Extraction Distribution of Microamounts of Strontium in the Two-Phase Water—NH$_4$Cl—15-Crown-5—Nitrobenzene—Ammonium Dicarbollylcobaltate System

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Extraction of microamounts of strontium with a nitrobenzene solution of ammonium dicarbollyl-cobaltate in the presence of 15-crown-5 (L) has been investigated. The equilibrium data have been explained assuming that the complexes NH_4L^+, $NH_4L_2^+$, 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.

In our previous works [1—4], we have studied the extraction distributions of H$^+$, Na$^+$, Cs$^+$, Sr^{2+}, and Ba^{2+} in the system water—15-crown-5 (L)—nitrobenzene using very hydrophobic dicarbollylcobaltate anion. The mentioned univalent cations (M$^+$ = H$^+$, Na$^+$, Cs$^+$) have been found to be extracted into the organic (org) phase in the forms of the ML_{org}^+ and $ML_{2,org}^+$ complexes [1—4], while the bivalent ions (M^{2+} = Sr^{2+}, Ba^{2+}) are present in the equilibrium nitrobenzene phase exclusively in the form of the complex species $ML_{2,org}^{2+}$ [1, 2].

The aim of the present communication is to study the extraction of microamounts of strontium with a nitrobenzene solution of ammonium dicarbollylcobaltate (NH$_4^+$B$^-$) in the presence of 15-crown-5 (L). We intended to find the composition of species present in the organic phase and to determine the respective equilibrium constants.

EXPERIMENTAL

15-Crown-5 (Ventron, Karlsruhe, Germany) was used without additional purification. Cesium dicarbollylcobaltate, Cs$^+$B$^-$, was synthesized in the Institute of Inorganic Chemistry, Řež, Czech Republic, using the method published by *Hawthorne et al.* [5]. The nitrobenzene solution of ammonium dicarbollylcobaltate $\left(NH_4^+B^-\right)$ was prepared from Cs$^+$B$^-$ by the procedure described in Ref. [6]. 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—NH$_4$Cl—Sr^{2+} (microamounts)—L—nitrobenzene—NH$_4^+$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 h at (25 ± 2) °C using a laboratory shaker. Under these conditions, an equilibrium in the system under study has established after approximately 30 min shaking. Then the phases were separated by centrifugation (5 min, 2500 min^{-1}). After centrifugation, 1 cm^3 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 a ratio of the measured radioactivities of ^{85}Sr in the nitrobenzene and aqueous samples.
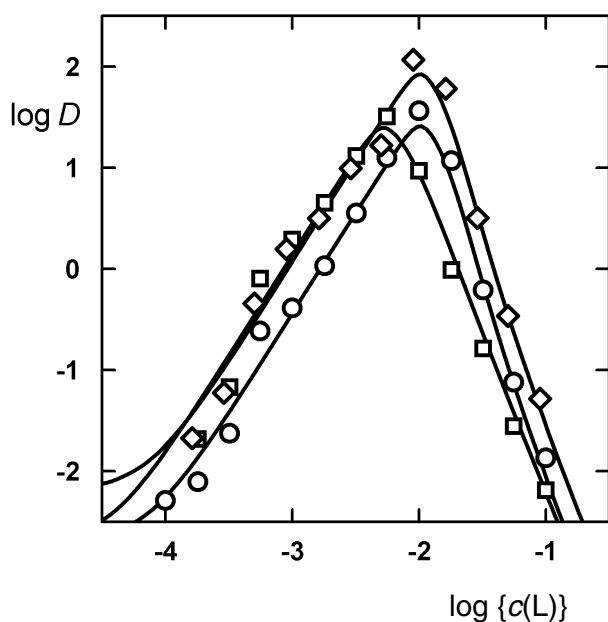
RESULTS AND DISCUSSION

The dependences of the logarithm of the strontium distribution ratios (log D) on the logarithm of the numerical value of total (analytical) concentration of the ligand 15-crown-5 in the initial aqueous phase, log$\{c(L)\}$, were measured for two concentrations of ammonium dicarbollylcobaltate in the nitrobenzene

Table 1. Log D as a Function of $\log\{c(\text{L})\}$ for Strontium Extraction from the Aqueous Solutions of Ammonium Chloride with the Nitrobenzene Solutions of NH_4^+B^-

