

Solvent extraction of univalent cations into nitrobenzene using sodium dicarbollylcobaltate and tetraphenyl *p*-*tert*-butylcalix[4]arene tetraketone

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Abstract From extraction experiments and γ -activity measurements, the exchange extraction constants corresponding to the equilibrium $M^+(\text{aq}) + \mathbf{1} \cdot \text{Na}^+(\text{nb}) \rightleftharpoons \mathbf{1} \cdot M^+(\text{nb}) + \text{Na}^+(\text{aq})$ taking place in the two-phase water-nitrobenzene system ($M^+ = \text{Li}^+, \text{H}_3\text{O}^+, \text{NH}_4^+, \text{Ag}^+, \text{K}^+, \text{Rb}^+, \text{Tl}^+, \text{Cs}^+$; $\mathbf{1}$ = tetraphenyl *p*-*tert*-butylcalix[4]arene tetraketone; aq = aqueous phase, nb = nitrobenzene phase) were evaluated. Moreover, the stability constants of the $\mathbf{1} \cdot M^+$ complexes in water saturated nitrobenzene were calculated; they were found to increase in the order $\text{Cs}^+ < \text{Rb}^+ < \text{Tl}^+ < \text{K}^+ < \text{NH}_4^+ < \text{Ag}^+ < \text{H}_3\text{O}^+ < \text{Li}^+$.

Keywords Calixarenes; Macrocycles; Complexation; Univalent cations; Stability constants.

Introduction

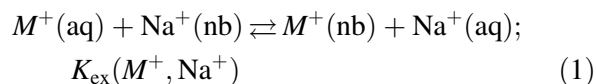
Calixarene-based molecules have received intense attention in the recent decades. One of the most important features of these compounds is their diversity. Calixarenes find applications as selective binders and carriers, analytical sensors, catalysts, and model structures for biomimetic studies [1, 2].

Recently, the interactions of the H_3O^+ cation with some calix[4]arenes have been investigated [3–6]. In

the present work, the stability constants of some univalent cations with tetraphenyl *p*-*tert*-butylcalix[4]arene tetraketone (**1**) (*cf.* Scheme 1) are determined in nitrobenzene saturated with water.

Results and discussion

With regard to the previous results [7, 8], the two-phase water- MNO_3 ($M^+ = \text{Li}^+, \text{H}^+, \text{NH}_4^+, \text{Ag}^+, \text{K}^+, \text{Rb}^+, \text{Tl}^+, \text{Cs}^+$)/nitrobenzene-sodium dicarbollylcobaltate (NaDCC) extraction system can be described by the following equilibrium (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.

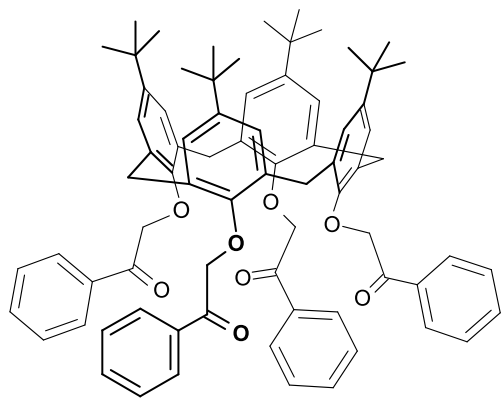


For the constant $K_{\text{ex}}(M^+, \text{Na}^+)$ one can write Eq. (2) where $K_{M^+}^i$ and $K_{\text{Na}^+}^i$ are the individual extraction constants for M^+ and Na^+ in the water-nitrobenzene system [7, 8].

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

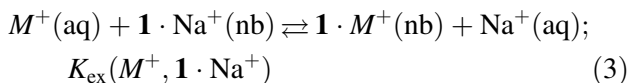
Knowing the values $\log K_{M^+}^i$ ($M^+ = \text{Li}^+, \text{Na}^+, \text{H}_3\text{O}^+, \text{NH}_4^+, \text{Ag}^+, \text{K}^+, \text{Rb}^+, \text{Tl}^+, \text{Cs}^+$) [7, 8], we calculated the single exchange extraction constants $K_{\text{ex}}(M^+, \text{Na}^+)$ on the basis of Eq. (2). The corresponding data are given in Table 1.

