



Interaction of the cesium cation with hexaethyl calix[6]arene hexaacetate: Extraction and DFT study



Emanuel Makrlík^a, Stanislav Böhm^b, Petr Vaňura^{b,*}

^a Faculty of Environmental Sciences, Czech University of Life Sciences, Prague, Czech Republic

^b University of Chemistry and Technology, Prague, Czech Republic

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ABSTRACT

On the basis of extraction experiments and γ -activity measurements, the extraction constant corresponding to the equilibrium $\text{Cs}^+(\text{aq}) + \text{A}^-(\text{aq}) + \mathbf{1}(\text{nb}) \rightleftharpoons \mathbf{1}\cdot\text{Cs}^+(\text{nb}) + \text{A}^-(\text{nb})$ occurring in the two-phase water–nitrobenzene system ($\mathbf{1}$ = hexaethyl calix[6]arene hexaacetate; A^- = picrate, aq = aqueous phase, nb = nitrobenzene phase) was evaluated as $\log K_{\text{ex}}(\mathbf{1}\cdot\text{Cs}^+, \text{A}^-) = 6.8 \pm 0.1$. Further, the very high stability constant of the $\mathbf{1}\cdot\text{Cs}^+$ complex in nitrobenzene saturated with water was calculated for a temperature of 25 °C: $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Cs}^+) = 8.7 \pm 0.1$. Finally, applying quantum mechanical DFT calculations, the most probable structure of the proven $\mathbf{1}\cdot\text{Cs}^+$ cationic complex species was derived. In the resulting complex, the “central” cation Cs^+ is bound by six very strong bonding interactions to the corresponding six oxygen atoms of the parent ligand $\mathbf{1}$. The interaction energy of the considered $\mathbf{1}\cdot\text{Cs}^+$ complex was found to be -308.0 kJ/mol, confirming the formation of this complex as well.

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1. Introduction

Calixarenes are a well-known family of macrocyclic molecules with many potential applications in various branches of chemistry and biology. Because of their one-pot preparation, easy derivatization and unique complexation abilities, calixarenes are widely used as the building blocks for the construction of more sophisticated molecular systems. Their unique three-dimensional pre-organization makes them very attractive as the receptors for the complexation of cations, anions, and even neutral molecules. Calixarenes find applications as selective binders and carriers, as analytical sensors, as catalysts and model structures for biomimetic studies [1,2], and finally, as effective and selective extractants for nuclear waste treatment [3,4].

New cesium-selective extractants, especially from the calixarene-crown-6 and the calixarene-bis(crown-6) families, have been introduced [3,5–10]. The corresponding crystal structures of model complexes with cesium salts have demonstrated significant π -interaction between the facing aromatic rings and the Cs^+ guest cation [3,5,6]. Besides, the calix[4]arene-crown-6 family of the mentioned compounds gives Cs^+/Na^+ separation factors exceeding 10^4 [5].

In the current work, the solvent extraction of cesium picrate (abbrev. CsA) into nitrobenzene by means of hexaethyl calix[6]arene hexaacetate (abbrev. $\mathbf{1}$; see Scheme 1) was investigated. Furthermore, the stability constant of the proven cationic complex species $\mathbf{1}\cdot\text{Cs}^+$ in the organic phase of the water–nitrobenzene extraction system was

determined. Finally, employing quantum mechanical DFT calculations, the most probable structure of the considered $\mathbf{1}\cdot\text{Cs}^+$ complex was solved.

