

SHORT COMMUNICATION

Extraction of calcium from water into nitrobenzene using strontium dicarbollylcobaltate in the presence of 18-crown-6

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From extraction experiments and γ -activity measurements, the extraction constant corresponding to the equilibrium $\text{Ca}^{2+}(\text{aq}) + \text{SrL}^{2+}(\text{nb}) \rightleftharpoons \text{CaL}^{2+}(\text{nb}) + \text{Sr}^{2+}(\text{aq})$ taking place in the two-phase water–nitrobenzene system (L = 18-crown-6, aq = aqueous phase, nb = nitrobenzene phase) was evaluated as $\log K_{\text{ex}}(\text{Ca}^{2+}, \text{SrL}^{2+}) = -1.9 \pm 0.1$. Furthermore, the stability constant of the calcium – 18-crown-6 complex in nitrobenzene saturated with water was calculated for the temperature of 25 °C: $\log \beta_{\text{nb}}(\text{CaL}^{2+}) = 10.1 \pm 0.1$.

Keywords: water-nitrobenzene system, calcium, 18-crown-6, stability constant.

The observation that macrocyclic polyethers form stable complexes with alkali and alkaline earth metal cations has stimulated a great deal of interest in these crown 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 special arrangements of the ligand bonding sites, the substitution on the macrocyclic ring and solvent effects.

The cyclic polyether 18-crown-6 has six oxygen atoms in the polyether ring, which are the bond sites of this ionophore.^{1,5}

The aim of the present communication was to determine the stability constant of the complex sites CaL^{2+} , where L is 18-crown-6, in water saturated nitrobenzene.

EXPERIMENTAL

18-crown-6 was supplied by Merck, Darmstadt, Germany. Caesium dicarbollylcobaltate (CsDCC) was synthesized in the Institute of Inorganic Chemistry, Rež, Czech Republic. The radionuclide ⁸⁵Sr (DuPont, Belgium) was of standard radiochemical purity. Nitrobenzene and all other chemicals (analytical grade, Lachema, Brno, Czech Republic) were used without further purification. In order to obtain a solution of HDCC in nitrobenzene, a solution of CsDCC in this medium (0.2 M)

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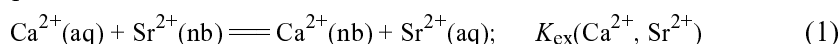
was twice equilibrated with equal volumes of 15 % (v/v) *n*-propanol in diluted H_2SO_4 of a concentration of about 1 M. The H_2SO_4 and *n*-propanol were removed from the organic phase by a ten-fold equilibration with a solution of H_2SO_4 in distilled water (about 1 M) of an equal volume, followed by two equilibrations with distilled water. The concentration of HDCC in the nitrobenzene solution was determined by neutralization titration (NaOH, bromocresol green) after a ten-fold dilution with ethanol or acetone. Equilibration of the nitrobenzene solution of HDCC with the stoichiometric amount of $\text{Sr}(\text{OH})_2$, which was dissolved in an aqueous solution of $\text{Sr}(\text{NO}_3)_2$ (0.2 M), yields the corresponding solution of $\text{Sr}(\text{DCC})_2$ in nitrobenzene.

The extraction experiment were carried out in 10 ml glass test tubes fitted with polyethylene stoppers: 2 ml of an aqueous solution of $\text{Ca}(\text{NO}_3)_2$ in the concentration range from 1×10^{-4} to 1×10^{-3} M and microamounts of ^{85}Sr were added to 2 ml of the nitrobenzene solution of 18-crown-6 and $\text{Sr}(\text{DCC})_2$, the initial concentration of which varied from 1×10^{-4} to 1×10^{-3} M (in all experiments, the initial concentration of 18-crown-6 in nitrobenzene, $c_{\text{L}}^{\text{in,nb}}$, was always equal to the initial concentration of $\text{Sr}(\text{DCC})_2$ in this medium, $c_{\text{Sr}(\text{DCC})_2}^{\text{in,nb}}$). The test tubes filled with the solutions 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 was already established after approximately 20 min 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 analyzer RFT Strahlungsmessgerät 20026 (RFT, Dresden, Germany).

