Solvent Extraction of Calcium into Nitrobenzene by Using an Anionic Ligand Based on Cobalt Bis(Dicarbollide) Anion with Covalently Bonded CMPO Function

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Abstract

From extraction experiments and γ-activity measurements, the exchange extraction constantcorresponding to the general equilibrium $Ca^{2+}(aq) + 2HL(nb) \Leftrightarrow CaL_2(nb) + 2H^+(aq)$ taking place in the two–phase water–nitrobenzene (L^- = anionic ligand based on cobalt bis(dicarbollide) anion with covalently bonded CMPO function; aq = aqueous phase, nb = nitrobenzene phase) was evaluated as $\log K_{ex}(Ca^{2+}, 2HL) = 0.0 \pm 0.1$. Further, the stability constant of the electroneutral complex species CaL_2 in water-saturated nitrobenzene was calculated for a temperature of 25 °C : $\log \beta_{nb}(CaL_2) = 11.0 \pm 0.2$.

Keywords: Calcium, anionic ligand with CMPO function, complexation, extraction and stability constants, water–nitrobenzene system

1. Introduction

Bidentate phosphonates, phosphine oxides and malonamides have been intensively studied for the extraction of trivalent lanthanides and actinides from acidic media.[1–13] Recently, also TODGA (*N,N,N´,N´*-tetraoctyl diglycolamide),[14–16] CMPO substituted calixarenes [17] and several other promising compounds have been investigated for this purpose. Moreover, a process involving chlorinated cobalt dicarbollide, polyethylene glycol (PEG 400) and diphenyl-*N,N*-dibutylcarbamoylmethyl phosphine oxide (DPDBCMPO), also called UNEX, has been reported for the simultaneous recovery of cesium, strontium, lanthanides and actinides from highly acidic media into phenyltrifluoromethyl sulfone.[18,19]

The dicarbollylcobaltate anion[20] and some of its halogen derivatives are very useful reagents for the extraction of various metal cations (especially Cs^+, Sr^{2+}, Ba^{2+}, Eu^{3+} and Am^{3+}) from aqueous solutions into a polar organic phase, both under laboratory conditions for purely theoretical or analytical purposes,[21–36] and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.[18,19]

The anionic ligand based on cobalt bis(dicarbollide) anion with covalently bonded CMPO function (abbrev. L^-; see Scheme 1) has been synthesized with the aim to develop an efficient extraction agent for liquid-liquid extraction of lanthanides and actinides from high-level activity nuclear waste. The molecular structure of the sodium complex of this anionic ligand has been determined by single crystal X-ray diffraction analysis. The results on the separation of the fission products from the simulated PUREX feed by using the mentioned ligand have been presented with the procedure for

Eu^{3+} stripping.[37] On the other hand, in the current work, the solvent extraction of Ca^{2+} into nitrobenzene by means of the considered ligand L[−] (in the form of the electroneutral HL species) was studied. Furthermore, the stability constant of the electroneutral complex CaL$_2$ in the organic phase of the water–nitrobenzene extraction system was evaluated.
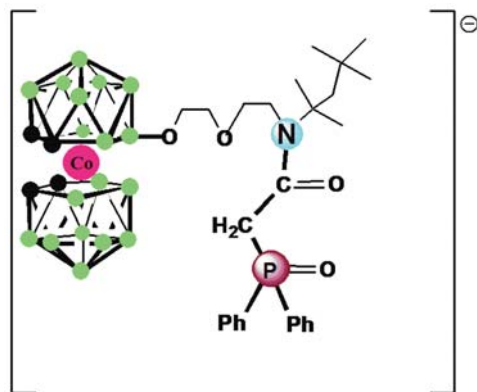
Scheme 1. Structural formula of an anionic ligand based on cobalt bis(dicarbollide) anion with covalently bonded CMPO function (abbrev. L[−]).

2. Experimental

A nitrobenzene solution of the species HL involving the anionic ligand L[−] based on cobalt bis(dicarbollide) anion with covalently bonded CMPO function (see Scheme 1) was supplied by Nuclear Research Institute, Řež, Czech Republic. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclide [45]Ca^{2+} was purchased from DuPont, Belgium.

The extraction experiments were carried out in 10 mL glass test-tubes with polyethylene stoppers: 2 mL of an aqueous solution of Ca(NO$_3$)$_2$ of the concentration in the range from 1×10^{-3} to 5×10^{-3} mol/L and microamounts of [45]Ca^{2+} were added to 2 mL of the nitrobenzene solution of HL, the initial concentration of which varied also from 1×10^{-3} to 5×10^{-3} mol/L. The test-tubes filled with the solutions were shaken for 12 h at 25 ± 1 °C, using a laboratory shaker. Then the phases were separated by centrifugation. After evaporating aliquots (1 mL) of the respective phases on Al plates, their β-activities were measured by means of the apparatus NRB-213 (Tesla Přemyšlení, Czech Republic).

The equilibrium distribution ratios of calcium, D$_{Ca}$, were determined as the ratios of the corresponding measured radioactivities of [45]Ca^{2+} in the nitrobenzene and aqueous samples.

