Short communication

Stability Constants of Some Univalent Cation Complexes of Tetra-*tert*-butyl *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^+ (aq) + NaL^+ (nb) $\Leftrightarrow$ ML^+ (nb) + Na^+ (aq) taking place in the two–phase water–nitrobenzene system ($M^+ = Li^+$, NH_4^+, Ag^+, K^+ Rb^+, Tl^+, Cs^+; L = tetra-*tert*-butyl *p-tert*-butylcalix[4]arene tetraacetate; aq = aqueous phase, nb = nitrobenzene phase) were evaluated. Further, the stability constants of the ML^+ complexes in water saturated nitrobenzene were calculated; they were found to increase in the series $Cs^+ < Rb^+ < Tl^+ < K^+ < NH_4^+ < Ag^+ < Li^+$.

Keywords: Univalent cations, calix[4]arene, water-nitrobenzene system, extraction and stability constants

1. Introduction

Calixarene-based molecules have received intense attention in the last years. One of the most important features of these compounds is their diversity. Calixarenes find applications as selective binders and carriers, as analytical sensors, as catalysts and model structures for biomimetic studies.[1,2]

Recently, solvent extraction of Ba^{2+}, Pb^{2+} and Cd^{2+} into nitrobenzene by using strontium dicarbollylcobaltate and tetraethyl *p-tert*-butylcalix[4]arene tetraacetate has been investigated.[3] The aim of the present communication was to determine the stability constants of the complex species ML^+, where $M^+ = Li^+$, NH_4^+, Ag^+, K^+, Rb^+, Tl^+, Cs^+ and L is tetra-*tert*-butyl *p-tert*-butylcalix[4]arene tetraacetate (see Scheme 1), in nitrobenzene saturated with water.

2. Experimental

Tetra-*tert*-butyl *p-tert*-butylcalix[4]arene tetraacetate was synthesized as published in Reference 4. Cesium dicarbollylcobaltate, CsDCC, was supplied by Katchem, Řež, Czech Republic. A nitrobenzene solution of hydrogen dicarbollylcobaltate (HDCC)[5] was prepared from CsDCC by the method described in Reference 6. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The equilibration of the nitrobenzene solution of hydrogen dicarbollylcobaltate, HDCC, with stoichiometric NaOH, which was dissolved in an aqueous solution of NaCl (0.2 mol L^{-1}), yielded the corresponding solution in nitrobenzene. The radionuclide $^{22}Na^+$ (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 MNO_3 ($M^+ = Li^+$, NH_4^+, Ag^+, K^+, Rb^+, Tl^+, Cs^+) of the concentration in the range from 1×10^{-3} to 1×10^{-2} mol L^{-1} and microamounts of $^{22}Na^+$ were added to 2 mL of a nitrobenzene solution of tetra-*tert*-butyl *p-tert*-butylcalix[4]arene tetraacetate and NaDCC, whose initial concentrations varied also from 1×10^{-3} to 1×10^{-2} mol L^{-1} (in all experiments, the initial concentration of tetra-*tert*-butyl *p-tert*-butylcalix[4]arene tetraacetate in nitrobenzene, $C_L^{in,nb}$, was always equal to the initial concentration of NaDCC in this medium, $C_{NaDCC}^{in,\,nb}$). 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(T1) scintillation detector connected to a γ-analyzer NK/350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratio of sodium, D_{Na}, was determined as the ratio of the measured radioactivities of $^{22}Na^+$ in the nitrobenzene and aqueous samples.

3. Results and Discussion

Regarding the results of previous papers,[7–9] the two–phase water–MNO_3 ($M^+ = Li^+$, NH_4^+, Ag^+, K^+, Rb^+, Tl^+, Cs^+)-nitrobenzene- NaDCC extraction system can be described by the following general equilibrium

$$M^+(aq) + Na^+(nb) \Leftrightarrow M^+(nb) + Na^+(aq)\,; \qquad K_{ex}(M^+, Na^+) \tag{1}$$

with the corresponding exchange extraction constant K_{ex} (M^+, Na^+); aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively. For the constant K_{ex} (M^+, Na^+) one can write[7]

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

where $K_{M^+}^{i}$ and $K_{Na^+}^{i}$ are the individual extraction constants for M^+ and Na^+, respectively, in the water–nitrobenzene system.[7] Knowing the values log $K_{M^+}^{i}$ ($M^+ = Li^+$, Na^+, NH_4^+, Ag^+, K^+, Rb^+, Tl^+, Cs^+),[7,9] the single exchange extraction constants K_{ex} (M^+, Na^+) were simply calculated on the basis of Eq. (2). The corresponding data are given in Table 1.

