Stability constants of the Li$^+$, Na$^+$, H$_3$O$^+$, NH$_4^+$, Ag$^+$, and K$^+$ complexes of the *cone* conformer of tetraethyl *p-tert*-butyltetrathiacalix[4]arene tetraacetate in nitrobenzene saturated with water

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Abstract From extraction experiments in the two-phase water–nitrobenzene system and γ-activity measurements, the stability constants of the tetraethyl *p-tert*-butyltetrathiacalix[4]arene tetraacetate (*cone*)·M$^+$ complexes (M$^+$ = Li$^+$, H$_3$O$^+$, NH$_4^+$, Ag$^+$, or K$^+$) were determined in water-saturated nitrobenzene. It was found that these constants increase in the cation order NH$_4^+$ < K$^+$ < H$_3$O$^+$ < Ag$^+$ < Li$^+$ < Na$^+$.

Keywords Calixarenes · Macrocycles · Complexation · Univalent cations · Stability constants

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 building blocks for the construction of more sophisticated molecular systems. Their unique 3D pre-organization makes them very attractive as receptors for the complexation of cations, anions, and even neutral molecules [1].

The well-established chemistry of the "classical" calix[*n*]arenes family has been "rejuvenated" by the discovery of so-called thiacalix[4]arenes. The presence of four sulfur atoms instead of methylene groups makes thiacalix[4]arenes [2] very promising molecules with many novel features if their chemistry is compared with that of "classical" calixarenes.

Recently, the interactions of some cations with "classical" calixarenes have been investigated by using solvent-extraction methods and DFT calculations [3–13]. In the current work, the stability constants of the **1**·M$^+$ complex species, where M$^+$ = Li$^+$, H$_3$O$^+$, NH$_4^+$, Ag$^+$, or K$^+$ and **1** is the *cone* conformer of tetraethyl *p-tert*-butyltetrathiacalix[4]arene tetraacetate (Scheme 1), are evaluated in the organic phase of the water–nitrobenzene extraction system.

Results and discussion

On the basis of previous results [14–16], the two-phase water–MNO$_3$ (M$^+$ = Li$^+$, H$^+$, NH$_4^+$, Ag$^+$, or K$^+$)–nitrobenzene–sodium dicarbollylcobaltate (NaDCC) extraction system can be described by the equilibrium represented by Eq. 1 with the corresponding exchange extraction constant K_{ex} (M$^+$, Na$^+$), where "aq" and "nb" denote the presence of the species in the aqueous and nitrobenzene phases.

$$M^+(aq) + Na^+(nb) \rightleftarrows M^+(nb) + Na^+(aq); K_{ex}(M^+, Na^+) \tag{1}$$
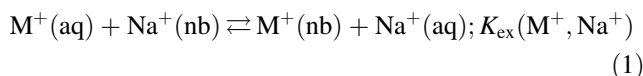
For the constant K_{ex} (M$^+$, Na$^+$) one can write Eq. 2 where $K_{M^+}^i$ and $K_{Na^+}^i$ are the individual extraction constants for M$^+$ and Na$^+$ in the water–nitrobenzene system [14, 16].

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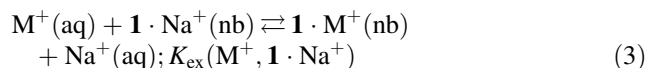Nuclear Research Institute, Řež, Czech Republic
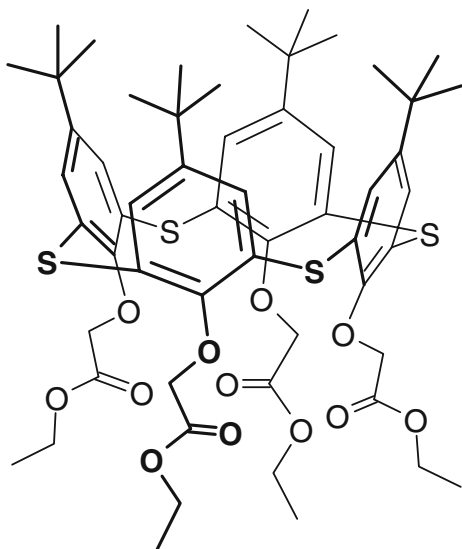
Scheme 1

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

Knowing the values of $\log K_{M^+}^i$ ($M^+ = Li^+$, Na^+, H^+, NH_4^+, Ag^+, or K^+) [14, 16], we calculated the single exchange extraction constants $K_{\text{ex}}(M^+, Na^+)$ on the basis of Eq. 2. The corresponding data are given in Table 1.