3. Results and Discussion

Previous results[38–42] indicated that the two–phase water–Ca(NO$_3$)$_2$–nitrobenzene–HL (L[−] = anionic ligand

based on cobalt bis(dicarbollide) anion with covalently bonded CMPO function) extraction system (see Experimental), chosen for determination of the stability constant of the electroneutral complex CaL$_2$ in nitrobenzene saturated with water, can be characterized by the chemical equilibrium

$$Ca^{2+}(aq) + 2HL(nb) \Leftrightarrow CaL_2(nb) + 2H^+(aq);$$
$$K_{ex}(Ca^{2+}, 2HL) \tag{1}$$
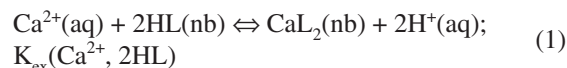
with the equilibrium extraction constant $K_{ex}(Ca^{2+}, 2HL)$:

$$K_{ex}(Ca^{2+}, 2HL) = \frac{[CaL_2]_{nb}[H^+]_{aq}^2}{[Ca^{2+}]_{aq}[HL]_{nb}^2} \tag{2}$$

where aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively.

It is necessary to emphasize that L[−] is a considerably hydrophobic anionic ligand, practically present in the nitrobenzene phase only, where it forms the very stable electroneutral species HL and CaL$_2$.

Taking into account the mass balances of the H^{+} and Ca^{2+} cations and the anionic ligand L[−] studied at equal volumes of the nitrobenzene and aqueous phases

$$[H^+]_{aq} + [HL]_{nb} = C_{HL}^{in,nb} \tag{3}$$

$$[Ca^{2+}]_{aq} + [CaL_2]_{nb} = C_{Ca(NO_3)_2}^{in,aq} \tag{4}$$

$$[HL]_{nb} + 2[CaL_2]_{nb} = C_{HL}^{in,nb} \tag{5}$$

as well as the measured equilibrium distribution ratio of calcium

$$D_{Ca} = [CaL_2]_{nb} / [Ca^{2+}]_{aq} \tag{6}$$

then combination of relationships (3) – (6) with Eq. (2) yielded the final expression for $K_{ex}(Ca^{2+}, 2HL)$ in the form

$$K_{ex}(Ca^{2+}, 2HL) =$$
$$= D_{Ca}^3 \left\{ \frac{2 C_{Ca(NO_3)_2}^{in,aq}}{(1 + D_{Ca}) C_{HL}^{in,nb} - 2D_{Ca} C_{Ca(NO_3)_2}^{in,aq}} \right\}^2 \tag{7}$$

where $C_{Ca(NO3)_2}^{in,aq}$ is the initial concentration of Ca(NO$_3$)$_2$ in the aqueous phase and $C_{HL}^{in,nb}$ denotes the initial concentration of HL in the nitrobenzene phase of the system under consideration.

In this study, from the extraction experiments and γ-activity measurements (see Experimental) by means of Eq. (7), the logarithm of the constant $K_{ex}(Ca^{2+}, 2HL)$ was determined: log $K_{ex}(Ca^{2+}, 2HL) = 0.0 \pm 0.1$.

Moreover, with respect to References 38 – 42, for the exchange extraction constant $K_{ex}(Ca^{2+}, 2H^+)$ corresponding to the equilibrium $Ca^{2+}(aq) + 2H^+(nb) \Leftrightarrow$

Ca^{2+}(nb) + 2H$^+$(aq) and for the extraction constant K_{ex} (Ca^{2+}, 2HL) defined above, as well as for the stability constants of the electroneutral species HL and CaL$_2$, denoted by β_{nb} (HL) and β_{nb} (CaL$_2$), respectively, one gets

$$\log \beta_{nb} (CaL_2) = 2 \log \beta_{nb} (HL) + \log K_{ex} (Ca^{2+}, 2HL) - \log K_{ex} (Ca^{2+}, 2H^+) \quad (8)$$

Finally, using the constants $\log K_{ex}$(Ca^{2+}, 2H$^+$) = 0.2[43] and $\log K_{ex}$ (Ca^{2+}, 2HL) given above, the value $\log \beta_{nb}$ (HL) = 5.6 ± 0.1,[44] and applying Eq. (8), we obtain the stability constant of the electroneutral complex species CaL$_2$ in water-saturated nitrobenzene at 25 °C as $\log \beta_{nb}$ (CaL$_2$) = 11.0 ± 0.2. In this context it should be noted that the stability constant of the cationic complex CaL$_2^{2+}$, where L denotes the electroneutral 15-crown-5 ligand, determined previously in the same nitrobenzene medium, is $\log \beta_{nb}$ (CaL$_2^{2+}$) = 11.57.[45] This means that the stabilities of the mentioned complexes CaL$_2$, where L$^-$ is the considered anionic ligand, and CaL$_2^{2+}$ (L = 15-crown-5) are comparable in nitrobenzene saturated with water.

4. Acknowledgements

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Povzetek

S pomočjo ekstrakcijskih eksperimentov in meritev γ-aktivnosti smo v dvofaznem sistemu voda-nitrobenzen raziskovali ravnotežje $Ca^{2+}(aq) + 2HL(nb) \Leftrightarrow CaL_2(nb) + 2H^+(aq)$ ($L^- =$ anionski ligand na osnovi cobaltovega bisdikarbolida, aq = vodna faza, nb = faza nitrobenzena). Določili smo konstanto ekstrakcije, log K_{ex} (Ca^{2+}, 2HL) = 0.0 ± 0.1 in konstanto stabilnosti kompleksov, β_{nb} (CaL_2), v vodni fazi, nasičeni z nitrobenzenom, log β_{nb} (CaL_2, 25 °C) = 11.0 ± 0.2.