

Short communication

Solvent Extraction of Ba²⁺, Pb²⁺ and Cd²⁺ into Nitrobenzene by Using Strontium Dicarbolylcobaltate in the Presence of Tetraethyl *p*-*tert*-Butylcalix[4]arene Tetraacetate

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Abstract

From extraction experiments and γ -activity measurements, the exchange extraction constants corresponding to the general equilibrium $M^{2+}(\text{aq}) + \text{SrL}^{2+}(\text{nb}) \rightleftharpoons \text{ML}^{2+}(\text{nb}) + \text{Sr}^{2+}(\text{aq})$ taking place in the two-phase water-nitrobenzene system ($M^{2+} = \text{Ba}^{2+}, \text{Pb}^{2+}, \text{Cd}^{2+}$; L = tetraethyl *p*-*tert*-butylcalix[4]arene tetraacetate; aq = aqueous phase, nb = nitrobenzene phase) were evaluated. Further, the stability constants of the ML^{2+} complexes in water saturated nitrobenzene were calculated; they were found to increase in the order $\text{Ba}^{2+} < \text{Cd}^{2+} < \text{Pb}^{2+}$.

Keywords: Barium, lead, cadmium, strontium dicarbolylcobaltate, nitrobenzene, calix[4]arene, extraction and stability constants

1. Introduction

Calixarenes (products of the base condensation reaction between *p*-substituted phenols and formaldehyde) and their lower rim as well as upper rim derivatives have found widespread applications.^{1,2}

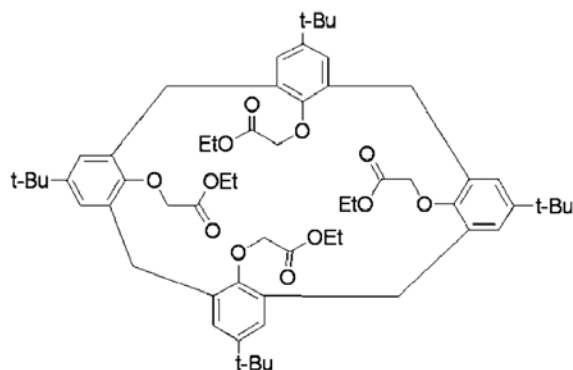
The presence of a hydrophobic cavity (able to host neutral species) besides the hydrophilic one (able to interact with ionic species) confers outstanding properties to calix[4]arene derivatives in their “cone” conformation relative to macrocycles such as crown ethers and cryptands. Calix[4]arenes containing ester and ketone functional groups at the lower rim have shown pronounced selectivity for alkali – metal cations in different media, particularly in acetonitrile.^{3,4}

In the present work, stability constants of Ba²⁺, Pb²⁺ and Cd²⁺ complexes of tetraethyl *p*-*tert*-butylcalix[4]arene tetraacetate (see Scheme 1) in the organic phase of the water – nitrobenzene extraction system were determined.

2. Experimental

Tetraethyl *p*-*tert*-butylcalix[4]arene tetraacetate, called also sodium ionophore X, was purchased from Fluka, Buchs, Switzerland. Cesium dicarbolylcobaltate, Cs-DCC, was supplied by Katchem, Řež, Czech Republic. A nitrobenzene solution of hydrogen dicarbolylcobaltate (HDCC) was prepared from CsDCC by the method described in Reference 5. 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 an aqueous solution of Sr(NO₃)₂ (0.2 mol L⁻¹), yielded the corresponding Sr(DCC)₂ solution in nitrobenzene. The radionuclide ⁸⁵Sr²⁺ (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 an aqueous solution of M(NO₃)₂ ($M^{2+} = \text{Ba}^{2+}, \text{Pb}^{2+}, \text{Cd}^{2+}$) of the concentration in the range from 1×10^{-4} to 1



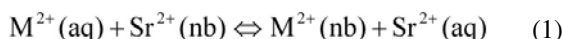
Scheme 1. Structural formula of tetraethyl *p-tert-butylcalix[4]arene* tetraacetate.

$\times 10^{-3}$ mol L⁻¹ and microamounts of ⁸⁵Sr²⁺ were added to 2 mL of a nitrobenzene solution of tetraethyl *p-tert-butylcalix[4]arene* tetraacetate and Sr(DCC)₂, whose initial concentrations varied also from 1×10^{-4} to 1×10^{-3} mol L⁻¹ (in all experiments, the initial concentration of tetraethyl *p-tert-butylcalix[4]arene* tetraacetate in nitrobenzene, C_L, was always equal to the initial concentration of Sr(DCC)₂ in this medium, C_{Sr(DCC)₂}^{in,nb}). The test-tubes filled with the solutions were shaken for 12 hours at 25 ± 1 °C, using a laboratory shaker. Then the phases were separated by centrifugation. 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 ⁸⁵Sr²⁺ in the nitrobenzene and aqueous samples.

