Short communication

Extraction of Strontium Into Nitrobenzene in the Presence of *p*-nonylphenylnonaethylene Glycol

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Abstract

The extraction of microamounts of strontium by a nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-) in the presence of Slovafol 909 (*p*-nonylphenylnonaethylene glycol, L) as a synergic agent has been investigated. The equilibrium data have been explained assuming that the complexes HL^+, HL_2^+, SrL^{2+} and SrL_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.

Keywords: Strontium, nitrobenzene, hydrogen dicarbollylcobaltate, *p*-nonylphenylnonaethylene glycol, extraction and stability constants

1. Introduction

The observation that macrocyclic polyethers form stable complexes with alkali and alkaline earth metal cations has stimulated a great deal of interest in these compounds for their possible applications in various branches of chemistry and biology.[1,2] Extensive thermodynamic data[3,4] suggest that the stability of macrocyclic complexes depends on the relative cation and ligand cavity size, the number and arrangements of the ligand bonding sites, the substitution on the macrocyclic ring and the solvent effects.

The dicarbollylcobaltate anion and some of its halogen derivatives are very useful reagents for the extraction of alkali metal cations (especially Cs^+), and also – in the presence of polyoxyethylene compounds – for the extraction of Sr^{2+} and Ba^{2+} from aqueous solutions into an organic polar phase, both under laboratory conditions for purely theoretical or analytical purposes,[5–7] and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.[8–10]

The aim of the present communication was to study the solvent extraction of microamounts of strontium using a nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-) in the presence of Slovafol 909 (*p*-nonylphenylnonaethylene glycol, L) as a synergic agent. We intended to find the composition of the species present in the nitrobenzene phase and to determine the corresponding equilibrium constants.

2. Experimental

p-Nonylphenylnonaethylene glycol (Slovafol 909) was supplied by Chemical Works, Nováky, Slovakia. Cesium dicarbollylcobaltate, Cs^+B^-, was synthesized in the Institute of Inorganic Chemistry, Řež, Czech Republic, using the method published by Hawthorne et al.[11] The nitrobenzene solution of hydrogen dicarbollylcobaltate (H^+B^-) was prepared from Cs^+B^- by the procedure described in Reference 12. 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 in the two-phase water-HNO_3–Sr^{2+} (microamounts) –Slovafol 909-nitrobenzene-H^+B^- system were performed in 10 mL glass test-tubes covered with polyethylene stoppers, using 2 mL of each phase. The test-tubes filled with the solutions were shaken for 2 h at a temperature of 25 ± 2 °C, using a laboratory shaker. Under these conditions, equilibrium in the system under study has been established already after approximately 20 min of shaking. Then the phases were separated by centrifugation (2 min, 2500 rpm). 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 single-channel γ-analyzer NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratio of strontium, D, was determined as the ratio of the measured radioactivities of ^{85}Sr in the nitrobenzene and aqueous samples.

3. Results and Discussion

The dependences of the logarithm of the strontium distribution ratios (log D) on the logarithm of the numerical value of the total (analytical) concentration of the ligand Slovafol 909 in the initial aqueous phase, log c(L), were measured for two initial concentrations of hydrogen dicarbollylcobaltate in the nitrobenzene phase (c_B = 0.001 and 0.002 mol L^{-1}) and two initial concentrations of nitric acid in the aqueous phase ($c(HNO_3)$ = 0.05 and 0.10 mol L^{-1}) in the presence of Slovafol 909 ($c(L) = 3.2 \times 10^{-5}$ – 5.6×10^{-5} mol L^{-1}). The mentioned initial concentrations c_B, $c(HNO_3)$ and c(L) are always related to the volume of one phase. The results are given in Figure 1.

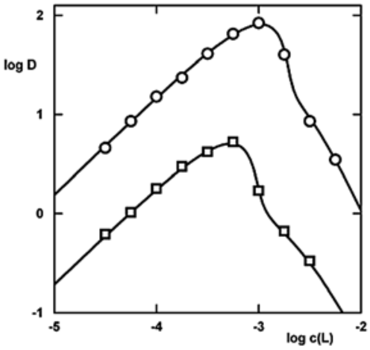

Figure 1. Log D as a function of log c(L), where L = Slovafol 909, for the water-HNO_3–Sr^{2+} (microamounts) –Slovafol 909-nitrobenzene-H^+B^- extraction system. ○$c(HNO_3)$ = 0.05 mol L^{-1}, c_B = 0.002 mol L^{-1}; □ $c(HNO_3)$ = 0.10 mol L^{-1}, c_B = 0.001 mol L^{-1}. The curves were calculated using the constants given in Table 2.

