tubes with polyethylene stoppers, using 2 mL 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 equilibria in the systems under study were established after approximately 20 min of shaking. Then the phases were separated by centrifugation. Afterwards, 1 mL samples were taken from each phase and their γ-activities were measured using a well-type NaI(Tl) scintillation detector connected to a γ-analyzer NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratios of strontium, D_{Sr}, were determined as the ratios of the measured radioactivities of $^{85}Sr^{2+}$ in the nitrobenzene and aqueous samples.

3. Results and Discussion

The dependence of the logarithm of the strontium distribution ratio (log D) on the logarithm of the numerical value of the total (analytical) concentration of the DB30C10 ligand in the initial nitrobenzene phase, log c(L), is given in Fig 1. The initial concentration of hydrogen dicarbollylcobaltate in the organic phase, $c_B = 0.001$ mol/L, as well as the initial concentration of HCl in the aqueous phase, c(HCl) = 0.01 mol/L, are always related to the volume of one phase.

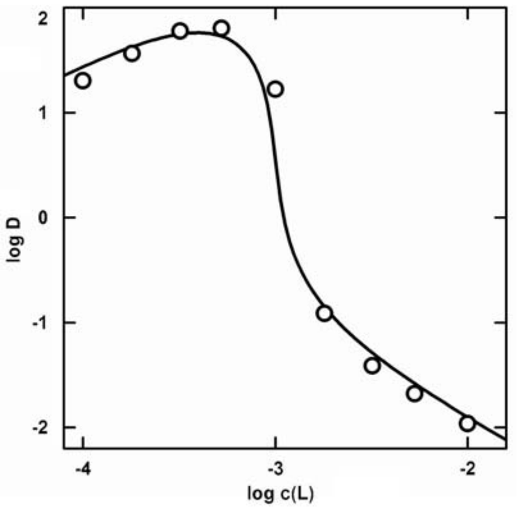


Fig. 1. Log D as a function of log c(L), where L is DB30C10, for the water–HCl–Sr^{2+} (microamounts) – nitrobenzene – DB30C10 – H^+B^- system; c(HCl) = 0.01 mol/L, $c_B = 0.001$ mol/L. The curve was calculated using the constants given in Table 2.

With respect to the results of previous papers,[7,10,29,34–44] the considered water– HCl–Sr^{2+} (microamounts)–nitrobenzene– DB30C10 (L)– H^+B^- system can be described by the set of reactions:

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

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

$$Sr^{2+}_{aq} + 2H^+_{org} \Leftrightarrow Sr^{2+}_{org} + 2H^+_{aq} \tag{3}$$

$$Sr^{2+}_{aq} + (r+2)H^+_{org} + sL_{org} \Leftrightarrow SrH_rL^{(r+2)+}_{s,org} + 2H^+_{aq} \tag{4}$$

to which the following equilibrium constants correspond:

$$K_D = \frac{[L_{org}]}{[L_{aq}]} \tag{5}$$

$$\beta(HL^+_{org}) = \frac{[HL^+_{org}]}{[H^+_{org}][L_{org}]} \tag{6}$$

$$K_{ex}(Sr^{2+}_{org}) = \frac{[Sr^{2+}_{org}][H^+_{aq}]^2}{[Sr^{2+}_{aq}][H^+_{org}]^2} \tag{7}$$

$$K_{ex}(SrH_rL^{(r+2)+}_{s,org}) = \frac{[SrH_rL^{(r+2)+}_{s,org}][H^+_{aq}]^2}{[Sr^{2+}_{aq}][H_{org}]^{(r+2)}[L_{org}]^s} \tag{8}$$

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

A subroutine UBBE, based on the relations given above, the mass balance of the DB30C10 ligand and the electroneutrality conditions in both phases of the system under consideration, was formulated [35,39] and introduced into a more general least-squares minimizing program LETAGROP [45] used for determination of the "best" values of the extraction constants $K_{ex}(SrH_rL^{(r+2)+}_{s,org})$ (L = DB30C10). The minimum of the sum of errors in log D, i.e., the minimum of the expression

$$U = \Sigma(\log D_{calc} - \log D_{exp})^2 \tag{9}$$

was sought.