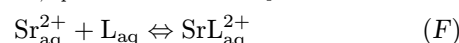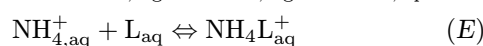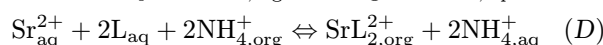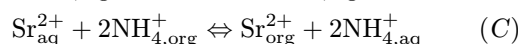| $c(\text{NH}_4\text{Cl}) = 0.0450$ mol dm^{-3} $c_\text{B} = 0.010$ mol dm^{-3}		$c(\text{NH}_4\text{Cl}) = 0.0225$ mol dm^{-3}			
		$c_\text{B} = 0.005$ mol dm^{-3}		$c_\text{B} = 0.010$ mol dm^{-3}	
$\log\{c(\text{L})\}$	$\log D$	$\log\{c(\text{L})\}$	$\log D$	$\log\{c(\text{L})\}$	$\log D$
−4.000	−2.289	−3.745	−1.684	−3.790	−1.671
−3.745	−2.104	−3.495	−1.170	−3.541	−1.222
−3.495	−1.624	−3.252	−0.098	−3.298	−0.338
−3.252	−0.613	−3.000	0.289	−3.046	0.196
−3.000	−0.384	−2.745	0.651	−2.790	0.502
−2.745	0.032	−2.495	1.114	−2.541	0.994
−2.495	0.550	−2.252	1.506	−2.298	1.223
−2.252	1.100	−2.000	0.970	−2.046	2.067
−2.000	1.563	−1.745	−0.011	−1.790	1.781
−1.745	1.070	−1.495	−0.786	−1.541	0.505
−1.495	−0.208	−1.252	−1.553	−1.298	−0.464
−1.252	−1.119	−1.000	−2.188	−1.046	−1.279
−1.000	−1.869				

Fig. 1. Log D as a function of $\log\{c(\text{L})\}$ for the water—NH$_4$Cl—Sr^{2+} (microamounts)—L—nitrobenzene—NH$_4^+$B$^-$ system. ○ $c(\text{NH}_4\text{Cl}) = 0.0450$ mol dm^{-3}, $c_\text{B} = 0.010$ mol dm^{-3}; □ $c(\text{NH}_4\text{Cl}) = 0.0225$ mol dm^{-3}, $c_\text{B} = 0.005$ mol dm^{-3}; ◇ $c(\text{NH}_4\text{Cl}) = 0.0225$ mol dm^{-3}, $c_\text{B} = 0.010$ mol dm^{-3}. The curves were calculated using the constants given in Table 3.

phase ($c_\text{B} = 0.005$ mol dm^{-3} and 0.010 mol dm^{-3}) and two initial concentrations of ammonium chloride in the aqueous phase ($c(\text{NH}_4\text{Cl}) = 0.0225$ mol dm^{-3} and 0.0450 mol dm^{-3}) in the presence of 15-crown-5 ($c(\text{L}) = 0.0001$—0.10 mol dm^{-3}). The mentioned initial concentrations c_B, $c(\text{NH}_4\text{Cl})$, and $c(\text{L})$ are always related to the volume of one phase. The results are given in Table 1 and Fig. 1.

With regard to the results of previous papers [1—4, 7—10], the considered water—NH$_4$Cl—Sr^{2+} (microamounts)—L—nitrobenzene—NH$_4^+$B$^-$ system can be described by the set of reactions

$$\text{L}_\text{aq} \Leftrightarrow \text{L}_\text{org} \qquad (A)$$

$$\text{NH}_{4,\text{org}}^+ + n\text{L}_\text{aq} \Leftrightarrow \text{NH}_4\text{L}_{n,\text{org}}^+ \qquad (B)$$

$$\text{Sr}_\text{aq}^{2+} + 2\text{NH}_{4,\text{org}}^+ \Leftrightarrow \text{Sr}_\text{org}^{2+} + 2\text{NH}_{4,\text{aq}}^+ \qquad (C)$$