With regard to the results of previous papers,[13–20] the considered water-HNO_3–Sr^{2+} (microamounts)-Slovafol 909-nitrobenzene-H^+B^- extraction system can be described by the set of reactions

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

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

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

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

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

to which the following equilibrium constants correspond:

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

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

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

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

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

The subscripts aq and org denote the aqueous and organic phases, respectively. In this context, it is necessary to emphasize that the formation of the strontium complexes with Slovafol 909, as well as the formation of HL^+ and HL_2^+ (L = Slovafol 909) in the aqueous phase of the system under consideration could be neglected as a consequence of the very low values of the stability constants of the mentioned complex species with linear polyethers in water.[14,16,17]

A subroutine UBBE, based on the relations given above, the mass balance of the Slovafol 909 ligand and the electroneutrality conditions in both phases, was formulated[14,18] and introduced into a more general least-squares minimizing program LETAGROP[21] used for determination of the "best" values of the constants $K_{ew}(SrL^{2+}_{n,org})$. 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.

Table 1. Comparison of three different models of strontium extraction from aqueous solutions of nitric acid by nitrobenzene solutions of H^+B^- in the presence of Slovafol 909.

Strontium complexes in the organic phase	**logK_{ex}** [a]	***U*** [b]
SrL^{2+}	11.23 (11.52)	6.09
SrL_2^{2+}	16.39 (16.65)	24.10
SrL^{2+}, SrL_2^{2+}	10.92 ± 0.02, 15.22 ± 0.03	0.01

[a] The values of the extraction constants are given for each complex. The reliability interval of the constants is given as 3 σ(K), where σ(K) is the standard deviation of the constant K.[21] These values are given in the logarithmic scale using the approximate expression logK ± {log[K + 1.5σ(K)] – log[K – 1.5σ(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 logK(log[K + 3σ(K)]).[21]
[b] The error-square sum $U = \Sigma(\log D_{calc} - \log D_{exp}$.

The values $\log K_D = 1.38$,[13] $\log \beta(HL^{+}_{org}) = 5.64$,[13] $\log \beta(HL^{+}_{2,org}) = 8.27$,[13] and $\log K_{ex}(Sr^{2+}_{org}) = 0.7$ (from References 14 and 15) 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 complex species SrL^{2+} and SrL^{2+}_{2} to be extracted into the nitrobenzene phase.

Figure 2 presents the contributions of the species H^{+}_{org}, HL^{+}_{org} and $HL^{+}_{2,org}$ to the total hydrogen concentration in the equilibrium nitrobenzene phase while Figure 3 shows the contributions of the particles Sr^{2+}_{org}, SrL^{2+}_{org} and $SrL^{2+}_{2,or}$ to the total strontium concentration in the equilibrium organic phase. From both of these figures it follows that the complexes $HL^{+}_{2,org}$ and $SrL^{2+}_{2,org}$ are present in significant concentrations only at relatively high amounts of the Slovafol 909 ligand in the system under consideration.

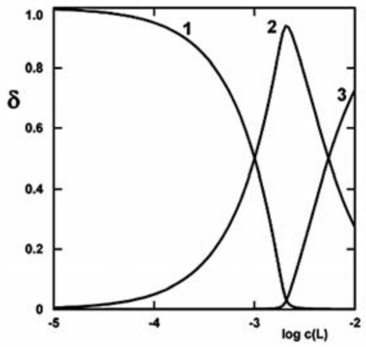

Figure 2. Distribution diagram of hydrogen in the equilibrium nitrobenzene phase of the water–HNO_3–Sr^{2+} (microamounts)–Slovafol 909–nitrobenzene–H^+B^- extraction system in the forms of H^+, HL^+ and HL^{+}_{2}. $c(HNO_3) = 0.05$ mol L^{-1}, $c_B = 0.002$ mol L^{-1}. 1 $\delta(H^+) = [H^{+}_{org}]/c(H^+)_{org}$, 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.