2. Experimental section

2.1. Chemicals

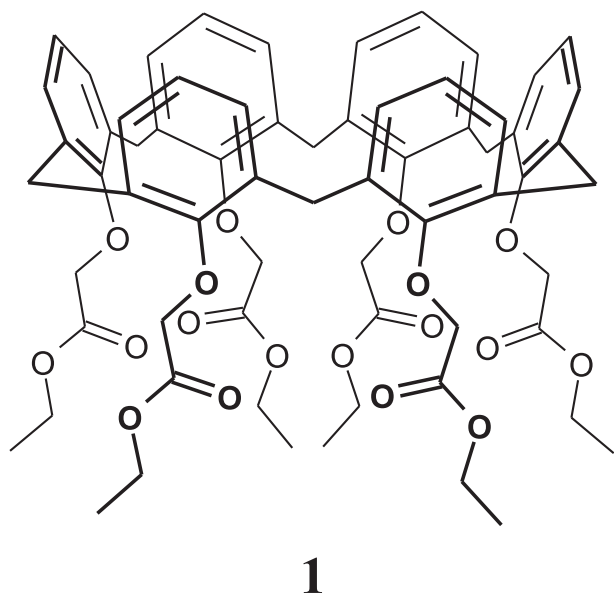
Compound $\mathbf{1}$ (purity, $\geq 98\%$; see Scheme 1) was supplied by Fluka and it was employed as received. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. A solution of cesium picrate, CsA, in water was prepared by dissolving a stoichiometric amount of picric acid in an aqueous solution of CsOH. The carrier-free radionuclide $^{137}\text{Cs}^+$ (in the chemical form of $^{137}\text{Cs}^+\text{Cl}^-$) was purchased from Techsnaveksport, Russia; its radionuclidic purity was 99.9%.

2.2. Extraction

The extraction experiments were carried out in 10 mL polypropylene test-tubes with polypropylene stoppers: 2 mL of an aqueous solution of CsA (A^- = picrate) of the concentration in the range from 1×10^{-3} to 3×10^{-3} mol/L and 10 kBq of $^{137}\text{Cs}^+$ (in the form of $^{137}\text{Cs}^+\text{Cl}^-$) were added to 2 mL of a nitrobenzene solution of $\mathbf{1}$, the initial concentration of which varied from 2×10^{-3} to 6×10^{-3} mol/L (in all experiments, the initial concentration of $\mathbf{1}$ in nitrobenzene, $C_{\mathbf{1}}^{\text{in,nb}}$, was always higher than the initial concentration of CsA in water, $C_{\text{CsA}}^{\text{in,aq}}$). The test-tubes filled with the solutions were shaken for 3 h at 25 ± 1 °C, using a laboratory shaker. Then the phases were separated by

* Corresponding author.

E-mail address: petr.vanura@vscht.cz (P. Vaňura).



Scheme 1. Structural formula of hexaethyl calix[6]arene hexaacetate (abbrev. **1**).

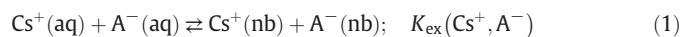
centrifugation. Finally, 1 mL samples were taken from each phase and their γ -activities were measured by means of a well-type NaI(Tl) scintillation detector connected to a γ -analyzer Triathler (Hidex, Turku, Finland).

The equilibrium distribution ratios of cesium, D_{Cs} , were determined as the ratios of the measured radioactivities of $^{137}Cs^+$ in the nitrobenzene and aqueous samples.

3. Results and discussion

3.1. Extraction experiments

Regarding the results of previous papers [11,12], the two-phase water–CsA ($A^- = \text{picrate}$)–nitrobenzene extraction system can be described by the following equilibrium

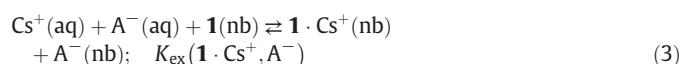


with the corresponding extraction constant $K_{ex}(Cs^+, A^-)$; aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively. For the constant $K_{ex}(Cs^+, A^-)$ one can write [11]

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

where $K_{Cs^+}^i$ and $K_{A^-}^i$ are the individual extraction constants for Cs^+ and A^- , respectively, in the water–nitrobenzene system [11]. Knowing the values $\log K_{Cs^+}^i = -2.7$ [11] and $\log K_{A^-}^i = 0.8$ ($A^- = \text{picrate}$) [11], the extraction constant $K_{ex}(Cs^+, A^-)$ was simply calculated from Eq. (2) as $\log K_{ex}(Cs^+, A^-) = -1.9$.

Our previous results [13,14] indicated that the two-phase water–CsA ($A^- = \text{picrate}$)–nitrobenzene–**1** (hexaethyl calix[6]arene hexaacetate) extraction system, chosen for determination of the stability constant of the complex $\mathbf{1} \cdot Cs^+$ in nitrobenzene saturated with water (see Experimental section), can be characterized by the main chemical equilibrium



to which the equilibrium extraction constant

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

corresponds. It is necessary to emphasize that **1** is a considerably lipophilic ligand, practically present in the nitrobenzene phase only, where this ligand forms – with the Cs^+ cation – the very stable complex $\mathbf{1} \cdot Cs^+$, as given below.