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Tetraphenyl *p*-*tert*-butylcalix[4]arene tetraketone (**1**)

Scheme 1

In terms of previous papers [9–12], the two-phase water- MNO_3 ($M^+ = Li^+, H^+, NH_4^+, Ag^+, K^+, Rb^+, Tl^+, Cs^+$)/nitrobenzene-**1**-NaDCC extraction system (see Experimental Section), chosen for determination of stability of the complex $\mathbf{1} \cdot M^+$ in water saturated nitrobenzene, can be characterized by the main chemical equilibrium (3) to which the general equilibrium extraction constant as shown by Eq. (4) corresponds.



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

It is necessary to emphasize that **1** is a considerably hydrophobic ligand, practically present in the nitrobenzene phase only, where this ligand forms the very stable complexes $\mathbf{1} \cdot M^+$ and $\mathbf{1} \cdot Na^+$ with the mentioned univalent cations. 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, $D_{Na} = [\mathbf{1} \cdot Na^+]_{nb} / [Na^+]_{aq}$, combined with Eq. (4), we obtain the final expression for the exchange extraction constant (Eq. (5)); $C_{MNO_3}^{in, aq}$ is the initial concentration of MNO_3 ($M^+ = Li^+, H^+, NH_4^+, Ag^+, K^+, Rb^+, Tl^+, Cs^+$) in the aqueous phase and $C_{NaDCC}^{in, nb}$ denotes the initial concentration of NaDCC in the organic phase of the system under consideration.

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

In this study, from the extraction experiments and γ -activity measurements by using Eq. (5), the logarithms of the constants $K_{ex}(M^+, \mathbf{1} \cdot Na^+)$ were determined and given in Table 1.

Furthermore, with respect to Refs. [9–12], for the extraction constants $K_{ex}(M^+, Na^+)$ and $K_{ex}(M^+, \mathbf{1} \cdot Na^+)$ defined above, as well as for the stability constants of the complexes $\mathbf{1} \cdot M^+$ and $\mathbf{1} \cdot Na^+$ in nitrobenzene saturated with water, denoted by $\beta_{nb}(\mathbf{1} \cdot M^+)$ and $\beta_{nb}(\mathbf{1} \cdot Na^+)$, one gets Eq. (6).

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

Using the constants $\log K_{ex}(M^+, Na^+)$ and $\log K_{ex}(M^+, \mathbf{1} \cdot Na^+)$ given in Table 1, $\log \beta_{nb}(\mathbf{1} \cdot Na^+) = 10.5$ [13], 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 $\mathbf{1} \cdot M^+$ ($M^+ = Li^+, H_3O^+, NH_4^+, Ag^+, K^+, Rb^+, Tl^+, Cs^+$) in nitrobenzene saturated with water at 25°C. These data are also sum-

Table 1 Equilibrium data for the M^+ and $\mathbf{1} \cdot M^+$ cations in the two-phase water/nitrobenzene extraction system at 25°C (for the meaning of the constants see text)

Quantity	M^+								
	Li^+	Na^+	H_3O^+	NH_4^+	Ag^+	K^+	Rb^+	Tl^+	Cs^+
$\log K_{M^+}^i$ ^a	−6.7	−6.0	−5.7	−4.7	−4.5 ^b	−4.1	−3.4	−3.4 ^b	−2.7
$\log K_{ex}(M^+, Na^+)$ ^c	−0.7	–	0.3	1.3	1.5	1.9	2.6	2.6	3.3
$\log K_{ex}(M^+, \mathbf{1} \cdot Na^+)$ ^d	−0.9	–	−0.6	−0.4	0.0	−0.3	−0.4	−0.1	−0.4
$\log \beta_{nb}(\mathbf{1} \cdot M^+)$ ^e	10.3	10.5 ^f	9.6	8.8	9.0	8.3	7.5	7.8	6.8