$$\text{Sr}_\text{aq}^{2+} + 2\text{L}_\text{aq} + 2\text{NH}_{4,\text{org}}^+ \Leftrightarrow \text{SrL}_{2,\text{org}}^{2+} + 2\text{NH}_{4,\text{aq}}^+ \qquad (D)$$

$$\text{NH}_{4,\text{aq}}^+ + \text{L}_\text{aq} \Leftrightarrow \text{NH}_4\text{L}_\text{aq}^+ \qquad (E)$$

$$\text{Sr}_\text{aq}^{2+} + \text{L}_\text{aq} \Leftrightarrow \text{SrL}_\text{aq}^{2+} \qquad (F)$$

to which the following equilibrium constants

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

$$K_\text{ex}(\text{NH}_4\text{L}_{n,\text{org}}^+) = \frac{[\text{NH}_4\text{L}_{n,\text{org}}^+]}{[\text{NH}_{4,\text{org}}^+][\text{L}_\text{aq}]^n} \qquad (2)$$

$$K_\text{ex}(\text{Sr}_\text{org}^{2+}) = \frac{[\text{Sr}_\text{org}^{2+}][\text{NH}_{4,\text{aq}}^+]^2}{[\text{Sr}_\text{aq}^{2+}][\text{NH}_{4,\text{org}}^+]^2} \qquad (3)$$

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

$$\beta(\text{NH}_4\text{L}_\text{aq}^+) = \frac{[\text{NH}_4\text{L}_\text{aq}^+]}{[\text{NH}_{4,\text{aq}}^+][\text{L}_\text{aq}]} \qquad (5)$$

$$\beta(\text{SrL}_\text{aq}^{2+}) = \frac{[\text{SrL}_\text{aq}^{2+}]}{[\text{Sr}_\text{aq}^{2+}][\text{L}_\text{aq}]} \qquad (6)$$

correspond; subscripts aq and org denote the aqueous and organic phases, respectively.

Table 2. Comparison of Three Different Models of Strontium Extraction from the Aqueous Solutions of Ammonium Chloride with the Nitrobenzene Solutions of $NH_4^+B^-$ in the Presence of 15-Crown-5

Ammonium complexes in the organic phase	$\log\{K_{ex}\}^a$	U^b
NH_4L^+	5.16 (5.43)	61.70
$NH_4L_2^+$	8.67 (9.01)	70.69
NH_4L^+, $NH_4L_2^+$	4.68 ± 0.06, 7.88 ± 0.10	1.31

a) The values of the extraction constants are given for each complex. The reliability interval of the constants is given – in agreement with Ref. [12] – 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 $\log\{K\} \pm (\log\{[K + 1.5\sigma(K)]\} - \log\{[K - 1.5\sigma(K)]\})$ [12]. 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 of $\log\{K\}$ $(\log\{[K + 3\sigma(K)]\})$ [12].
b) The error-square sum $U = \sum (\log D_{calc} - \log D_{exp})^2$.

A subroutine UBBE, based on the relations given above, mass balance of the crown ligand, and the electroneutrality conditions in both phases, was formulated [8, 11] and introduced into a more general least-squares minimizing program LETAGROP [12] used for determination of the "best" values of the constants $K_{ex}(NH_4L_{n,org}^+)$. The minimum of the sum of errors in $\log D$, *i.e.* the minimum of the expression

$$U = \sum (\log D_{calc} - \log D_{exp})^2 \qquad (7)$$

was sought.

The values $K_D = 0.22$ [7], $\log K_{ex}(Sr_{org}^{2+}) = -1.3$ (inferred from Refs. [8] and [9]), $\log\{K_{ex}(SrL_{2,org}^{2+})\} = 12.27$ (inferred from Refs. [1] and [9]), $\log\{\beta(NH_4L_{aq}^+)\} = 1.71$ [10], and $\log\{\beta(SrL_{aq}^{2+})\} = 1.95$ [10] were used for the respective calculations. The results are listed in Table 2, from which it is evident that the extraction data can be explained assuming the ammonium complex species NH_4L^+ and $NH_4L_2^+$ to be extracted into the nitrobenzene phase.

Fig. 2 presents the contributions of the species $NH_{4,org}^+$, $NH_4L_{org}^+$, and $NH_4L_{2,org}^+$ to the total ammonium concentration in the equilibrium nitrobenzene phase. From this figure it follows that the "sandwich"-type complex $NH_4L_{2,org}^+$ is present in significant concentrations only at relatively high amounts of the 15-crown-5 ligand in the system under study.