The values log K_D = 3.8 (see Table 2, footnote *a*), log $\beta(HL^+_{org}) = 6.0$[47] and log $K_{ex}(Sr^{2+}_{org}) = 0.7$[35] 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 species SrL^{2+}, $SrHL^{3+}$ and $SrHL_2^{3+}$ (L = DB30C10) to be extracted into the nitrobenzene phase.

Knowing the value log $K_{ex}(Sr^{2+}_{org}) = 0.7$,[35] as well as the extraction constant log $K_{ex}(SrL^{2+}_{org}) = 9.98$[35] determined

Table 1. Comparison of various models of strontium extraction from aqueous solution of HCl by nitrobenzene solution of H^+B^- in the presence of DB30C10.

Strontium complexes in the organic phase	**log K_{ex}** [a]	**U** [b]
SrL^{2+}	10.22 (10.47)	0.92
SrL_2^{2+}	14.47 (15.36)	39.40
$SrHL^{3+}$	14.99 (15.62)	16.32
$SrHL_2^{3+}$	19.50 (19.88)	2.97
SrL^{2+}, SrL_2^{2+}	Transformed to SrL^{2+}	
SrL^{2+}, $SrHL^{3+}$	10.06 (10.35), 13.32 (13.81)	0.95
SrL^{2+}, $SrHL_2^{3+}$	Transformed to SrL^{2+}	
SrL_2^{2+}, $SrHL^{3+}$	12.44 (12.97), 13.90 (14.39)	3.04
SrL_2^{2+}, $SrHL_2^{3+}$	Transformed to $SrHL_2^{3+}$	
$SrHL^{3+}$, $SrHL_2^{3+}$	13.51 (13.86), 19.06 (19.45)	0.65
SrL^{2+}, SrL_2^{2+}, $SrHL^{3+}$	Transformed to SrL^{2+}, $SrHL^{3+}$	
SrL^{2+}, SrL_2^{2+}, $SrHL_2^{3+}$	Transformed to SrL^{2+}	
SrL^{2+}, $SrHL^{3+}$, $SrHL_2^{3+}$	9.98 (10.21), 13.36 (13.64), 18.27 (18.56)	0.03
SrL^{2+}, SrL_2^{2+}, $SrHL^{3+}$, $SrHL_2^{3+}$	Transformed to SrL^{2+}, $SrHL^{3+}$, $SrHL_2^{3+}$	

[a] The values of the extraction constants are given for each complex. The reliability interval of the constants is given as 3σ(K), where σ(K) is the standard deviation of the constant K.[45] These values are given in the logarithmic scale using the approximate expression log K ± {log [K + 1.5 σ(K)] – log [K – 1.5 σ(K)]}. For σ(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 + 3σ(K)]).[45]

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

here (see Table 1), the stability constant of the complex SrL^{2+} (L = DB30C10) in the nitrobenzene phase defined as

$$\beta(SrL^{2+}_{org}) = \frac{[SrL^{2+}_{org}]}{[Sr^{2+}_{org}][L_{org}]} \qquad (10)$$

can be evaluated applying the following simple relation:

$$\log \beta\,(SrL^{2+}_{org}) = \log K_{ex}(SrL^{2+}_{org}) - \log K_{ex}(Sr^{2+}_{org}) \qquad (11)$$

Similarly, the protonation constant of the cation SrL^{2+}_{org} (L = DB30C10) in nitrobenzene saturated with water, i. e., the equilibrium constant of the following reaction:

$$SrL^{2+}_{org} + H^+_{org} \Leftrightarrow SrHL^{3+}_{org} \qquad (12)$$

defined as

$$K(SrHL^{3+}_{org}) = \frac{[SrHL^{3+}_{org}]}{[SrL^{2+}_{org}][H^+_{org}]} \qquad (13)$$

was calculated on the basis of Relation (14):

$$\log K(SrHL^{3+}_{org}) = \log K_{ex}(SrHL^{3+}_{org}) - \log K_{ex}(SrL^{2+}_{org}) \qquad (14)$$

The respective equilibrium constants are summarized in Table 2.