In terms of previous papers,[7–11] the two-phase water-MNO_3 ($M^+ = Li^+$, NH_4^+, Ag^+, K^+, Rb^+, Tl^+, Cs^+)–nitrobenzene–L (L = tetra-*tert*-butyl *p-tert*-butylcalix[4]arene tetraacetate)-NaDCC extraction system (see Experimental), chosen for determination of stability of the complexes ML^+ in nitrobenzene saturated with water, can be characterized by the main chemical equilibrium

$$M^+(aq) + NaL^+(nb) \Leftrightarrow ML^+(nb) + Na^+(aq); \qquad K_{ex}(M^+, NaL^+) \tag{3}$$

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

$$K_{ex}(M^+, NaL^+) = \frac{[ML^+]_{nb}[Na^+]_{aq}}{[M^+]_{aq}[NaL^+]_{nb}} \tag{4}$$

It is necessary to emphasize that the tetra-*tert*-butyl *p-tert*-butylcalix[4]arene tetraacetate ligand forms – with the mentioned univalent cations – the very stable complexes ML^+ and NaL^+ in the nitrobenzene phase. Taking into account the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of the considered univalent cations at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratio of sodium, $D_{Na} = [NaL^+]_{nb} / [Na^+]_{aq}$, combined with Eq. (4), we gain the final expression for K_{ex} (M^+, NaL^+) in the form

$$K_{ex}(M^+, NaL^+) = \frac{1}{D_{Na}} \frac{C_{NaDCC}^{in,nb}}{(1 + D_{Na})\, C_{MNO_3}^{in,aq} - C_{NaDCC}^{in,nb}} \tag{5}$$

where $C_{MNO_3}^{in,\,aq}$ is the initial concentration of MNO_3 in the aqueous phase of the system under consideration.

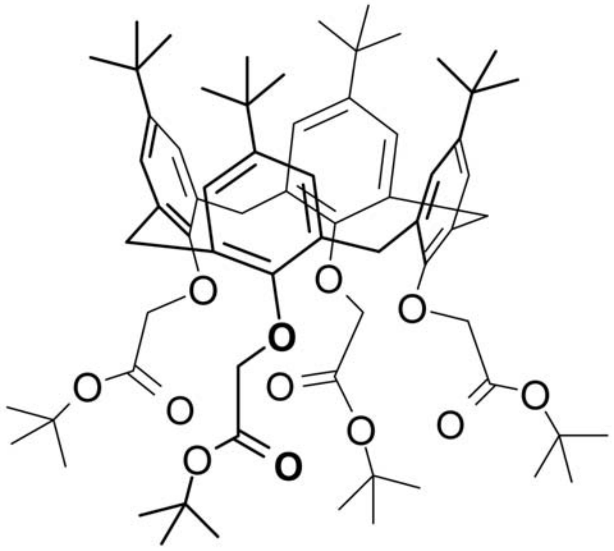
In this study, from the extraction experiments and γ-activity measurements by means of Eq. (5), the logarithms of the constants K_{ex} (M^+, NaL^+) ($M^+ = Li^+$, NH_4^+, Ag^+, K^+, Rb^+, Tl^+, Cs^+) were determined and given in Table 1.

Moreover, with respect to References 10 and 11, for the extraction constants K_{ex} (M^+, Na^+) and K_{ex} (M^+, NaL^+) defined above, as well as for the stability constants of the

Table 1. Equilibrium data for the M^+ and ML^+ cations in the two–phase water– nitrobenzene extraction system at 25 °C ($M^+ = Li^+$, Na^+, NH_4^+, Ag^+, K^+, Rb^+, Tl^+, Cs^+; L = tetra–*tert*–butyl *p–tert*–butylcalix[4]arene tetraacetate; for the meaning of the constants see text).

Quantity	Li^+	Na^+	NH_4^+	Ag^+	K^+	Rb^+	Tl^+	Cs^+
log $K_{M^+}^{i}$ [a]	–6.7	–6.0	–4.7	–4.5 [b]	–4.1	–3.4	–3.4 [b]	–2.7
log K_{ex} (M^+, Na^+) [c]	–0.7	–	1.3	1.5	1.9	2.6	2.6	3.3
log K_{ex} (M^+, NaL^+) [d]	–1.1	–	–0.6	–0.1	–0.4	–0.5	–0.4	–0.4
log β_{ex} (ML^+) [e]	10.8	11.2 [f]	9.3	9.6	8.9	8.1	8.2	7.5

[a] Ref. 7.
[b] Ref. 9.
[c] Calculated from Eq. (2) using data from Refs 7 and 9.
[d] Calculated from Eq. (5).
[e] Calculated from Eq. (6) using data from Refs 7, 9 and 12.
[f] Ref. 12.