Knowing the value $K_D = 0.22$ [7] as well as the extraction constants $\log\{K_{ex}(NH_4L_{org}^+)\} = 4.68$ and $\log\{K_{ex}(NH_4L_{2,org}^+)\} = 7.88$ determined here (see Table 2), the stability constants of the complexes $NH_4L_{org}^+$ and $NH_4L_{2,org}^+$ in the nitrobenzene phase defined as

$$\beta(NH_4L_{org}^+) = \frac{[NH_4L_{org}^+]}{[NH_{4,org}^+][L_{org}]} \qquad (8)$$

$$\beta(NH_4L_{2,org}^+) = \frac{[NH_4L_{2,org}^+]}{[NH_{4,org}^+][L_{org}]^2} \qquad (9)$$

can be evaluated applying the simple relations
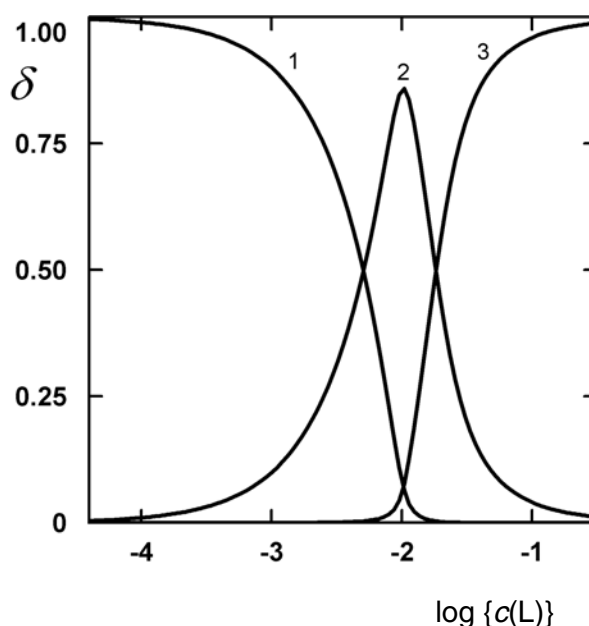
Fig. 2. Distribution diagram of ammonium in the equilibrium nitrobenzene phase of the system water—NH_4Cl—Sr^{2+} (microamounts)—L—nitrobenzene—$NH_4^+B^-$ in the forms of NH_4^+, NH_4L^+, and $NH_4L_2^+$. $c(NH_4Cl) = 0.0225$ mol dm^{-3}, $c_B = 0.010$ mol dm^{-3}. $1 - \delta(NH_4^+) = [NH_{4,org}^+]/c(NH_4^+)_{org}$, $2 - \delta(NH_4L^+) = [NH_4L_{org}^+]/c(NH_4^+)_{org}$, $3 - \delta(NH_4L_2^+) = [NH_4L_{2,org}^+]/c(NH_4^+)_{org}$, where $c(NH_4^+)_{org} = [NH_{4,org}^+] + [NH_4L_{org}^+] + [NH_4L_{2,org}^+]$. The distribution curves were calculated using the constants given in Table 3.

$$\log\{\beta(NH_4L_{org}^+)\} = \log\{K_{ex}(NH_4L_{org}^+)\} - \\ - \log K_D \qquad (10)$$

$$\log\{\beta(NH_4L_{2,org}^+)\} = \log\{K_{ex}(NH_4L_{2,org}^+)\} - \\ - 2\log K_D \qquad (11)$$

Furthermore, the individual extraction constant of the cation NH_4L^+ in the water—nitrobenzene system, denoted $K_i(NH_4L^+)$, corresponding to the following

Table 3. Equilibrium Constants for the Water—NH_4Cl—Sr^{2+} (Microamounts)—15-Crown-5—Nitrobenzene— $NH_4^+B^-$ System