On the basis of previous results [17–19], the two-phase water–MNO_3 ($M^+ = Li^+$, H^+, NH_4^+, Ag^+, or K^+)–nitrobenzene–**1**–NaDCC extraction system (see "Experimental"), chosen for determination of the stability of the complex **1**·M^+ in water-saturated nitrobenzene, can be characterized by the main chemical equilibrium (Eq. 3) to which the general equilibrium extraction constant shown by Eq. 4 corresponds.

Table 1 Equilibrium data for the M^+ and **1**·M^+ cations in the two-phase water–nitrobenzene extraction system at 25 °C (for the meaning of the constants see the text)

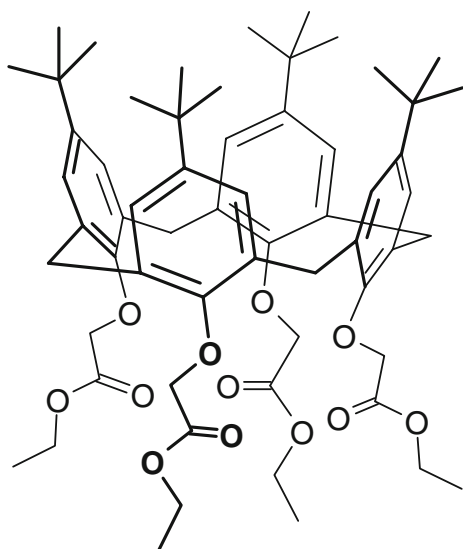| Quantity	M^+					
	Li^+	Na^+	H_3O^+	NH_4^+	Ag^+	K^+
$\log K_{M^+}^i$ [a]	−6.7	−6.0	−5.7	−4.7	−4.5[b]	−4.1
$\log K_{\text{ex}}(M^+, Na^+)$[c]	−0.7	–	0.3	1.3	1.5	1.9
$\log K_{\text{ex}}(M^+, \mathbf{1}\cdot Na^+)$[d]	−1.1	–	−0.8	−0.6	1.0	0.1
$\log \beta_{\text{nb}}(\mathbf{1}\cdot M^+)$[e]	5.8	6.2[f]	5.1	4.3	5.7	4.4

[a] Ref. [14]

[b] Ref. [16]

[c] Calculated from Eq. 2 using data from Refs. [14, 16]

[d] Calculated from Eq. 5

[e] Calculated from Eq. 6 using data from Refs. [14, 16]

[f] Unpublished results

$$M^+(aq) + \mathbf{1}\cdot Na^+(nb) \rightleftarrows \mathbf{1}\cdot M^+(nb)$$
$$+ Na^+(aq); K_{\text{ex}}(M^+, \mathbf{1}\cdot Na^+) \qquad (3)$$

$$K_{\text{ex}}(M^+, \mathbf{1}\cdot Na^+) = \frac{[\mathbf{1}\cdot M^+]_{\text{nb}}[Na^+]_{\text{aq}}}{[M^+]_{\text{aq}}[\mathbf{1}\cdot Na^+]_{\text{nb}}} \qquad (4)$$

It is necessary to emphasize that **1** is an extremely hydrophobic ligand, practically present in the nitrobenzene phase only, where this ligand forms relatively stable complexes **1**·M^+ and **1**·Na^+ with the univalent cations mentioned. Taking into account the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of these univalent cations for equal volumes of the nitrobenzene and aqueous phases, and the measured equilibrium distribution ratio of sodium, $D_{Na} = [\mathbf{1}\cdot Na^+]_{\text{nb}}/[Na^+]_{\text{aq}}$, combined with Eq. 4, we obtain the final expression for the exchange extraction constant (Eq. 5); $C_{MNO_3}^{\text{in,aq}}$ is the initial concentration of MNO_3 ($M^+ = Li^+$, H^+, NH_4^+, Ag^+, or K^+) in the aqueous phase and $C_{NaDCC}^{\text{in,nb}}$ denotes the initial concentration of NaDCC in the organic phase of the system under consideration.