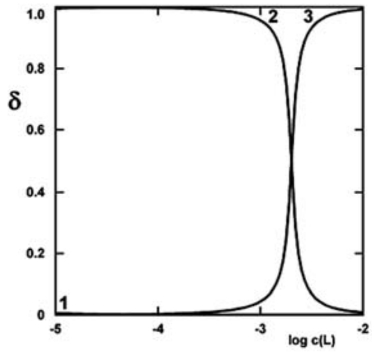

Figure 3. Distribution diagram of strontium in the equilibrium nitrobenzene phase of the water–HNO_3 – Sr^{2+}) (microamounts)–Slovafol 909–nitrobenzene–H^+B^- -extraction system in the forms of Sr^{2+}, SrL^{2+} and SrL^{2+}_{2} . $c(HNO_3) = 0.05$ mol L^{-1}, $c_B = 0.002$ mol L^{-1}. 1 $\delta(Sr^{2+}) = [Sr^{2+}_{org}]/c(Sr^{2+})_{org}$, 2 $\delta(SrL^{2+}) = [SrL^{2+}_{org}]/c(Sr^{2+})_{org}$, 3 $\delta(SrL^{2+}_{2}) = [SrL^{2+}_{2,org}]/c(Sr^{2+})_{org}$, where $c(Sr^{2+})_{org} = [SrL^{2+}_{org}] + (SrL^{2+}_{org}) + [SrL^{2+}_{2,org}]$. The distribution curves were calculated using the constants given in Table 2.

Knowing the value $\log K_{ex}(Sr^{2+}_{org}) = 0.7$ (inferred from References 14 and 15) as well as the extraction constants $\log K_{ex}(SrL^{2+}_{org}) = 12.92$ and $\log K_{ex}(SrL^{2+}_{2,org}) = 15.22$ determined here (Table 1), the stability constants of the complexes Sr^{2+}_{org} and $SrL^{2+}_{2,org}$ in the nitrobenzene phase defined as

$$\beta(SrL^{2+}_{org}) = \frac{[SrL^{2+}_{org}]}{[Sr^{2+}_{org}][L_{org}]}, \tag{12}$$

$$\beta(SrL^{2+}_{2,org}) = \frac{[SrL^{2+}_{2,org}]}{[Sr^{2+}_{org}][L_{org}]^2}, \tag{13}$$

can be evaluated applying the simple relations:

$$\log \beta(SrL^{2+}_{org}) = \log K_{ex}(SrL^{2+}_{org}) - \log K_{ex}(Sr^{2+}_{org}), \tag{14}$$

$$\log \beta(SrL^{2+}_{2,org}) = \log K_{ex}(SrL^{2+}_{2,org}) - \log K_{ex}(Sr^{2+}_{org}). \tag{15}$$

The respective equilibrium constants are summarized in Table 2.

Table 2. Equilibrium constants in the water–HNO_3–Sr^{2+} (microamounts)–Slovafol 909–nitrobenzene–H^+B^- extraction system.

Equilibrium	**log *K***
$L_{aq} \Leftrightarrow L_{org}$	1.38 [a]
$Sr^{2+}_{aq} + 2H^{+}_{org} \Leftrightarrow Sr^{2+}_{org} + 2H^{+}_{aq}$	0.7 [b]
$Sr^{2+}_{aq} + L_{org} + 2H^{+}_{org} \Leftrightarrow SrL^{2+}_{org} + 2H^{+}_{aq}$	10.92
$Sr^{2+}_{aq} + 2L_{org} + 2H^{+}_{org} \Leftrightarrow SrL^{2+}_{2,org} + 2H^{+}_{aq}$	15.22
$H^{+}_{org} + L_{org} \Leftrightarrow HL^{+}_{org}$	5.64 [a]
$H^{+}_{org} + 2L_{org} \Leftrightarrow HL^{+}_{2,org}$	8.27 [a]
$Sr^{2+}_{org} + L_{org} \Leftrightarrow SrL^{2+}_{org}$	10.22
$Sr^{2+}_{org} + 2L_{org} \Leftrightarrow SrL^{2+}_{2,org}$	14.52

[a] Ref. 13.
[b] From Refs 14 and 15.

In conclusion, it should be noted that in the system water–$HClO_4$–Sr^{2+} (microamounts)–PEG 300–nitrobenzene–hydrogen dicarbollylcobaltate, the stability constant of the complex SrL^{2+} (L = PEG 300) in water saturated nitrobenzene was evaluated as $\log \beta(SrL^{2+}_{org}) = 10.4$.[17] It means that the stability constants of the species SrL^{2+} (L = PEG 300) and the analogous complex SrL^{2+} (L = Slovafol 909) in the mentioned medium are comparable since $\log \beta(SrL^{2+}_{org}) = 10.22$, where L = Slovafol 909 (see Table 2).

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5. References

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Povzetek

Raziskovali smo mikroekstrakcijo stroncija z raztopino vodikovega dikarbolilkobaltata (H^+B^-) v nitrobenzen ob prisotnosti Slovafol 909 (*p*-nonilfenilnonaetilen glikol, L) kot sinergijskega agensa. Dobljena ravnotežja smo opisali s pomočjo predpostavke, da se v organsko fazo ekstrahirajo kompleksi HL^+, HL_2^+, SrL^{2+} and SrL_2^{2+} Določili smo konstante stabilnosti speciesov v nasičeni vodni raztopini nitrobenzena.