3. Results and Discussion

Regarding the results of previous papers,^{6–10} the two-phase water- M(NO₃)₂ (M²⁺ = Ba²⁺, Pb²⁺, Cd²⁺)-nitrobenzene-Sr(DCC)₂ extraction system can be described by the following general equilibrium



with the corresponding exchange extraction constant K_{ex}(M²⁺, Sr²⁺); aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively.

The changes of the standard Gibbs energies corresponding to the transfer of the ions M²⁺ (M²⁺ = Ba²⁺, Pb²⁺, Cd²⁺) and Sr²⁺ from the aqueous into the nitrobenzene phase, expressed by



are given by definitions

$$\Delta G_{\text{tr},M^{2+}}^{0,\text{aq} \rightarrow \text{nb}} = \mu_{M^{2+}}^{0,\text{nb}} - \mu_{M^{2+}}^{0,\text{aq}} \quad (4)$$

$$\Delta G_{\text{tr},\text{Sr}^{2+}}^{0,\text{aq} \rightarrow \text{nb}} = \mu_{\text{Sr}^{2+}}^{0,\text{nb}} - \mu_{\text{Sr}^{2+}}^{0,\text{aq}} \quad (5)$$

Here μ^0 – s are the standard chemical potentials of the ions M²⁺ and Sr²⁺ in the two phases concerned.

The individual extraction constants K_{M²⁺}ⁱ (M²⁺ = Ba²⁺, Pb²⁺, Cd²⁺) and K_{Sr²⁺}ⁱ for the divalent metal cations in the water-nitrobenzene extraction system are defined by⁶

$$\Delta G_{\text{tr},M^{2+}}^{0,\text{aq} \rightarrow \text{nb}} = -RT \ln K_{M^{2+}}^i \quad (6)$$

$$\Delta G_{\text{tr},\text{Sr}^{2+}}^{0,\text{aq} \rightarrow \text{nb}} = -RT \ln K_{\text{Sr}^{2+}}^i \quad (7)$$

Combination of the relation

$$\begin{aligned} -RT \ln K_{\text{ex}}(M^{2+}, \text{Sr}^{2+}) &= \mu_{M^{2+}}^{0,\text{nb}} + \mu_{\text{Sr}^{2+}}^{0,\text{aq}} - \\ &- \mu_{M^{2+}}^{0,\text{aq}} - \mu_{\text{Sr}^{2+}}^{0,\text{nb}} \end{aligned} \quad (8)$$

corresponding to Equilibrium (1) with Eqs (4)–(7) yields

$$\log K_{\text{ex}}(M^{2+}, \text{Sr}^{2+}) = \log K_{M^{2+}}^i - \log K_{\text{Sr}^{2+}}^i \quad (9)$$

Knowing the values $\log K_{\text{Ba}^{2+}}^i = -10.5$,⁹ $\log K_{\text{Pb}^{2+}}^i = -10.6$,¹⁰ $\log K_{\text{Cd}^{2+}}^i = -11.5$,¹⁰ and $\log K_{\text{Sr}^{2+}}^i = -10.7$, which was inferred from References 6 and 8, the single exchange extraction constants K_{ex}(M²⁺, Sr²⁺) were simply calculated on the basis of Eq. (9). The corresponding data are given in Table 1.

Table 1. Equilibrium data for the M²⁺ and ML²⁺ cations in the two-phase water- nitrobenzene extraction system at 25 °C (M²⁺ = Sr²⁺, Ba²⁺, Pb²⁺, Cd²⁺; L = tetraethyl *p-tert-butylcalix[4]arene* tetraacetate; for the meaning of the constants see text).

Quantity	Sr ²⁺	Ba ²⁺	Pb ²⁺	Cd ²⁺
$\log K_{M^{2+}}^i$	-10.7 ^a	-10.5 ^b	-10.6 ^c	-11.5 ^c
$\log K_{\text{ex}}(M^{2+}, \text{Sr}^{2+})^d$	–	0.2	0.1	-0.8
$\log K_{\text{ex}}(M^{2+}, \text{SrL}^{2+})^e$	–	0.6	1.6	-1.2
$\log \beta_{\text{nb}}(\text{ML}^{2+})^f$	6.2 ^g	6.6	7.7	5.8

^a Inferred from Refs 6 and 8.

^b Ref. 9.

^c Ref. 10.