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

RESULTS AND DISCUSSION

According to the results of previous papers,^{6,7} the two-phase water – $\text{Ca}(\text{NO}_3)_2$ – nitrobenzene – $\text{Sr}(\text{DCC})_2$ extraction system can be described by the following equilibrium



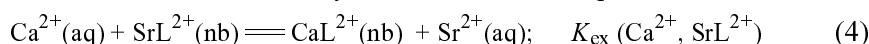
with the corresponding exchange extraction constant $K_{\text{ex}}(\text{Ca}^{2+}, \text{Sr}^{2+})$; aq and nb denote the presence of the particles in the aqueous and nitrobenzene phases, respectively. The constant $K_{\text{ex}}(\text{Ca}^{2+}, \text{Sr}^{2+})$ can be written as⁶

$$\log K_{\text{ex}}(\text{Ca}^{2+}, \text{Sr}^{2+}) = \log K_{\text{Ca}^{2+}}^{\text{i}} - \log K_{\text{Sr}^{2+}}^{\text{i}} \quad (2)$$

where $K_{\text{Ca}^{2+}}^{\text{i}}$ and $K_{\text{Sr}^{2+}}^{\text{i}}$ are the individual extraction constants for Ca^{2+} and Sr^{2+} , respectively, in the water–nitrobenzene system.⁶ Knowing $\log K_{\text{Ca}^{2+}}^{\text{i}} = -11.2$,⁸ and $\log K_{\text{Sr}^{2+}}^{\text{i}} = -10.7$, which was inferred from previous results,^{6,9} the exchange extraction constant $K_{\text{ex}}(\text{Ca}^{2+}, \text{Sr}^{2+})$ was simply calculated from Eq. (2):

$$\log K_{\text{ex}}(\text{Ca}^{2+}, \text{Sr}^{2+}) = -0.5 \quad (3)$$

In terms of previous papers,^{7,10} the two-phase water – $\text{Ca}(\text{NO}_3)_2$ – nitrobenzene L (L = 18-crown-6) – $\text{Sr}(\text{DCC})_2$ extraction system (see Experimental Section), chosen for the determination of the stability of the complex CaL^{2+} in water saturated nitrobenzene, can be characterized by the main chemical equilibrium



to which the equilibrium extraction constant

$$K_{\text{ex}}(\text{Ca}^{2+}, \text{SrL}^{2+}) = \frac{[\text{CaL}^{2+}]_{\text{nb}} [\text{Sr}^{2+}]_{\text{aq}}}{[\text{Ca}^{2+}]_{\text{aq}} [\text{SrL}^{2+}]_{\text{nb}}} \quad (5)$$

corresponds; aq and nb refer to the aqueous and nitrobenzene phases, respectively. The 18-crown-6 ligand forms very stable complexes CaL^{2+} and SrL^{2+} with Ca^{2+} and Sr^{2+} in the nitrobenzene phase.¹⁰

Taking into account the conditions of electroneutrality of the organic and aqueous phases

$$[\text{SrL}^{2+}]_{\text{nb}} + [\text{CaL}^{2+}]_{\text{nb}} = c_{\text{Sr}(\text{DCC})_2}^{\text{in, nb}} \quad (6)$$

$$[\text{Sr}^{2+}]_{\text{aq}} + [\text{Ca}^{2+}]_{\text{aq}} = c_{\text{Ca}(\text{NO}_3)_2}^{\text{in, aq}} \quad (7)$$

the mass balances of calcium and strontium for equal volumes of the nitrobenzene and aqueous phases

$$[\text{Ca}^{2+}]_{\text{aq}} + [\text{CaL}^{2+}]_{\text{nb}} = c_{\text{Ca}(\text{NO}_3)_2}^{\text{in, aq}} \quad (8)$$

$$[\text{Sr}^{2+}]_{\text{aq}} + [\text{SrL}^{2+}]_{\text{nb}} = c_{\text{Sr}(\text{DCC})_2}^{\text{in, nb}} \quad (9)$$