Moreover, Fig. 2 depicts the contributions of the species Sr^{2+}_{org} (curve 1), SrL^{2+}_{org} (curve 2), $SrHL^{3+}_{org}$ (curve 3) and $SrHL^{3+}_{2,org}$ (curve 4) to the total strontium cation concentration in the equilibrium organic phase. From this figure it follows that the distribution curve 3 is decreasing, whereas the distribution curves 2 and 4 are increasing.

Table 2. Equilibrium constants in the water –HCl– Sr^{2+} (microamounts) – nitrobenzene – DB30C10 – H^+B^- system.

Equilibrium	**log K**
$L_{aq} \Leftrightarrow L_{org}$	3.8 [a]
$H^+_{org} + L_{org} \Leftrightarrow HL^+_{org}$	6.0 [b]
$Sr^{2+}_{aq} + 2H^+_{org} \Leftrightarrow Sr^{2+}_{org} + 2H^+_{aq}$	0.7 [c]
$Sr^{2+}_{aq} + L_{org} + 2H^+_{org} \Leftrightarrow SrL^{2+}_{org} + 2H^+_{aq}$	9.98
$Sr^{2+}_{aq} + L_{org} + 3H^+_{org} \Leftrightarrow SrHL^{3+}_{org} + 2H^+_{aq}$	13.36
$Sr^{2+}_{aq} + 2L_{org} + 3H^+_{org} \Leftrightarrow SrHL^{3+}_{2,org} + 2H^+_{aq}$	18.27
$Sr^{2+}_{org} + L_{org} \Leftrightarrow SrL^{2+}_{org}$	9.28
$SrL^{2+}_{org} + H^+_{org} \Leftrightarrow SrHL^{3+}_{org}$	3.38

[a] Determined by the method of the concentration dependent distribution.[46] [b] Ref. 47. [c] Ref. 35.

Finally, Table 3 summarizes stability constants of the complexes SrL^{2+}_{org} and $SrL^{2+}_{2,org}$ with 18 oxyethylene ligands L, denoted by the symbols diglyme, triglyme, tetraglyme, PEG 200, PEG 300, PEG 400, Slovafol 909, 15C5, B15C5, N15C5, 18C6, B18C6, DB18C6, DCH18C6, DB21C7, DB24C8, DCH24C8 and DB30C10, in nitrobenzene saturated with water. From the data reviewed in this table it follows that in the mentioned nitrobenzene medium, the stability constants of the complexes SrL^{2+}_{org} increase in the series of diglyme < triglyme < tetraglyme < DB18C6 < DB21C7 < DB24C8 < PEG 200 < DB30C10 ≈ B18C6 < DCH24C8 < Slovafol 909 < PEG 300 < PEG 400 < DCH18C6 < 18C6, whereas the