^d Calculated from Eq. (9) using data from Refs 6 and 8–10.

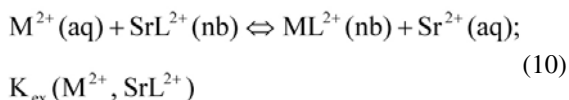
^e Calculated from Eq. (17).

^f Calculated from Eq. (18) using data from Refs 6, 8–10 and 14.

^g Ref. 14.

With respect to previous results,^{11–13} the two-phase water-M(NO₃)₂ (M²⁺ = Ba²⁺, Pb²⁺, Cd²⁺)-nitrobenzene-L (L = tetraethyl *p-tert-butylcalix[4]arene* tetraacetate)-

Sr(DCC)₂ extraction systems (see Experimental), chosen for determination of stability of the ML²⁺ complexes in nitrobenzene saturated with water, can be characterized by the main chemical equilibrium



with the general equilibrium constant $K_{\text{ex}}(M^{2+}, \text{SrL}^{2+})$:

$$K_{\text{ex}}(M^{2+}, \text{SrL}^{2+}) = \frac{[\text{ML}^{2+}]_{\text{nb}}[\text{Sr}^{2+}]_{\text{aq}}}{[\text{M}^{2+}]_{\text{aq}}[\text{SrL}^{2+}]_{\text{nb}}} \quad (11)$$

It is necessary to emphasize that tetraethyl *p*-*tert*-butylcalix[4]arene tetraacetate is a considerably hydrophobic ligand, practically present in the nitrobenzene phase only, where it forms the very stable complexes ML²⁺ with the mentioned divalent cations.

Taking into account the conditions of electroneutrality in the organic and aqueous phases of the system under study

$$[\text{ML}^{2+}]_{\text{nb}} + [\text{SrL}^{2+}]_{\text{nb}} = C_{\text{Sr(DCC)}_2}^{\text{in,nb}} \quad (12)$$

$$[\text{M}^{2+}]_{\text{aq}} + [\text{Sr}^{2+}]_{\text{aq}} = C_{\text{M(NO}_3)_2}^{\text{in,aq}} \quad (13)$$

the mass balances of the divalent cations studied at equal volumes of the nitrobenzene and aqueous phases

$$[\text{M}^{2+}]_{\text{aq}} + [\text{ML}^{2+}]_{\text{nb}} = C_{\text{M(NO}_3)_2}^{\text{in,aq}} \quad (14)$$

$$[\text{Sr}^{2+}]_{\text{aq}} + [\text{SrL}^{2+}]_{\text{nb}} = C_{\text{Sr(DCC)}_2}^{\text{in,nb}} \quad (15)$$

as well as the measured equilibrium distribution ratio of strontium

$$D_{\text{Sr}} = [\text{SrL}^{2+}]_{\text{nb}} / [\text{Sr}^{2+}]_{\text{aq}} \quad (16)$$

then combination of Relations (11) – (16) gives the final expression for the exchange extraction constant $K_{\text{ex}}(M^{2+}, \text{SrL}^{2+})$:

$$K_{\text{ex}}(M^{2+}, \text{SrL}^{2+}) =$$

$$= \frac{1}{D_{\text{Sr}}(1 + D_{\text{Sr}})} \frac{C_{\text{Sr(DCC)}_2}^{\text{in,nb}}}{C_{\text{M(NO}_3)_2}^{\text{in,aq}} - C_{\text{Sr(DCC)}_2}^{\text{in,nb}}} \quad (17)$$

where $C_{\text{M(NO}_3)_2}^{\text{in,aq}}$ is the initial concentration of M(NO₃)₂ in the aqueous phase of the system under consideration.

In this study, from the extraction experiments and γ -activity measurements (see Experimental) by means of Eq.

(17), the logarithms of the constants $K_{\text{ex}}(M^{2+}, \text{SrL}^{2+})$ were determined as reviewed in Table 1.

Moreover, with regard to References 11 and 13, for the extraction constants $K_{\text{ex}}(M^{2+}, \text{SrL}^{2+})$ and $K_{\text{ex}}(M^{2+}, \text{SrL}^{2+})$ defined above, as well as for the stability constants of the complexes ML²⁺ and SrL²⁺ in nitrobenzene saturated with water, denoted by $\beta_{\text{nb}}(\text{ML}^{2+})$ and $\beta_{\text{nb}}(\text{SrL}^{2+})$, respectively, one gets

$$\log \beta_{\text{nb}}(\text{ML}^{2+}) = \log \beta_{\text{nb}}(\text{SrL}^{2+}) +$$

$$+ \log K_{\text{ex}}(M^{2+}, \text{SrL}^{2+}) - \log K_{\text{ex}}(M^{2+}, \text{Sr}^{2+}) \quad (18)$$