Applying the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of **1** and CsA ($A^- = \text{picrate}$) at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratio of cesium, $D_{Cs} = [\mathbf{1} \cdot Cs^+]_{nb} / [Cs^+]_{aq}$, combined with Eq. (4), we gain the final expression for the extraction constant $K_{ex}(\mathbf{1} \cdot Cs^+, A^-)$:

$$K_{ex}(\mathbf{1} \cdot Cs^+, A^-) = D_{Cs}^2 / \left\{ C_{\mathbf{1}}^{in,nb} - \frac{D_{Cs}}{1 + D_{Cs}} C_{CsA}^{in,aq} \right\} \quad (5)$$

where $C_{CsA}^{in,aq}$ is the initial concentration of CsA in the aqueous phase and $C_{\mathbf{1}}^{in,nb}$ denotes the initial concentration of **1** in the organic phase of the system under consideration.

In this work, from the extraction experiments and γ -activity measurements (see Experimental section) by means of Eq. (5), the following value of the constant $K_{ex}(\mathbf{1} \cdot Cs^+, A^-)$ was determined: $\log K_{ex}(\mathbf{1} \cdot Cs^+, A^-) = 6.8 \pm 0.1$ (see Table 1). This constant experimentally proves the justifying of the extraction mechanism and the presentation of the corresponding species, expressed by the two-phase chemical equilibrium (3).

Moreover, with respect to our previous results [13,14], for the extraction constants $K_{ex}(Cs^+, A^-)$ and $K_{ex}(\mathbf{1} \cdot Cs^+, A^-)$ defined above, as well as for the stability constant of the complex $\mathbf{1} \cdot Cs^+$ in nitrobenzene saturated with water, denoted by $\beta_{nb}(\mathbf{1} \cdot Cs^+)$, corresponding to the equilibrium $\mathbf{1}(nb) + Cs^+(nb) \rightleftharpoons \mathbf{1} \cdot Cs^+(nb)$, one gets

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

Using the constants $\log K_{ex}(Cs^+, A^-)$ and $\log K_{ex}(\mathbf{1} \cdot Cs^+, A^-)$ given above, and applying Eq. (6), we obtain the stability constant of the $\mathbf{1} \cdot Cs^+$ complex in water-saturated nitrobenzene at 25 °C as $\log \beta_{nb}(\mathbf{1} \cdot Cs^+) = 8.7 \pm 0.1$. In this context it should be noted that the stability constant of the complex species $\mathbf{2} \cdot Cs^+$, where **2** denotes 1,3-alternate-25,27-bis(1-octyloxy)calix[4]arene-crown-6 (see Scheme 2), in nitrobenzene saturated with water is $\log \beta_{nb}(\mathbf{2} \cdot Cs^+) = 8.8 \pm 0.1$, as reported recently [15]. It means that in this nitrobenzene medium, the stabilities of the considered cationic complexes $\mathbf{1} \cdot Cs^+$ and $\mathbf{2} \cdot Cs^+$ are nearly the same.

3.2. Quantum mechanical DFT calculations

The theoretical calculations were performed at the density functional level of theory (DFT, B3LYP functional) [16,17], employing the Gaussian 09 suite of programs [18]. The LanL2DZ basis set was used and the optimizations were unconstrained. In order to increase the numerical accuracy and to reduce oscillations during the molecular geometry optimization, two-electron integrals and their derivatives

Table 1

Experimental data concerning determination of $\log K_{ex}(\mathbf{1} \cdot Cs^+, A^-)$ on the basis of Eq. (5).

| $C_{CsA}^{in,aq}$ (mol/L) | $C_{\mathbf{1}}^{in,nb}$ (mol/L) | D_{Cs} | $\log K_{ex}(\mathbf{1} \cdot Cs^+, A^-)$ |
|---------------------------|----------------------------------|----------|---|
| 1.0×10^{-3} | 2.0×10^{-3} | 82.7 | 6.8 |
| 1.5×10^{-3} | 3.0×10^{-3} | 105.1 | 6.9 |
| 2.0×10^{-3} | 4.0×10^{-3} | 123.8 | 6.9 |
| 2.5×10^{-3} | 5.0×10^{-3} | 131.6 | 6.8 |
| 3.0×10^{-3} | 6.0×10^{-3} | 128.3 | 6.7 |

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