^a Ref. [7]; ^b Ref. [8]; ^c Calculated from Eq. (2) using data from Refs. [7, 8]; ^d Calculated from Eq. (5); ^e Calculated from Eq. (6) using data from Refs. [7, 8, 13]; ^f Ref. [13]

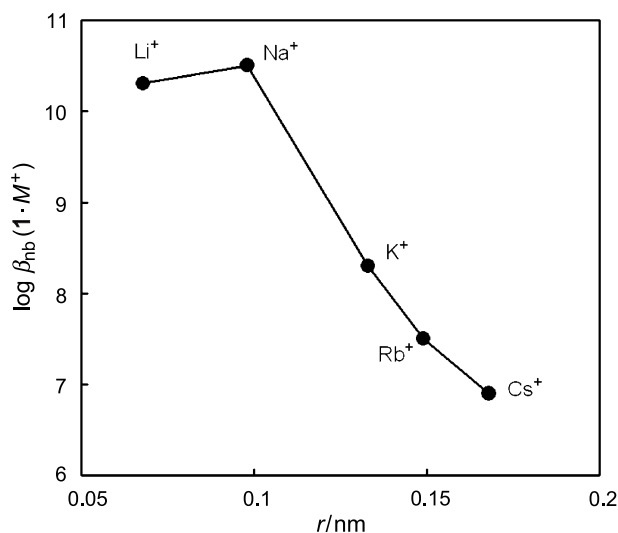


Fig. 1 Dependence of the logarithm of the stability constant of the $1 \cdot M^+$ complex cation ($M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+$) in nitrobenzene saturated with water, $\log \beta_{nb}(1 \cdot M^+)$, on the crystallographic radius of the alkali metal cation M^+

marized in Table 1. Thus, the $\log \beta_{nb}(1 \cdot M^+)$ values from this table indicate that the stability of the complex cation $1 \cdot M^+$ in nitrobenzene saturated with water increases in the series $Cs^+ < Rb^+ < Tl^+ < K^+ < NH_4^+ < Ag^+ < H_3O^+ < Li^+ < Na^+$. Besides, as depicted in Fig. 1, the dependence of $\log \beta_{nb}(1 \cdot M^+)$ 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 alkali metal complex formation with calix[4]arenes [14, 15] similarly as in the case of cyclic or acyclic polyethers [16].

Experimental

Caesium dicarbollylcobaltate was supplied by Katchem, Řež, Czech Republic. A nitrobenzene solution of HDCC [17] was prepared from CsDCC by the method described elsewhere [18]. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The equilibration of the nitrobenzene solution of HDCC with stoichiometric NaOH, which was dissolved in an aqueous solution of $NaNO_3$ (0.2M), yielded the corresponding NaDCC solution in nitrobenzene. Compound **1** was synthesized using the procedures described elsewhere [19]. The radionuclide $^{22}Na^+$ (DuPont, Belgium) was of standard radiochemical purity.

The extraction experiments were carried out in 10 cm³ glass test-tubes covered with polyethylene stoppers: 2 cm³ of an aqueous solution of MNO_3 ($M^+ = Li^+, H^+, NH_4^+, Ag^+, K^+, Rb^+, Tl^+, Cs^+$) of the concentration in the range from $1 \times$

10^{-3} to 1×10^{-2} M and microamounts of $^{22}Na^+$ were added to 2 cm³ of a nitrobenzene solution of **1** and NaDCC, whose initial concentrations varied also from 1×10^{-3} to 1×10^{-2} M (in all experiments, the initial concentration of **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 24 h at $25 \pm 1^\circ C$, using a laboratory shaker. Then the phases were separated by centrifugation. Afterwards, 1 cm³ 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 sodium, D_{Na} , was determined as the ratio of the measured radioactivities of $^{22}Na^+$ in the nitrobenzene and aqueous samples.

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