

Extraction Distribution of Microamounts of Strontium in the Two-Phase Water—HCl—Nitrobenzene—Benzo-15-crown-5—Hydrogen Dicarbolylcobaltate System

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Extraction of microamounts of strontium with a nitrobenzene solution of hydrogen dicarbolylcobaltate in the presence of benzo-15-crown-5 (L) has been investigated. The equilibrium data have been explained assuming that the complexes HL^+ , $HL\frac{1}{2}$, and $SrL\frac{2}{2}^+$ are extracted into the organic phase. The values of extraction and stability constants of the species in nitrobenzene saturated with water have been determined.

The dicarbolylcobaltate 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 [1–3] and on the technological scale for the separation of some high-activity isotopes in the reprocessing of irradiated nuclear fuel [4–6].

In the present communication, the solvent extraction of microamounts of strontium using a nitrobenzene solution of hydrogen dicarbolylcobaltate (H^+B^-) in the presence of benzo-15-crown-5 (L) was studied. We intended to find the composition of the species present in the nitrobenzene phase and to determine the corresponding equilibrium constants.

EXPERIMENTAL

Benzo-15-crown-5 (B15C5) was supplied by Ventron, Karlsruhe, Germany. Cesium dicarbolylcobaltate, Cs^+B^- , was synthesized in the Institute of Inorganic Chemistry, Řež, Czech Republic, using the method published by Hawthorne *et al.* [7]. The nitrobenzene solution of hydrogen dicarbolylcobaltate (H^+B^-) was prepared from Cs^+B^- by the procedure described in Ref. [8]. 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—HCl— Sr^{2+} (microamounts)—nitrobenzene— H^+B^-

—B15C5 system 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 ± 1) °C using a laboratory shaker (under these conditions, an equilibrium in the system under study has established after approximately 30 min of shaking). Then the phases were separated by centrifugation (5 min, 2 500 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 to a single-channel γ -analyzer Strahlungsmessgerät 20 026 (RFT, Dresden, Germany).

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

RESULTS AND DISCUSSION

The dependence of the logarithm of the strontium distribution ratio ($\log D$) on the logarithm of the numerical value of total (analytical) concentration of the ligand B15C5 in the initial nitrobenzene phase, $\log \{c(L)\}$, is given in Fig. 1. The initial concentration of HCl in the aqueous phase, $c(HCl) = 0.10$ mol dm⁻³, and the initial concentration of hydrogen dicarbolylcobaltate in the organic phase, $c_B = 0.003$ mol dm⁻³, are related to the volume of one phase.

With regard to the results of previous papers [9–11], the considered water—HCl— Sr^{2+} (microamounts)—nitrobenzene— H^+B^- —B15C5 extraction system can be described by the set of reactions

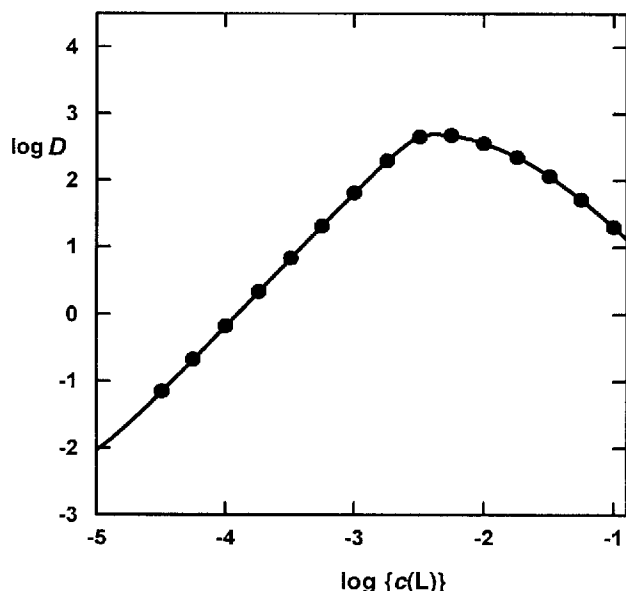


Fig. 1. Log D as a function of $\log\{c(L)\}$ for the system water—HCl— Sr^{2+} (microamounts)—nitrobenzene— H^+B^- —B15C5. $c(\text{HCl}) = 0.10 \text{ mol dm}^{-3}$, $c_{\text{B}} = 0.003 \text{ mol dm}^{-3}$. The curve was calculated using the constants given in Table 2.

