Stability Constants of Ca²⁺, Cu²⁺, Zn²⁺, UO₂²⁺, Mn²⁺, Co²⁺ and Ni²⁺ Complexes of Tetraethyl *p-tert*-Butylcalix[4]arene Tetraacetate in Nitrobenzene Saturated with Water

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Abstract

From extraction experiments and γ-activity measurements, the exchange extraction constants corresponding to the general equilibrium M^{2+} (aq) + SrL^{2+} (nb) $\Leftrightarrow$ ML^{2+} (nb) + Sr^{2+} (aq) taking place in the two–phase water–nitrobenzene system ($M^{2+} = Ca^{2+}, Cu^{2+}, Zn^{2+}, UO_2^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}$; 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 cation order $Mn^{2+} < Co^{2+} < Cu^{2+} < Zn^{2+} < UO_2^{2+}$, $Ni^{2+} < Ca^{2+}$.
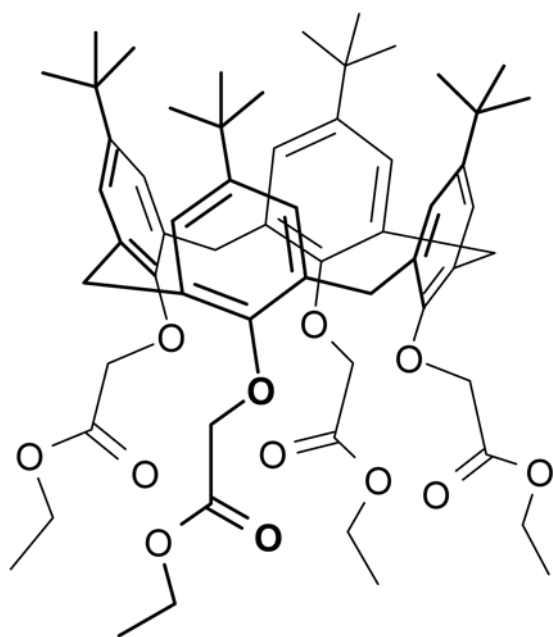
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1. Introduction

Calix[n]arenes are a well-known family of macrocyclic molecules with many potential applications in various branches of chemistry. Because of their simple one-pot preparation, easy derivatization and unique complexation abilities, calix[n]arenes are widely used as the building blocks for the constructions of more sophisticated molecular systems. Their unique three-dimensional pre-organization make them very attractive as the receptors for the complexation of cations, anions, and even neutral molecules. Calix[n]arenes find applications as selective binders and carriers, as analytical sensors, as catalysts and model structures for biomimetic studies.[1,2] In the field of host-guest chemistry, many studies have focused on the binding ability of calixarene derivatives with carbonyl groups at their lower rims toward metal ions, predominantly alkali and alkaline-earth, but also transition and heavy metal cations,[3–12] and even toward H_3O^+.[13–21]

Dicarbollylcobaltate anion and some of its halogen derivatives are very useful reagents for the extraction of alkali metal cations (especially Cs⁺), and also-in the presence of polyoxyethylene compounds (e.g., crown ethers, PEG 400, Slovafol 909) – for the extraction of Sr²⁺ and Ba²⁺ from aqueous solutions into an organic polar phase, both under laboratory conditions for purely theoretical or analytical purposes,[22,23] and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.[24,25]

Recently, the solvent extraction of Ba²⁺, Pb²⁺ and Cd²⁺ into nitrobenzene by using synergistic mixture of strontium dicarbollylcobaltate and tetraethyl *p-tert*-butylcalix[4]arene tetraacetate (see Scheme 1) has been investigated.[26] In the present work, the stability constants of Ca²⁺, Cu²⁺, Zn²⁺, UO₂²⁺, Mn²⁺, Co²⁺ and Ni²⁺ complexes with the mentioned calix[4]arene ligand were determined in the organic phase of the water–nitrobenzene extraction system.

Zn^{2+}, UO_2^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}) of the concentration in the range from 1×10^{-3} to 1×10^{-2} mol dm^{-3} and micro-mounts of $^{85}Sr^{2+}$ were added to 2 cm^3 of a nitrobenzene solution of tetraethyl *p-tert*-butylcalix[4]arene tetraacetate and $Sr(DCC)_2$, whose initial concentrations varied also from 1×10^{-3} to 1×10^{-2} mol dm^{-3} (in all experiments, the initial concentration of tetraethyl *p-tert*-butylcalix[4]arene tetraacetate in nitrobenzene, $C_L^{in,nb}$, 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 °C, using a laboratory shaker. Then the phases were separated by centrifugation. Afterwards, 1 cm^3 samples were taken from each phase and their γ–activities were measured using a well-type NaI(T1) scintillation detector connected to a γ–analyzer NK/350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratios of strontium, D_{Sr}, were determined as the ratios of the measured radioactivities of $^{85}Sr^{2+}$ in the nitrobenzene and aqueous samples.