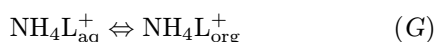| Equilibrium	$\log\{K\}$
$L_{aq} \Leftrightarrow L_{org}$	-0.66^a
$NH_{4,aq}^+ + L_{aq} \Leftrightarrow NH_4L_{aq}^+$	1.71^b
$Sr_{aq}^{2+} + L_{aq} \Leftrightarrow SrL_{aq}^{2+}$	1.95^b
$NH_{4,org}^+ + L_{aq} \Leftrightarrow NH_4L_{org}^+$	4.68
$NH_{4,org}^+ + 2L_{aq} \Leftrightarrow NH_4L_{2,org}^+$	7.88
$Sr_{aq}^{2+} + 2NH_{4,org}^+ \Leftrightarrow Sr_{org}^{2+} + 2NH_{4,aq}^+$	-1.3^c
$Sr_{aq}^{2+} + 2L_{aq} + 2NH_{4,org}^+ \Leftrightarrow SrL_{2,org}^{2+} + 2NH_{4,aq}^+$	12.27^d
$NH_{4,org}^+ + L_{org} \Leftrightarrow NH_4L_{org}^+$	5.34
$NH_{4,org}^+ + 2L_{org} \Leftrightarrow NH_4L_{2,org}^+$	9.20
$Sr_{org}^{2+} + 2L_{org} \Leftrightarrow SrL_{2,org}^{2+}$	14.89^e
$NH_4L_{aq}^+ \Leftrightarrow NH_4L_{org}^+$	-1.7

a) Ref. [7], *b*) Ref. [10], *c*) inferred from Refs. [8] and [9], *d*) inferred from Refs. [1] and [9], *e*) Ref. [1].

Table 4. Stability Constants of the Complexes ML^+ and ML_2^+ in Nitrobenzene Saturated with Water at $25\,°C$

M^+	H^+	Na^+	Cs^+	NH_4^+
$\log\{\beta(ML_{org}^+)\}$	4.27^a (4.21^b)	7.33^c	4.24^d	5.34
$\log\{\beta(ML_{2,org}^+)\}$	6.32^a (6.23^b)	8.63^c	6.72^d	9.20

a) Ref. [1], *b*) Ref. [2], *c*) Ref. [3], *d*) Ref. [4].

equilibrium
$$NH_4L_{aq}^+ \Leftrightarrow NH_4L_{org}^+ \quad\quad (G)$$

was calculated employing the relationship

$$\log K_i(NH_4L^+) = \log\{K_{ex}(NH_4L_{org}^+)\} - \quad\quad (12)$$
$$- \log\{\beta(NH_4L_{aq}^+)\} + \log K_i(NH_4^+)$$

where $\log\{\beta(NH_4L_{aq}^+)\} = 1.71$ [10] and $\log K_i(NH_4^+) = -4.7$ [9]. The respective equilibrium constants are summarized in Table 3.

On the basis of the data given in Table 4, the following interesting stability constant comparisons can be written

$$\log\{\beta(HL_{org}^+)\} \approx \log\{\beta(CsL_{org}^+)\}$$
$$\log\{\beta(HL_{2,org}^+)\} \approx \log\{\beta(CsL_{2,org}^+)\}$$
$$\log\{\beta(NaL_{2,org}^+)\} \approx \log\{\beta(NH_4L_{2,org}^+)\}$$
$$\log\{\beta(NaL_{org}^+)\} > \log\{\beta(NH_4L_{org}^+)\}$$

On the other hand, it is noteworthy that in aqueous solutions, the complex NH_4L^+ is somewhat more stable than the analogous species NaL^+ including the same ligand L since $\log\{\beta(NH_4L_{aq}^+)\} = 1.71$ [10] and $\log\{\beta(NaL_{aq}^+)\} = 0.70$ [10].

The selectivity shown by certain cyclic polyethers toward cations is well documented and constitutes one of the interesting features which distinguish them from most noncyclic ligands [13—15]. The demonstration of cation selectivity by these compounds has resulted in much interest in them for possible use in many areas where this property is important, *e.g.* sensing elements in cation selective electrodes, study of biological transport mechanisms, solubilization of salts in solvents of low polarity making possible new organic reactions with increased yields, and development of carrier-membrane systems [13—15].

In conclusion, it should be noted that further experimental research on cation complexation selectivity and ligating ability of various crown ligands toward metal cations in the nitrobenzene medium is in progress.

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