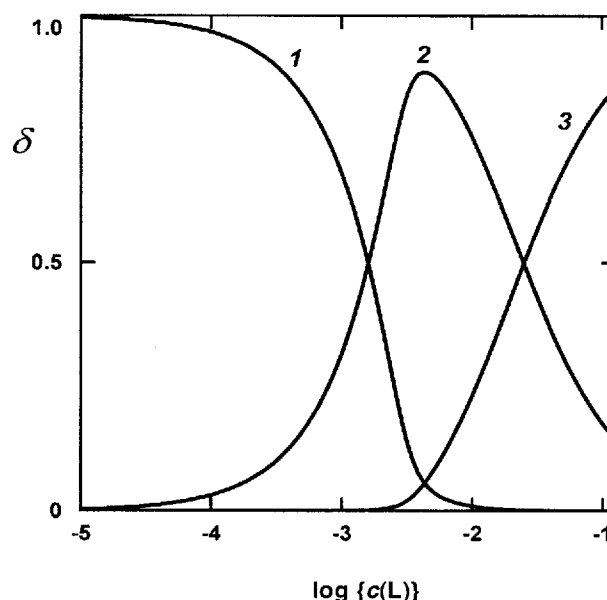
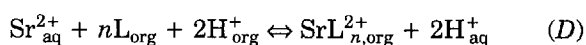
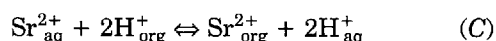
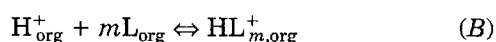


Fig. 2. Distribution diagram of hydrogen in the equilibrium nitrobenzene phase of the system water—HCl— Sr^{2+} (microamounts)—nitrobenzene— H^+B^- —B15C5 in the forms of H^+ , HL^+ , and HL_2^+ . $c(\text{HCl}) = 0.10 \text{ mol dm}^{-3}$, $c_{\text{B}} = 0.003 \text{ mol dm}^{-3}$.

1. $\delta(\text{H}^+) = [\text{H}_{\text{org}}^+]/c(\text{H}^+)_{\text{org}}$, 2. $\delta(\text{HL}^+) = [\text{HL}_{\text{org}}^+]/c(\text{H}^+)_{\text{org}}$, 3. $\delta(\text{HL}_2^+) = [\text{HL}_{2,\text{org}}^+]/c(\text{H}^+)_{\text{org}}$, where $c(\text{H}^+)_{\text{org}} = [\text{H}_{\text{org}}^+] + [\text{HL}_{\text{org}}^+] + [\text{HL}_{2,\text{org}}^+]$. The distribution curves were calculated using the constants given in Table 2.



to which the following equilibrium constants

$$K_{\text{D}} = \frac{[\text{L}_{\text{org}}]}{[\text{L}_{\text{aq}}]} \quad (1)$$

$$\beta(\text{HL}_{m,\text{org}}^+) = \frac{[\text{HL}_{m,\text{org}}^+]}{[\text{H}_{\text{org}}^+][\text{L}_{\text{org}}]^m} \quad (2)$$

$$K_{\text{ex}}(\text{Sr}_{\text{org}}^{2+}) = \frac{[\text{Sr}_{\text{org}}^{2+}][\text{H}_{\text{aq}}^+]^2}{[\text{Sr}_{\text{aq}}^{2+}][\text{H}_{\text{org}}^+]^2} \quad (3)$$

$$K_{\text{ex}}(\text{SrL}_{n,\text{org}}^{2+}) = \frac{[\text{SrL}_{n,\text{org}}^{2+}][\text{H}_{\text{aq}}^+]^2}{[\text{Sr}_{\text{aq}}^{2+}][\text{L}_{\text{org}}]^n[\text{H}_{\text{org}}^+]^2} \quad (4)$$

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 formulat-

Table 1. Comparison of Various Models of Strontium Extraction from the Aqueous Solution of HCl Using the Nitrobenzene Solution of H^+B^- in the Presence of Benzo-15-crown-5

Hydrogen and strontium complexes in the organic phase	$\log\{\beta\}$, $\log\{K_{\text{ex}}\}^a$	U^b
HL^+ , SrL^{2+}	1.82 (2.28), 7.56 (7.97)	5.05
HL^+ , SrL_2^{2+}	6.40 (7.45), 18.34 (19.63)	3.09
HL_2^+ , SrL^{2+}	3.13 (3.56), 7.44 (7.78)	4.04
HL_2^+ , SrL_2^{2+}	4.46 ± 0.15 , 10.93 ± 0.16	0.27
HL^+ , HL_2^+ , SrL^{2+}	transforms to HL_2^+ , SrL^{2+}	
HL^+ , HL_2^+ , SrL_2^{2+}	4.25 ± 0.16 , 5.97 ± 0.15 , $14.34 (14.57)$	0.01
HL^+ , HL_2^+ , SrL^{2+} , SrL_2^{2+}	transforms to HL^+ , HL_2^+ , SrL_2^{2+}	

^a) The values of the extraction constants are given for each complex. The reliability interval is given – in agreement with Ref. [13] – as $3\sigma(K)$, where $\sigma(K)$ is the standard deviation of the constant K . These values are expressed in the logarithmic scale using the approximate relation $\log\{K\} \pm (\log\{[K + 1.5\sigma(K)]\} - \log\{[K - 1.5\sigma(K)]\})$. For $\sigma(K) > 0.2K$, the previous relation is not valid and then only the upper limit is given in the parentheses in the form $\log\{K\}(\log\{[K + 3\sigma(K)]\})$ [13].

