*Acta Chim. Slov.* **2007,** *54,* 375–377

*Short communication*

# Extraction of Zinc from Water into Nitrobenzene Using Strontium Dicarbollylcobaltate in the Presence of Valinomycin

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*Received: 19-02-2007*

## Abstract

From extraction experiments and γ-activity measurements, the extraction constant corresponding to the equilibrium $Zn^{2+}(aq) + SrL^{2+}(nb) \Leftrightarrow ZnL^{2+}(nb) + Sr^{2+}(aq)$ taking place in the two-phase water-nitrobenzene system (L = valinomycin; aq = aqueous phase, nb = nitrobenzene phase) was evaluated as $\log K_{ex}(Zn^{2+},SrL^{2+}) = -0.1$. Furthermore, the stability constant of the valinomycin-zinc complex in nitrobenzene saturated water was calculated for a temperature of 25 °C: $\log \beta_{nb}(ZnL^{2+}) = 6.2$.

**Keywords:** Zinc, valinomycin, water-nitrobenzene system, extraction and stability constants.

## 1. Introduction

The antibiotic valinomycin was discovered in cultures *Streptomyces fulvissimus*[1]. It is a macrocyclic depsipeptide exhibiting the threefold symmetry.[2] It forms complexes with alkali metal ions, the stability of which shows a pronounced dependence on the ion radius.[2–5] Because of the lipophilic outer envelope of the complex, valinomycin enables univalent cations to be transported across membranes of cells and cell organelles[3], and consequently, it is a powerful uncoupler of oxidative phosphorylation in mitochondria[6]. The very large difference in stability of the potassium and the sodium complexes is the cause of the high potassium selectivity of the valinomycin-based ion-selective electrode.[7]

Up to now, a complex species of zinc with valinomycin has not been obviously proved. In the present communication, stability of the valinomycin-zinc complex in the organic phase of the water-nitrobenzene extraction system was determined.

## 2. Results and Discussion

Regarding the results of previous papers[8–11], the two-phase water-$Zn(NO_3)_2$-nitrobenzene-$Sr(DCC)_2$extraction system can be described by the following equilibrium

$$Zn^{2+}(aq) + Sr^{2+}(nb) \Leftrightarrow Zn^{2+}(nb) + Sr^{2+}(aq); \quad K_{ex}(Zn^{2+},Sr^{2+}) \qquad (1)$$

with the corresponding exchange extraction constant $K_{ex}(Zn^{2+},Sr^{2+})$; aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively. For the constant $K_{ex}(Zn^{2+},Sr^{2+})$ it can be written[8]

$$\log K_{ex}(Zn^{2+},Sr^{2+}) = \log K^{i}_{Zn^{2+}} - \log K^{i}_{Sr^{2+}} \qquad (2)$$

where $K^{i}_{Zn^{2+}}$ and $K^{i}_{Sr^{2+}}$ are the individual extraction constans for $Zn^{2+}$ and $Sr^{2+}$, respectively, in the water-nitrobenzene system[8]. Knowing $\log K^{i}_{Zn^{2+}} = -11.6$[10] and $\log K^{i}_{Sr^{2+}} = -10.7$ (inferred from References 8 and 11), the exchange extraction constant $K_{ex}(Zn^{2+},Sr^{2+})$ was simply calculated from Eq.(2):

$$\log K_{ex}(Zn^{2+},Sr^{2+}) = -0.9 \qquad (3)$$

In terms of previous results[9,12], the two-phase water-$Zn(NO_3)_2$-nitrobenzene-L (L = valinomycin) -$Sr(DCC)_2$ extraction system (see Experimental), chosen for determination of stability of the complex $ZnL^{2+}$ in water saturated nitrobenzene, can be characterized by the main chemical equilibrium

$$Zn^{2+}(aq) + SrL^{2+}(nb) \Leftrightarrow ZnL^{2+}(nb) + Sr^{2+}(aq) \; ; \quad K_{ex}(Zn^{2+},SrL^{2+}) \qquad (4)$$

with the equilibrium extraction constant $K_{ex}(Zn^{2+},SrL^{2+})$:

$$K_{ex}(\mathrm{Zn}^{2+},\mathrm{SrL}^{2+}) = \frac{[\mathrm{ZnL}^{2+}]_{nb}[\mathrm{Sr}^{2+}]_{aq}}{[\mathrm{Zn}^{2+}]_{aq}[\mathrm{SrL}^{2+}]_{nb}} \qquad (5)$$

It is necessary to emphasize that the valinomycin ligand forms-with $Zn^{2+}$ and $Sr^{2+}$ – the relatively stable complexes $ZnL^{2+}$ and $SrL^{2+}$ in the nitrobenzene phase.

Following the conditions of electroneutrality in the organic and aqueous phases of the system under study

$$[\mathrm{ZnL}^{2+}]_{nb} + [\mathrm{SrL}^{2+}]_{nb} = C^{in,nb}_{\mathrm{Sr(DCC)_2}} \qquad (6)$$

$$[\mathrm{Zn}^{2+}]_{aq} + [\mathrm{Sr}^{2+}]_{aq} = C^{in,aq}_{\mathrm{Zn(NO_3)_2}} \qquad (7)$$