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

complexes ML^+ and NaL^+ in nitrobenzene saturated with water, denoted by $\beta_{nb}(ML^+)$ and $\beta_{nb}(NaL^+)$, respectively, one gets

$$\log \beta_{nb}(ML^+) = \log \beta_{nb}(NaL^+) + \\ + \log K_{ex}(M^+, NaL^+) - \log K_{ex}(M^+, Na^+) \qquad (6)$$

Using the constants og K_{ex} (M^+, Na^+) and log K_{ex} (M^+, NaL^+) given in Table 1, the value log $\beta_{nb}(NaL^+)$ = 11.2 (L = tetra-*tert*-butyl *p*-*tert*-butylcalix[4]arene tetraacetate),[12] determined from the distribution of sodium picrate in the water–nitrobenzene system containing tetra-*tert*-butyl *p*-*tert*-butylcalix[4]arene tetraacetate, and applying Eq. (6), we obtain the stability constants of the complexes ML^+ ($M^+ = Li^+, NH_4^+, Ag^+, K^+, Rb^+, Tl^+, Cs^+$) in water saturated nitrobenzene. These data are also summarized in Table 1. Thus, the log $\beta_{nb}(ML^+)$ values from this table indicate that the stability of the complex cation ML^+ in nitrobenzene saturated with water increases in the $Cs^+ < Rb^+ < Tl^+ < K^+ < NH_4^+ < Ag^+ < Li^+ < Na^+$ order. Besides, as depicted in Fig. 1, the dependence of log $\beta_{nb}(ML^+)$ on the crystallographic radius of the alkali metal cation displays a maximum for $M^+ = Na^+$. In organic solvents, the occurrence of such maxima seems to be a general feature also in the case of the alkali metal complex formation with calix[4]arenes[13,14] similarly as in the case of cyclic or acyclic polyethers.[15]

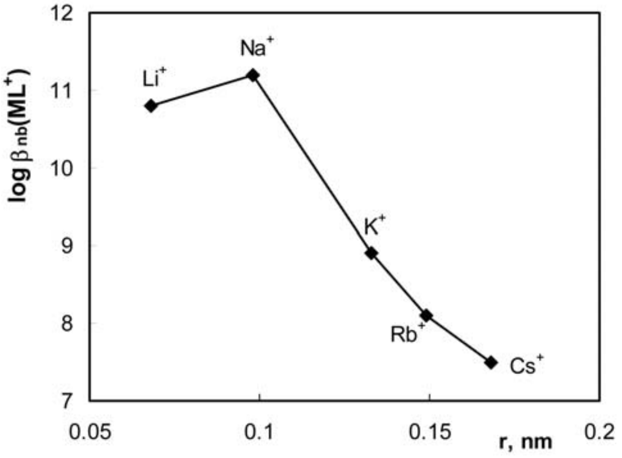


Figure 1. Dependence of the logarithm of the stability constant of the ML^+ complex cation ($M^+ = Li^+, Na^+, K^+ Rb^+, Cs^+$; L = tetra-*tert*-butyl *p*-*tert*-butylcalix[4]arene tetraacetate) in nitrobenzene saturated with water, log $\beta_{nb}(ML^+)$, on the crystallographic radius of the alkali metal cation M^+.

4. Acknowledgement

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5. References

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Povzetek

Iz podatkov, dobljenih pri eksperimentih ekstrakcije ter meritvah γ-aktivnosti, smo določili konstante ekstrakcijskih ravnotežij, ki jih za dvofazni sistem voda-nitrobenzen lahko zapišemo splošno kot $M^+(aq) + NaL^+(nb) \Leftrightarrow ML^+(nb) + Na^+(aq)$; ($M^+ = Li^+, NH_4^+, Ag^+, K^+, Rb^+, Tl^+, Cs^+$; L = tetra-*tert*-butil *p*-*tert*-butilcalix[4]aren tetraacetate; aq = vodna faza, nb = faza nitrobenzena). Izračunali smo konstante stabilnosti kompleksov tipa ML^+ v vodi, nasičeni z nitrobenzenom. Izkaže se, da konstante stabilnosti naraščajo v smeri $Cs^+ < Rb^+ < Tl^+ < K^+ < NH_4^+ < Ag^+ < Li^+$.