

SHORT COMMUNICATION

Stability of the barium–benzo-15-crown-5 complex in nitrobenzene saturated with water

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Abstract: From extraction experiments and γ -activity measurements, the exchange extraction constant corresponding to the equilibrium $\text{Ba}^{2+}(\text{aq}) + \text{SrL}_2^{2+}(\text{nb}) \rightleftharpoons \text{BaL}_2^{2+}(\text{nb}) + \text{Sr}^{2+}(\text{aq})$ occurring in the two-phase water–nitrobenzene system (L = benzo-15-crown-5; aq = aqueous phase, nb = nitrobenzene phase) was evaluated as $\log K_{\text{ex}}(\text{Ba}^{2+}, \text{SrL}_2^{2+}) = 0.3 \pm 0.1$. Furthermore, the stability constant of the benzo-15-crown-5–barium complex in nitrobenzene saturated with water was calculated for the temperature of 25 °C: $\log \beta_{\text{nb}}(\text{BaL}_2^{2+}) = 13.3 \pm 0.1$.

Keywords: barium, benzo-15-crown-5, stability constant, nitrobenzene.

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 crown compounds because of their possible application 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 size of the cation and cavity, the number and arrangement of the ligand bonding sites, the substitution on the macrocyclic ring and solvent effects.

The cyclic polyether benzo-15-crown-5 has five oxygen atoms in the polyether ring, which are the bonding places of this ionophore.^{1,5}

The aim of the present communication was to determine the stability constant of the complex species BaL_2^{2+} , where L = benzo-15-crown-5, in water saturated nitrobenzene.

EXPERIMENTAL

Benzo-15-crown-5 was supplied by Fluka, Buchs, Switzerland. Cesium 3,3'-*commo*-bis(undecahydro-1,2-dicarba-3-cobalta-*closo*-dodecabor)ate, $\text{Cs}^+ \{[\pi-(3)-1,2-\text{B}_9\text{C}_2\text{H}_{11}]_2 \text{Co(III)}\}^-$ (also called cesium dicarbollylcobaltate, abbrev. CsDCC), was synthesized in the Institute of Inorganic

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Chemistry, Řež, Czech Republic, using the method published by Hawthorne *et al.*⁶ 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 hydrogen dicarbollylcobaltate in nitrobenzene, a solution of CsDCC in this medium (0.20 mol/l) was twice equilibrated with an equal volume of 15 % (v/v) *n*-propanol in dilute H₂SO₄ (about 1 mol/l H₂SO₄). The *n*-propanol was removed from the organic phase by a ten-fold equilibration with an equal volume of a solution of H₂SO₄ in distilled water (about 1 mol/l), 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 a stoichiometric amount of Sr(OH)₂, which was dissolved in an aqueous solution of Sr(NO₃)₂ (0.2 mol/l), yields the corresponding solution of Sr(DCC)₂ in nitrobenzene.

The extraction experiments were carried out in 10 ml glass test-tubes covered with polyethylene stoppers: 2 ml of an aqueous solution of Ba(NO₃)₂ having a concentration in the range from 2 × 10⁻⁴ to 2 × 10⁻³ mol/l and microamounts of ⁸⁵Sr were added to 2 ml of the nitrobenzene solution of benzo-15-crown-5 and Sr(DCC)₂, the initial concentrations of which varied from 1 × 10⁻⁴ to 1 × 10⁻³ mol/l (in all experiments, the initial concentration of benzo-15-crown-5 in nitrobenzene, *c*^{in,nb}_L, was always two times higher than that of Sr(DCC)₂ in nitrobenzene, *i.e.* *c*^{in,nb}_L = 2 *c*^{in,nb}_{Sr(DCC)₂}). 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, the equilibrium in the system under study was established after approximately 15 min of shaking. Then the phases were separated by centrifugation. Subsequently, 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 RFT Strahlungsmessgerät 20 026 (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,⁷⁻¹¹ the two-phase water–Ba(NO₃)₂–nitrobenzene–Sr(DCC)₂ extraction system can be described by the following equilibrium



with the corresponding exchange extraction constant *K*_{ex} (Ba²⁺, Sr²⁺), since Ba(DCC)₂ and Sr(DCC)₂ are fully dissociated in the nitrobenzene phase,⁹ aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively. The constant *K*_{ex} (Ba²⁺, Sr²⁺) is given by:⁷