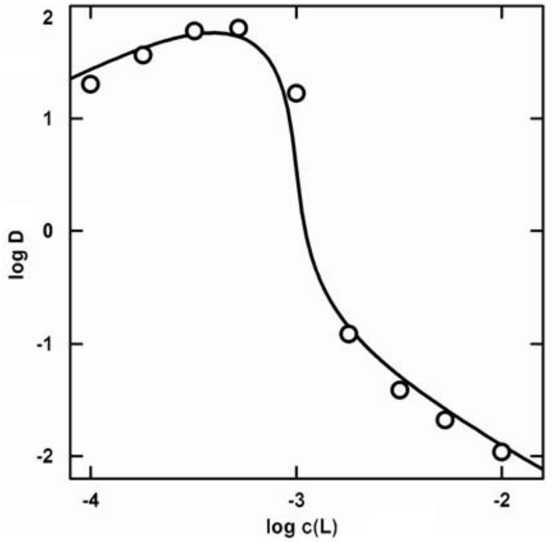


Fig. 2. Distribution diagram of strontium in the equilibrium organic phase of the water– HCl–Sr^{2+} (microamounts) –nitrobenzene–DB30C10 – H^+B^- extraction system in the forms of Sr^{2+}, SrL^{2+}, $SrHL^{3+}$, and $SrHL_2^{3+}$; c(HCl) = 0.01 mol/L, c_B = 0.001 mol/L.
1 $\delta(Sr^{2+}) = [Sr^{2+}_{org}]/c(Sr^{2+})_{org}$,
2 $\delta(SrL^{2+}) = [SrL^{2+}_{org}]/c(Sr^{2+})_{org}$,
3 $\delta(SrHL^{3+}) = [SrHL^{3+}_{org}]/c(Sr^{2+})_{org}$,
4 $\delta(SrHL_2^{3+}) = [SrHL^{3+}_{2,org}]/c(Sr^{2+})_{org}$,
where $c(Sr^{2+})_{org} = [Sr^{2+}_{org}] + [SrL^{2+}_{org}] + [SrHL^{3+}_{org}] + [SrHL^{3+}_{2,org}]$
The distribution curves were calculated using the constants given in Table 2.

Table 3. Stability constants of the complexes SrL^{2+} and SrL_2^{2+}[L = diglyme, triglyme, tetraglyme, PEG 200, PEG 300, PEG 400, Slovafol 909, 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), 2,3-naphtho-15-crown-5 (N15C5), 18-crown-6 (18C6), benzo-18-crown-6 (B18C6), dibenzo-18-crown-6 (DB18C6), dicyclohexano-18-crown-6 (DCH18C6), dibenzo-21-crown-7 (DB21C7), dibenzo-24-crown-8 (DB24C8), dicyclohexano-24-crown-8 (DCH24-C8), dibenzo-30-crown-10 (DB30C10)] in nitrobenzene saturated with water at 25 °C.

L	log $\beta(SrL^{2+}_{org})$	log $\beta(SrL^{2+}_{2,org})$	Ref.
diglyme	3.06	–	34
triglyme	4.34	6.77	34
tetraglyme	4.90	7.52	34
PEG 200	9.06	–	35
PEG 300	10.41	–	35
PEG 400	11.03	–	35
Slovafol 909	10.22	14.52	10
15C5	–	14.89	36
B15C5	–	13.20	37
N15C5	–	11.28	38
18C6	11.50	16.24	39
B18C6	9.29	13.68	40
DB18C6	6.38	8.94	41
DCH18C6	11.19	14.74	42
DB21C7	6.61	10.00	43
DB24C8	8.15	12.77	29
DCH24C8	9.99	14.44	44
DB30C10	9.28	–	This work

stability of the cationic complex species $SrL^{2+}_{2,org}$ increases in the following sequence: triglyme < tetraglyme < DB18C6 < DB21C7 < N15C5 < DB24C8 < B15C5 < B18C6 < DCH24C8 < Slovafol 909 < DCH18C6 < 15C5 < 18C6 .

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Povzetek

Proučevali smo ekstrakcijo mikrokoličin stroncija z raztopino hidrogen dikarbolilkobaltata (H^+B^-) v nitrobenzenu v prisotnosti dibenzo-30-crown-10 (DB30C10, L). Ob predpostavki, da so v ravnotežju v organski fazi prisotni kompleksi HL^+, SrL^{2+}, $SrHL^{3+}$ in $SrHL_2^{3+}$ smo določili konstante ekstrakcije in konstante stabilnosti navedenih komplekosv.