and the measured equilibrium distribution ratio of strontium

$$D_{\text{Sr}} = \frac{[\text{SrL}^{2+}]_{\text{nb}}}{[\text{Sr}^{2+}]_{\text{aq}}} \quad (10)$$

the combination of previous relationships (5) – (10) gives the final expression for the extraction constant $K_{\text{ex}}(\text{Ca}^{2+}, \text{SrL}^{2+})$:

$$K_{\text{ex}}(\text{Ca}^{2+}, \text{SrL}^{2+}) = \frac{1}{D_{\text{Sr}} (1 + D_{\text{Sr}})} \frac{c_{\text{Sr}(\text{DCC})_2}^{\text{in, nb}}}{c_{\text{Ca}(\text{NO}_3)_2}^{\text{in, aq}} - c_{\text{Sr}(\text{DCC})_2}^{\text{in, nb}}} \quad (11)$$

Using Eq. (11), the extraction experiments and subsequent γ -activity measurements (see Table I) result in determination of the following value of the extraction constant $\log K_{\text{ex}}(\text{Ca}^{2+}, \text{SrL}^{2+})$:

$$\log K_{\text{ex}}(\text{Ca}^{2+}, \text{SrL}^{2+}) = -1.9 \pm 0.1 \quad (12)$$

Furthermore, with respect to previous result,^{11,12} for the extraction constant $K_{\text{ex}}(\text{Ca}^{2+}, \text{Sr}^{2+})$ and $K_{\text{ex}}(\text{Ca}^{2+}, \text{SrL}^{2+})$ defined above, and for the stability constants of the complexes CaL^{2+} and SrL^{2+} in nitrobenzene saturated with water, denoted by $\beta_{\text{nb}}(\text{CaL}^{2+})$ and $\beta_{\text{nb}}(\text{SrL}^{2+})$, respectively, one obtains

$$\log \beta_{\text{nb}}(\text{CaL}^{2+}) = \log \beta_{\text{nb}}(\text{SrL}^{2+}) + \log K_{\text{ex}}(\text{Ca}^{2+}, \text{SrL}^{2+}) - \log K_{\text{ex}}(\text{Ca}^{2+}, \text{Sr}^{2+}) \quad (13)$$

TABLE I. Extraction experiments concerning the determination of $\log K_{\text{ex}}(\text{Ca}^{2+}, \text{SrL}^{2+})$ on the basis of Eq. (11)

$c_{\text{Ca}(\text{NO}_3)_2}^{\text{in, aq}} / \text{M}$	$c_{\text{Sr}(\text{DCC})_2}^{\text{in, nb}} / \text{M}$	D_{Sr}	$\log K_{\text{ex}}(\text{Ca}^{2+}, \text{SrL}^{2+})$
1×10^{-4}	1×10^{-4}	10.1	-2.0
3×10^{-4}	3×10^{-4}	6.3	-1.6
5×10^{-4}	5×10^{-4}	8.9	-1.9
7.5×10^{-4}	7.5×10^{-4}	11.1	-2.1
1×10^{-3}	1×10^{-3}	7.9	-1.8

Using the constants $\log K_{\text{ex}}(\text{Ca}^{2+}, \text{Sr}^{2+})$ and $\log K_{\text{ex}}(\text{Ca}^{2+}, \text{SrL}^{2+})$ given above, the value $\log \beta_{\text{nb}}(\text{SrL}^{2+}) = 11.5$ ($L = 18\text{-crown-6}$)¹⁰ and applying Eq. (13), the stability constant of the calcium – 18-crown-6 complex in nitrobenzene saturated with water at 25 °C is obtained:

$$\log \beta_{\text{nb}}(\text{CaL}^{2+}) = 10.1 \pm 0.1 \quad (14)$$

The stability constants of the complexes of Ca^{2+} , Sr^{2+} and Ba^{2+} with 18-crown-6 in water and nitrobenzene saturated with water together with the hydration numbers of the species M^{2+} and ML^{2+} ($\text{M}^{2+} = \text{Ca}^{2+}$, Sr^{2+} and Ba^{2+} ; $L = 18\text{-crown-6}$) in water saturated nitrobenzene are summarized with the corresponding references in Table II. The $\beta_{\text{aq}}(\text{ML}^{2+})$ and $\beta_{\text{nb}}(\text{ML}^{2+})$ values indicate that the stability of the complex cation ML^{2+} in both solvents increases in the series $\text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$, *i.e.*, in the order of increasing crystallographic radii of the alkaline earth cations. The solvent molecules always complete with the ligand bonding sites for the central cation, so the main reason for the $\beta_{\text{nb}}(\text{ML}^{2+})$ values in nitrobenzene saturated with water being several orders of magnitude higher than the corresponding $\beta_{\text{aq}}(\text{ML}^{2+})$ values may be due to the substantially higher basicity and solvating power of water as compared with nitrobenzene.

TABLE II. Logarithms of the stability constants of the complexes ML^{2+} ($\text{M}^{2+} = \text{Ca}^{2+}$, Sr^{2+} , Ba^{2+} ; $L = 18\text{-crown-6}$) in water, $\log \beta_{\text{aq}}(\text{ML}^{2+})$, and in nitrobenzene saturated with water, $\log \beta_{\text{nb}}(\text{ML}^{2+})$, and the hydration numbers of the species M^{2+} ($h_{\text{M}^{2+}}$) and ML^{2+} ($h_{\text{ML}^{2+}}$) in water saturated nitrobenzene

M^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
$\log \beta_{\text{aq}}(\text{ML}^{2+})$	0.48 ^a	2.72 ^b	3.87 ^b
$\log \beta_{\text{nb}}(\text{ML}^{2+})$	10.1 ^c	11.5 ^d	12.5 ^d
$h_{\text{M}^{2+}}$ ^c	13.0	12.1	10.5
$h_{\text{ML}^{2+}}$ ^c	4.7	4.6	3.4

^a Ref. 13; ^b Ref. 14; ^c This work; ^d Ref. 10; ^e Ref 15.

Škarda *et al.*¹⁶ and Iwachido *et al.*¹⁵ proved that alkali metal and alkaline earth cations in the equilibrium nitrobenzene phase of the water – nitrobenzene system are present in the hydrated state. This is also true for the complex species composed of alkali metal or alkaline earth cations and the electroneutral ionophores of the crown or cryptand type, and even of the crown or cryptand ligands themselves.^{15,17}

The average number of water molecules bonded to a species i in the nitrobenzene phase is expressed quantitatively by the hydration number h_i (Table II). For the complex species composed of alkali metal or alkali earth cations and crown-type ligands, the hydration numbers in the nitrobenzene phase are considerably lower than for the alkali metal or alkali earth cations themselves^{15–17} (Table II only includes data for the particular case of 18-crown-6 and Ca^{2+} , Sr^{2+} and Ba^{2+}). This indicates that the mentioned cyclic polyethers (similar to cryptand-type ligands) displace a fraction of the coextracted water from the hydration shells of the alkali metal or alkaline earth cations.

ИЗВОД

ЭКСТРАКЦИЈА КАЛЦИЈУМА ИЗ ВОДЕ НИТРОБЕНЗЕНОМ КОРИШЋЕЊЕМ СТРОНЦИЈУМА ДИКАРБОЛИЛКОБАЛТАТА У ПРИСУСТВУ 18-КРУНА-6

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На осанову екстракционих експеримената и мерења γ -активности изведена је константа екстракције као $\log K_{\text{ex}}(\text{Ca}^{2+}, \text{SrL}^{2+}) = 1,9 \pm 0,1$ за равнотежу $\text{Ca}^{2+}(\text{aq}) + \text{SrL}(\text{nb}) \rightleftharpoons \text{CaL}^{2+}(\text{nb}) + \text{Sr}^{2+}(\text{aq})$ у двофазном систему вода–нитробензен, где су: L = 18-круна-6, аq = водена фаза и nb = нитробензен. Затим, израчуната је константа стабилности за калцијум–18-круна-6 комплекс у нитробензену засићеним водом на 25 °C као: $\log \beta_{\text{nb}}(\text{CaL}^{2+}) = 10,1 \pm 0,1$.

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