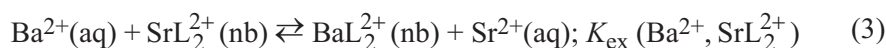
$$\log K_{\text{ex}}(\text{Ba}^{2+}, \text{Sr}^{2+}) = \log K_{\text{Ba}^{2+}}^{\text{i}} - \log K_{\text{Sr}^{2+}}^{\text{i}} \quad (2)$$

where *K*_{Ba²⁺}ⁱ and *K*_{Sr²⁺}ⁱ are the individual extraction constants for Ba²⁺ and Sr²⁺, respectively, in the water–nitrobenzene system.⁷ Knowing log *K*_{Ba²⁺}ⁱ = -10.5¹⁰ and log *K*_{Sr²⁺}ⁱ = -10.7, which was inferred from previous results,^{7,11} the exchange extraction constant *K*_{ex} (Ba²⁺, Sr²⁺) was simply calculated from Eq. (2):

$$\log K_{\text{ex}}(\text{Ba}^{2+}, \text{Sr}^{2+}) = 0.2$$

According to previous papers,^{8,12} the two-phase water–Ba(NO₃)₂–nitrobenzene–L (L = benzo-15-crown-5)–Sr(DCC)₂ extraction system (see Experimental

section), chosen for the determination of the stability of the complex BaL_2^{2+} in water saturated nitrobenzene, can be characterized by the main chemical equilibrium



for which the equilibrium extraction constant

$$K_{\text{ex}}(\text{Ba}^{2+}, \text{SrL}_2^{2+}) = \frac{[\text{BaL}_2^{2+}]_{\text{nb}} [\text{Sr}^{2+}]_{\text{aq}}}{[\text{Ba}^{2+}]_{\text{aq}} [\text{SrL}_2^{2+}]_{\text{nb}}} \quad (4)$$

corresponds; aq and nb refer to the aqueous and nitrobenzene phases, respectively. It is necessary to emphasize that the benzo-15-crown-5 ligand forms the very stable complexes BaL_2^{2+} and SrL_2^{2+} with Ba^{2+} and Sr^{2+} in the nitrobenzene phase.¹²

In accordance with the conditions of electroneutrality in the organic and aqueous phases

$$[\text{BaL}_2^{2+}]_{\text{nb}} + [\text{SrL}_2^{2+}]_{\text{nb}} = c_{\text{Sr}(\text{DCC})_2}^{\text{in,nb}} \quad (5)$$

$$[\text{Ba}^{2+}]_{\text{aq}} + [\text{Sr}^{2+}]_{\text{aq}} = c_{\text{Ba}(\text{NO}_3)_2}^{\text{in,aq}} \quad (6)$$

the mass balances of barium and strontium at equal volumes of the nitrobenzene and aqueous phases

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

$$[\text{Sr}^{2+}]_{\text{aq}} + [\text{SrL}_2^{2+}]_{\text{nb}} = c_{\text{Sr}(\text{DCC})_2}^{\text{in,nb}} \quad (8)$$

and the measured equilibrium distribution ratio of strontium

$$D_{\text{Sr}} = \frac{[\text{SrL}_2^{2+}]_{\text{nb}}}{[\text{Sr}^{2+}]_{\text{aq}}} \quad (9)$$