3. Results and Discussion

Regarding the results of previous papers,[22, 28–30] the two–phase water– $M(NO_3)_2$ ($M^{2+} = Ca^{2+}$, Cu^{2+}, Zn^{2+}, UO_2^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+})–nitrobenzene–$Sr(DCC)_2$ extraction system can be described by the following general equilibrium

$$M^{2+}(aq) + Sr^{2+}(nb) \Leftrightarrow M^{2+}(nb) + Sr^{2+}(aq) \quad (1)$$

with the corresponding exchange extraction constant $K_{ex}(M^{2+}, Sr^{2+})$; aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively. For the constant $K_{ex}(M^{2+}, Sr^{2+})$ one can write[22,28]

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

where $K_{M^{2+}}^i$ and $K_{Sr^{2+}}^i$ are the individual extraction constants for M^{2+} and Sr^{2+}, respectively, in the water–nitrobenzene system. Knowing $\log K_{Ca^{2+}}^i = -11.2$ (inferred from References 28 and 29), $\log K_{Cu^{2+}}^i = -11.5$,[31] $\log K_{Zn^{2+}}^i$ $\log K_{Ni^{2+}}^i = -11.6$,[31] $\log K_{UO_2^{2+}}^i = -11.8$,[31] $\log K_{Mn^{2+}}^i = -11.1$,[31]

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

2. Experimental

Tetraethyl *p-tert*-butylcalix[4]arene tetraacetate was purchased from Fluka, Buchs, Switzerland. Cesium dicarbollylcobaltate, CsDCC, was supplied by Katchem, Řež, Czech Republic. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. A nitrobenzene solution of hydrogen dicarbollylcobaltate (HDCC)[22] was prepared from CsDCC by the method described elsewhere.[27] The equilibration of the nitrobenzene solution of HDCC with stoichiometric $Sr(OH)_2$, which was dissolved in an aqueous solution of $Sr(NO_3)_2$ (0.2 mol dm^{-3}), yielded the corresponding $Sr(DCC)_2$ solution in nitrobenzene. The radionuclide $^{85}Sr^{2+}$ (DuPont, Belgium) was of standard radiochemical purity.

The extraction experiments were carried out in 10 cm^3 glass test-tubes covered with polyethylene stoppers: 2 cm^3 of an aqueous solution of $M(NO_3)_2$ ($M^{2+} = Ca^{2+}$, Cu^{2+},

Table 1. Equilibrium data for the M^{2+} and ML^{2+} cations in the two–phase water–nitrobenzene extraction system at 25 °C ($M^{2+} = Ca^{2+}$, Sr^{2+}, Cu^{2+}, Zn^{2+}, UO_2^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}; L = tetraethyl *p-tert*-butylcalix[4]arene tetraacetate; for the meaning of the constants see text).

Quantity	Ca^{2+}	Sr^{2+}	Cu^{2+}	Zn^{2+}	UO_2^{2+}	Mn^{2+}	Co^{2+}	Ni^{2+}
$\log K_{M^{2+}}^i$	–11.2[a]	–10.7[b]	–11.5[c]	–11.6[c]	–11.8[c]	–11.1[c]	–11.4[c]	–11.6[c]
$\log K_{ex}(M^{2+}, Sr^{2+})$[d]	–0.5	–	–0.8	–0.9	–1.1	–0.4	–0.7	–0.9
$\log K_{ex}(M^{2+}, SrL^{2+})$[e]	1.3	–	–0.7	–0.3	–0.3	–0.6	–0.7	–0.1
$\log \beta_{ub}(ML^{2+})$[f]	8.0	6.2[g]	6.3	6.8	7.0	6.0	6.2	7.0

[a] Inferred from Refs 28 and 29. [b] Inferred from Refs 28 and 30. [c] Ref. 31. [d] Calculated from Eq. (2) using data from Refs 28–31. [e] Calculated from Eq. (5). [f] Calculated from Eq. (6) using data from Refs 28–31 and 36. [g] Ref. 36.

log $K_{Co^{2+}}^i$ = –11.4[31] and finally, log $K_{Sr^{2+}}^i$ = –10.7, which was inferred from References 28 and 30, the single exchange extraction constants $K_{ex}(M^{2+}, Sr^{2+})$ were simply calculated on the basis of Eq. (2). The corresponding data are given in Table 1.