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

$$[\mathrm{Zn}^{2+}]_{aq} + [\mathrm{ZnL}^{2+}]_{nb} = C^{in,aq}_{\mathrm{Zn(NO_3)_2}} \qquad (8)$$

$$[\mathrm{Sr}^{2+}]_{aq} + [\mathrm{SrL}^{2+}]_{nb} = C^{in,nb}_{\mathrm{Sr(DCC)_2}} \qquad (9)$$

and the measured equilibrium distribution ratio of strontium

$$D_{Sr} = [\mathrm{SrL}^{2+}]_{nb} / [\mathrm{Sr}^{2+}]_{aq} \qquad (10)$$

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

$$K_{ex}(\mathrm{Zn}^{2+},\mathrm{SrL}^{2+}) = \\ = \frac{1}{D_{Sr}} \frac{C^{in,nb}_{\mathrm{Sr(DCC)_2}}}{(1+D_{Sr})C^{in,aq}_{\mathrm{Zn(NO_3)_2}} - C^{in,nb}_{\mathrm{Sr(DCC)_2}}} \qquad (11)$$

In this study, from the extraction experiments and γ-activity measurements (see Experimental) by using Eq. (11), the following value of the constant log $K_{ex}(Zn^{2+},SrL^{2+})$ was evaluated:

$$\log K_{ex}(\mathrm{Zn}^{2+},\mathrm{SrL}^{2+}) = -0.1 \qquad (12)$$

Moreover, with respect to previous results[12,13], for the extraction constants $K_{ex}(Zn^{2+},Sr^{2+})$ and $K_{ex}(Zn^{2+}, SrL^{2+})$ defined above, as well as for the stability constants of the complexes $ZnL^{2+}$ and $SrL^{2+}$ in nitrobenzene saturated with water, denoted by $\beta_{nb}(ZnL^{2+})$ and $\beta_{nb}(SrL^{2+})$, respectively, one gets

$$\log \beta_{nb}(\mathrm{ZnL}^{2+}) = \log \beta_{nb}(\mathrm{SrL}^{2+}) + \\ + \log K_{ex}(\mathrm{Zn}^{2}_{+},\mathrm{SrL}^{2}_{+}) - \log K_{ex}(\mathrm{Zn}^{2}_{+},\mathrm{Sr}^{2}_{+}) \qquad (13)$$

Using the constants log $K_{ex}(Zn^{2+},Sr^{2+})$ and log $K_{ex}(Zn^{2+},SrL^{2+})$ given above, the value log $\beta_{nb}(SrL^{2+})$ = 5.4 (L = valinomycin)[14] and applying Eq. (13), we obtain the stability constant of the valinomycin-zinc complex in water saturated nitrobenzene at 25 °C:

$$\log \beta_{nb}(\mathrm{ZnL}^{2+}) = 6.2 \qquad (14)$$

In conclusion, it should be noted that the stability constant of the complex species $BaL^{2+}$ (L = valinomycin) in nitrobenzene saturated with water is log $\beta_{nb}(BaL^{2+})$ = 6.5.[15] It means that the stability constants of the complexes $ZnL^{2+}$ and $BaL^{2+}$, where L is valinomycin, in the mentioned medium are comparable.

## 3. Experimental

Valinomycin was supplied by Merck, Darmstadt, Germany. Cesium dicarbollylcobaltate (abbrev. CsDCC) was synthesized in the Institute of Inorganic Chemistry, Řež, Czech Republic, using the method published by Hawthorne *et al.*[16] The nitrobenzene solution of hydrogen dicarbollylcobaltate, HDCC, was prepared from CsDCC by the procedure described in Reference 17. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The equilibration of the nitrobenzene solution of HDCC with stoichiometric $Sr(OH)_2$, which was dissolved in the aqueous solution of $Sr(NO_3)_2$ (0.2 mol/l), yields the corresponding $Sr(DCC)_2$ solution in nitrobenzene. The radionuclide $^{85}Sr$ (DuPont, Belgium) was of standard radiochemical purity.

The extraction experiments were carried out in 10 ml glass test-tubes covered with polyethylene stoppers: 2 ml of the aqueous solution of $Zn(NO_3)_2$ of the concentration in the range from $1 \times 10^{-4}$ to $1 \times 10^{-3}$ mol/l and microamounts of $^{85}Sr$ were added to 2 ml of the nitrobenzene solution of valinomycin and $Sr(DCC)_2$, whose initial concentrations varied also from $1 \times 10^{-4}$ to $1 \times 10^{-3}$ mol/l (in all experiments, the initial concentration of valinomycin in nitrobenzene, $C_L^{in,nb}$, was always equal to the initial concentration of $Sr(DCC)_2$ in this medium, $C^{in,nb}_{Sr(DCC)_2}$). The test-tubes filled with the solutions were shaken for 2 h at 25 ± 1 °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 (2 min, 2 500 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 γ-analyzer NK/350 (Gamma, Budapest, Hungary).

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

## 4. Acknowledgements

The present work was supported by the Czech Ministry of Education, Youth and Sports, Projects MSM 4977751303 and MSM 6046137307.

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## Povzetek

Z ekstrakcijo in meritvami γ-aktivnosti smo določili konstanto ekstrakcije v sistemu dveh faz (voda/nitrobenzen), ki jo ponazorimo z ravnotežjem $Zn^{2+}(aq) + SrL^{2+}(nb) \Longleftrightarrow ZnL^{2+}(nb) + Sr^{2+}(aq)$ (L = valinomicin; aq = vodna faza, nb = nitrobenzenova faza) in znaša $\log K_{ex} (Zn^{2+},SrL^{2+}) = -0.1$. Ocenili smo tudi konstanto stabilnosti kompleksa med valinomicinom in zinkom v nasičeni raztopini nitrobenzena v vodi, ki pri 25 °C znaša $\log \beta_{nb}(ZnL^{2+}) = 6.2$.