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

Table 2. Equilibrium Constants in the Water—HCl—Sr²⁺ (Micro-amounts)—Nitrobenzene—H⁺B⁻—B15C5 Extraction System

Equilibrium	log{K}
$L_{\text{aq}} \rightleftharpoons L_{\text{org}}$	1.60 ^a
$H_{\text{org}}^+ + L_{\text{org}} \rightleftharpoons HL_{\text{org}}^+$	4.25
$H_{\text{org}}^+ + 2L_{\text{org}} \rightleftharpoons HL_{2,\text{org}}^+$	5.97
$Sr_{\text{aq}}^{2+} + 2H_{\text{org}}^+ \rightleftharpoons Sr_{\text{org}}^{2+} + 2H_{\text{aq}}^+$	0.70 ^b
$Sr_{\text{aq}}^{2+} + 2L_{\text{org}} + 2H_{\text{org}}^+ \rightleftharpoons SrL_{2,\text{org}}^{2+} + 2H_{\text{aq}}^+$	14.34
$Sr_{\text{org}}^{2+} + 2L_{\text{org}} \rightleftharpoons SrL_{2,\text{org}}^{2+}$	13.64

a) Ref. [9], b) Ref. [10].

ed [10, 12] and introduced into a more general least-squares minimizing program LETAGROP [13] used for determination of the “best” values of the constants $\beta(HL_{m,\text{org}}^+)$ and $K_{\text{ex}}(SrL_{n,\text{org}}^{2+})$. The minimum of the sum of errors in log D , i.e. the minimum of the expression

$$U = \Sigma(\log D_{\text{calc}} - \log D_{\text{exp}})^2 \quad (5)$$

was sought.

The values $\log K_D = 1.60$ [9] and $\log K_{\text{ex}}(Sr_{\text{org}}^{2+})$ [10] were used for the respective calculations. The results are listed in Table 1, from which it is evident that the extraction data can be best explained assuming the complex species HL^+ , $HL_{2,\text{org}}^+$, and $SrL_{2,\text{org}}^{2+}$ to be extracted into the nitrobenzene phase.

Fig. 2 presents the contributions of the species H_{org}^+ , HL_{org}^+ , and $HL_{2,\text{org}}^+$ to the total hydrogen concentration in the equilibrium nitrobenzene phase. From this figure it follows that “sandwich” type complex $HL_{2,\text{org}}^+$ is present in significant concentrations only at relatively high amounts of the B15C5 ligand in the system under study.

Knowing the value $\log K_{\text{ex}}(Sr_{\text{org}}^{2+}) = 0.70$ [10] as well as the extraction constant $\log\{K_{\text{ex}}(SrL_{2,\text{org}}^{2+})\} = 14.34$ determined here (see Table 1), the stability constant of the complex $SrL_{2,\text{org}}^{2+}$ in the nitrobenzene phase defined as

$$\beta(SrL_{2,\text{org}}^{2+}) = \frac{[SrL_{2,\text{org}}^{2+}]}{[Sr_{\text{org}}^{2+}][L_{\text{org}}]^2} \quad (6)$$

can be evaluated applying the simple relation

$$\log\{\beta(SrL_{2,\text{org}}^{2+})\} = \log\{K_{\text{ex}}(SrL_{2,\text{org}}^{2+})\} - \log K_{\text{ex}}(Sr_{\text{org}}^{2+}) \quad (7)$$

The respective equilibrium constants are summarized in Table 2.

In conclusion, it should be noted that somewhat higher stability of the species $SrL_{2,\text{org}}^{2+}$, where $L = 15$ -crown-5, in nitrobenzene saturated with water ($\log\{\beta(SrL_{2,\text{org}}^{2+})\} = 14.89$) [11] in comparison with the stability of the analogous complex of Sr^{2+} with B15C5 in this medium determined here for the first time ($\log\{\beta(SrL_{2,\text{org}}^{2+})\} = 13.64$ – see Table 2) can be probably explained on the basis of the higher flexibility of the 15-crown-5 ligand than in the case of the more rigid structure of B15C5 [14].

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