On substitution of relationships (5) – (9) into Equation (4) and rearranging, the final expression for the extraction constant $K_{\text{ex}}(\text{Ba}^{2+}, \text{SrL}_2^{2+})$ is given by:

$$K_{\text{ex}}(\text{Ba}^{2+}, \text{SrL}_2^{2+}) = \frac{1}{D_{\text{Sr}} (1 + D_{\text{Sr}})} \frac{c_{\text{Sr}(\text{DCC})_2}^{\text{in,nb}}}{c_{\text{Ba}(\text{NO}_3)_2}^{\text{in,aq}} + c_{\text{Sr}(\text{DCC})_2}^{\text{in,nb}}} \quad (10)$$

In this study, from the extraction experiments and the γ -activity measurements (see Experimental section), using relation (10), the following value of the constant $\log K_{\text{ex}}(\text{Ba}^{2+}, \text{SrL}_2^{2+})$ was evaluated:

$$\log K_{\text{ex}}(\text{Ba}^{2+}, \text{SrL}_2^{2+}) = 0.3 \pm 0.1$$

Furthermore, with respect to previous results,¹³ for the extraction constants $K_{\text{ex}}(\text{Ba}^{2+}, \text{Sr}^{2+})$ and $K_{\text{ex}}(\text{Ba}^{2+}, \text{SrL}_2^{2+})$ defined above, as well as for the stability constants of the complexes BaL_2^{2+} and SrL_2^{2+} in nitrobenzene saturated with water, denoted by $\beta_{\text{nb}}(\text{BaL}_2^{2+})$ and $\beta_{\text{nb}}(\text{SrL}_2^{2+})$, respectively, the following expression is obtained:

$$\log \beta_{\text{nb}}(\text{BaL}_2^{2+}) = \log \beta_{\text{nb}}(\text{SrL}_2^{2+}) + \log K_{\text{ex}}(\text{Ba}^{2+}, \text{SrL}_2^{2+}) - \log K_{\text{ex}}(\text{Ba}^{2+}, \text{Sr}^{2+}) \quad (11)$$

Using the constants $\log K_{\text{ex}}(\text{Ba}^{2+}, \text{Sr}^{2+})$ and $\log K_{\text{ex}}(\text{Ba}^{2+}, \text{SrL}_2^{2+})$ given above, the value $\log \beta_{\text{nb}}(\text{SrL}_2^{2+}) = 13.2$ ($L = \text{benzo-15-crown-5}$)¹² and applying Eq. (11), the stability constant of the barium–benzo-15-crown-5 complex in nitrobenzene saturated with water at 25 °C is obtained as:

$$\log \beta_{\text{nb}}(\text{BaL}_2^{2+}) = 13.3 \pm 0.1$$

In conclusion, it should be emphasized that the stability constant of the benzo-15-crown-5 complex of strontium in water saturated nitrobenzene is $\log \beta_{\text{nb}}(\text{SrL}_2^{2+}) = 13.2$.¹² This means that the stability constants of the complexes BaL_2^{2+} and SrL_2^{2+} ($L = \text{benzo-15-crown-5}$) in the mentioned medium are nearly the same.

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ИЗВОД

СТАБИЛНОСТ БАРИЈУМ–БЕНЗО-15-КРУНА-5-КОМПЛЕКСА У НИТРОБЕНЗЕНУ ЗАСИЋЕНОМ ВОДОМ

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На основу екстракционих експеримената и мерења γ -активности одређена је вредност коефицијента расподеле који одговара равнотежи $\text{Ba}^{2+}(\text{aq}) + \text{Sr}^{2+}(\text{nb}) \rightleftharpoons \text{BaL}_2^{2+}(\text{nb}) + \text{Sr}^{2+}(\text{aq})$, а која се дешава у двофазном систему вода–нитробензен ($L = \text{бензо-15-круна-5}$; $\text{aq} = \text{водена фаза}$, $\text{nb} = \text{нитробензенска фаза}$): $\log K_{\text{ex}}(\text{Ba}^{2+}, \text{SrL}_2^{2+}) = 0,3 \pm 0,1$. Израчуната је константа стабилности бензо-15-круна-5–барјум комплекса у нитробензену засићеном водом на температури 25 °C: $\log \beta_{\text{nb}}(\text{BaL}_2^{2+}) = 13,3 \pm 0,1$.

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