Previous results[32–35] showed that the two–phase water–$M(NO_3)_2$ (M^{2+} = Ca^{2+}, Cu^{2+}, Zn^{2+}, UO_2^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+})–nitrobenzene–L (L = tetraethyl *p-tert*-butylcalix[4]arene tetraacetate)–$Sr(DCC)_2$ extraction system (see Experimental), chosen for determination of stability of the complex ML^{2+} in nitrobenzene saturated with water, can be characterized by the main chemical equilibrium

$$M^{2+}(aq) + SrL^{2+}(nb) \Leftrightarrow ML^{2+}(nb) + Sr^{2+}(aq) \quad (3)$$

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

$$K_{ex}(M^{2+}, SrL^{2+}) = \frac{[ML^{2+}]_{nb}[Sr^{2+}]_{aq}}{[M^{2+}]_{aq}[SrL^{2+}]_{nb}} \quad (4)$$

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 ML^{2+} with the mentioned divalent cations. Taking into account the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of the divalent cations studied at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratio of strontium, D_{Sr} = $[SrL^{2+}]_{nb}$/$[Sr^{2+}]_{aq}$, combined with Eq. (4), we gain the final expression for $K_{ex}(M^{2+}, SrL^{2+})$ in the form

$$K_{ex}(M^{2+}, SrL^{2+}) = \frac{1}{D_{Sr}} \frac{C_{Sr(DCC)_2}^{in,nb}}{(1+D_{Sr}) C_{M(NO_3)_2}^{in,aq} - C_{Sr(DCC)_2}^{in,nb}} \quad (5)$$

where $C_{M(NO_3)_2}^{in,aq}$ is the initial concentration of $M(NO_3)_2$ (M^{2+} = Ca^{2+}, Cu^{2+}, Zn^{2+}, UO_2^{2+}, Mn^{2+}, Co^{2+}, Ni^{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. (5), the logarithms of the constants $K_{ex}(M^{2+}, SrL^{2+})$ were determined as reviewed in Table 1. Moreover, with respect to References 32–35, for the extraction constants $K_{ex}(M^{2+}, Sr^{2+})$ and $K_{ex}(M^{2+}, SrL^{2+})$ defined above, as well as for the stability constants of the complexes ML^{2+} and SrL^{2+} in nitrobenzene saturated with water, denoted by $\beta_{nb}(ML^{2+})$ and $\beta_{nb}(SrL^{2+})$, respectively, one gets

$$\log \beta_{nb}(ML^{2+}) = \log \beta_{nb}(SrL^{2+}) + $$
$$+ \log K_{ex}(M^{2+}, SrL^{2+}) - \log K_{ex}(M^{2+}, Sr^{2+}) \quad (6)$$

Finally, using the constants log $K_{ex}(M^{2+}, Sr^{2+})$ and log $K_{ex}(M^{2+}, SrL^{2+})$ given in Table 1, log $\beta_{nb}(SrL^{2+})$ = 6.2(L = tetraethyl *p-tert*-butylcalix[4]arene tetraacetate),[36] determined from the distribution of strontium picrate in the water–nitrobenzene system containing the considered calix[4]arene ligand, and applying Eq. (6), we obtain the stability constants of the ML^{2+} complexes in water–saturated nitrobenzene. These data are also summarized in Table 1. The $\beta_{nb}(ML^{2+})$ values from this table indicate that the stability of the ML^{2+} complex cation in nitrobenzene saturated with water increases in the series of Mn^{2+} < Sr^{2+}, Co^{2+} < Cu^{2+} < Zn^{2+} < UO_2^{2+}, Ni^{2+} < Ca^{2+}.

In conclusion, it should be noted that the stability constants of the complex species ML^{2+}, where M^{2+} = Ba^{2+}, Cd^{2+}, Pb^{2+} and L is tetraethyl *p-tert*-butylcalix[4]arene tetraacetate, in water–saturated nitrobenzene are log $\beta_{nb}(BaL^{2+})$ = 6.6,[26] log $\beta_{nb}(CdL^{2+})$ = 5.8[26] and log $\beta_{nb}(PbL^{2+})$ = 7.7.[26] Thus, the previous data[26] and the data listed in Table 1 show that the stability of the complex cation ML^{2+} in the mentioned medium increases in the Cd^{2+} < Mn^{2+} < Sr^{2+}, Co^{2+} < Cu^{2+} < Ba^{2+} < Zn^{2+} < UO_2^{2+}, Ni^{2+} < Pb^{2+}< Ca^{2+} order.

4. Acknowledgement

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Povzetek

Raziskovali smo ekstrakcijska ravnotežja M^{2+} (aq) + SrL^{2+} (nb) $\Leftrightarrow$ ML^{2+} (nb) + Sr^{2+} (aq) v dvofaznem sistemu voda-nitrobenzen (M^{2+} = Ca^{2+}, Cu^{2+}, Zn^{2+}, UO_2^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}; L = tetraetil *p-tert*-butilcalix[4]aren tetraacetat; aq = vodna faza, nb = faza nitrobenzena). Določili smo konstante stabilnosti ML^{2+} kompleksov v vodni fazi, nasičeni z nitrobenzenom. Ugotovili smo, da te konstante naraščajo v smeri $Mn^{2+} < Co^{2+} < Cu^{2+} < Zn^{2+} < UO_2^{2+}$, $Ni^{2+} < Ca^{2+}$.