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

In this study, from the extraction experiments and γ-activity measurements (see "Experimental") by means of Eq. 5, the logarithms of the constants $K_{\text{ex}}(M^+, \mathbf{1}\cdot Na^+)$ were determined as reviewed in Table 1. Moreover, on the basis of Refs. [17–19], for the extraction constants $K_{\text{ex}}(M^+, Na^+)$ and $K_{\text{ex}}(M^+, \mathbf{1}\cdot Na^+)$ defined above, and for the stability constants of the complexes **1**·M^+ and **1**·Na^+ in nitrobenzene saturated with water, denoted by $\beta_{\text{nb}}(\mathbf{1}\cdot M^+)$ and $\beta_{\text{nb}}(\mathbf{1}\cdot Na^+)$, one obtains Eq. 6.

$$\log \beta_{\text{nb}}(\mathbf{1}\cdot M^+) = \log \beta_{\text{nb}}(\mathbf{1}\cdot Na^+) + \log K_{\text{ex}}(M^+, \mathbf{1}\cdot Na^+)$$
$$- \log K_{\text{ex}}(M^+, Na^+) \qquad (6)$$

Finally, using the constants $K_{\text{ex}}(M^+, Na^+)$ and $K_{\text{ex}}(M^+, \mathbf{1}\cdot Na^+)$ given in Table 1, $\log \beta_{\text{nb}}(\mathbf{1}\cdot Na^+) = 6.2$ (unpublished results), determined from the distribution of sodium picrate in the water–nitrobenzene system containing **1**, and applying Eq. 6, we obtain the stability constants of the complexes **1**·M^+ ($M^+ = Li^+$, H_3O^+, NH_4^+, Ag^+, or K^+) in nitrobenzene saturated with water at 25 °C. These data are also summarized in Table 1. Thus, the $\beta_{\text{nb}}(\mathbf{1}\cdot M^+)$ values from this table indicate that the stability of the complex cation **1**·M^+ in nitrobenzene saturated with water increases in the order $NH_4^+ < K^+ < H_3O^+ < Ag^+ < Li^+ < Na^+$.

In conclusion, it should be noted that the stability constants of the complexes **2**·M^+ ($M^+ = Li^+$, Na^+, or K^+; **2** = tetraethyl *p-tert*-butylcalix[4]arene tetraacetate; Scheme 2) in water-saturated nitrobenzene are $\log \beta_{\text{nb}}$

Scheme 2

($\mathbf{2} \cdot$Li$^+$) = 8.5 [5], log β_{nb} ($\mathbf{2} \cdot$Na$^+$) = 9.2 [5] and log β_{nb} ($\mathbf{2} \cdot$K$^+$) = 6.1 [5]. A means that in this medium the presence of four sulfur atoms in the considered ligand $\mathbf{1}$ (Scheme 1) instead of the four methylene groups in $\mathbf{2}$ (Scheme 2) reduces the stability of the respective cationic complex species $\mathbf{1} \cdot$M$^+$, where M$^+$ = Li$^+$, Na$^+$, or K$^+$, as follows from Table 1.

Experimental

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) [15] was prepared from CsDCC by the method described elsewhere [20]. Equilibration of the nitrobenzene solution of HDCC with stoichiometric NaOH, which was dissolved in an aqueous solution of NaCl (0.2 M), yielded the corresponding NaDCC solution in nitrobenzene. Compound $\mathbf{1}$ was supplied by Dr M. Kyrš, Prague. The radionuclide ^{22}Na$^+$ (DuPont, Belgium) was of standard radiochemical purity.

The extraction experiments were performed in 10 cm^3 glass test-tubes with polyethylene stoppers: 2 cm^3 of an aqueous solution of MNO$_3$ (M$^+$ = Li$^+$, H$^+$, NH$_4^+$, Ag$^+$, or K$^+$) with a concentration in the range 5×10^{-3} to 1×10^{-2} M and micro amounts of ^{22}Na$^+$ were added to 2 cm^3 of a nitrobenzene solution of $\mathbf{1}$ and NaDCC, the initial concentrations of which varied also from 5×10^{-3} to 1×10^{-2} M (in all experiments, the initial concentration of $\mathbf{1}$ in nitrobenzene, $C_1^{in,nb}$, 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 h at 25 ± 1 °C, using a laboratory shaker. The phases were then separated by centrifugation. Afterwards, 1 cm^3 samples were taken from each phase and their γ-activities were measured using a well-type NaI(Tl) scintillation detector connected to an NK 350 γ-analyser (Gamma, Budapest, Hungary).

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

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