Using the constants $\log K_{\text{ex}}(M^{2+}, \text{Sr}^{2+})$ and $\log K_{\text{ex}}(M^{2+}, \text{SrL}^{2+})$ given in Table 1, the value $\log \beta_{\text{nb}}(\text{SrL}^{2+}) = 6.2$, determined from the distribution of strontium picrate in the water-nitrobenzene system containing also tetraethyl *p*-*tert*-butylcalix[4]arene tetraacetate,¹⁴ and applying Eq. (18), we obtain the stability constants of the complexes ML²⁺ ($M^{2+} = \text{Ba}^{2+}, \text{Pb}^{2+}, \text{Cd}^{2+}$) in nitrobenzene saturated with water. These data are also summarized in Table 1. Thus, the $\beta_{\text{nb}}(\text{ML}^{2+})$ values from this table indicate that the stability of the complex cation ML²⁺ in water saturated nitrobenzene increases in the $\text{Cd}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+} < \text{Pb}^{2+}$ order. On the other hand, in the acetonitrile medium Danil de Namor et al.⁴ found that the stability of the mentioned complex species increases in the series $\text{Cd}^{2+} < \text{Ba}^{2+} < \text{Sr}^{2+} < \text{Pb}^{2+}$ as follows from Table 2.

Table 2. Stability constants of the ML²⁺ cations ($M^{2+} = \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Pb}^{2+}, \text{Cd}^{2+}$; L = tetraethyl *p*-*tert*-butylcalix[4]arene tetraacetate) in acetonitrile at 25 °C (taken from Ref. 4).

M^{2+}	Sr^{2+}	Ba^{2+}	Pb^{2+}	Cd^{2+}
$\log \beta_{\text{nb}}(\text{ML}^{2+})$	5.35	4.34	7.39	4.08

4. Acknowledgement

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5. References

1. V. Böhmer, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713–745.
2. C. D. Gutsche, *Calixarenes Revisited*. The Royal Society of Chemistry, Cambridge, 1998.
3. A. F. Danil de Namor, R. M. Cleverly, M. L. Zapata – Ormachea, *Chem. Rev.* **1998**, *98*, 2495–2525.
4. A. F. Danil de Namor, S. Chahine, D. Kowalska, E. E. Castellano, O. E. Piro, *J. Am. Chem. Soc.* **2002**, *124*, 12824–12836.

5. E. Makrlík, *Collect. Czech. Chem. Commun.* **1992**, 57, 289–295.
6. J. Rais, *Collect. Czech. Chem. Commun.* **1971**, 36, 3253–3262.
7. J. Rais, P. Selucký, M. Kyrš, *J. Inorg. Nucl. Chem.* **1976**, 38, 1376–1378.
8. P. Vaňura, E. Makrlík, J. Rais, M. Kyrš, *Collect. Czech. Chem. Commun.* **1982**, 47, 1444–1464.
9. I. Podzimek, M. Kyrš, J. Rais, *J. Inorg. Nucl. Chem.* **1980**, 42, 1481–1486.
10. E. Makrlík, P. Vaňura, *unpublished results*.
11. E. Makrlík, J. Hálová, M. Kyrš, *Collect. Czech. Chem. Commun.* **1984**, 49, 39–44.
12. E. Makrlík, P. Vaňura, *J. Radioanal. Nucl. Chem.* **2006**, 268, 155–157.
13. E. Makrlík, P. Vaňura, *J. Radioanal. Nucl. Chem.* **1996**, 214, 339–346.
14. P. Vaňura, E. Makrlík, P. Selucký, *unpublished results*.

Povzetek

Z ekstrakcijo in meritvami γ -aktivnosti smo določili konstante ekstrakcije v sistemu dveh faz (voda/nitrobenzen), ki jo ponazorimo z ravnotežjem $M^{2+}(aq) + SrL^{2+}(nb) \rightleftharpoons ML^{2+}(nb) + Sr^{2+}(aq)$; ($M^{2+} = Ba^{2+}, Pb^{2+}, Cd^{2+}$; L = tetraetil-*p-tert*-butil-kaliks[4]aren tetraacetat; aq = vodna faza, nb = nitrobenzen). Ocenili smo tudi konstante stabilnosti kompleksov ML^{2+} v nitrobenzenu nasičenem z vodo in ugotovili naslednje zaporedje konstant stabilnosti kompleksov: $Ba^{2+} < Cd^{2+} < Pb^{2+}$.