

# Experimental Evidence for a Calix[4]arene-Proton Complex

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**Summary.** From extraction experiments and  $\gamma$ -activity measurements, the extraction constant corresponding to the equilibrium  $\text{H}^+(\text{aq}) + \mathbf{1}\cdot\text{Na}^+(\text{nb}) \rightleftharpoons \mathbf{1}\cdot\text{H}^+(\text{nb}) + \text{Na}^+(\text{aq})$  taking place in the two-phase water-nitrobenzene system ( $\mathbf{1} = p$ -tert-butylcalix[4]arene-tetrakis(*N,N*-diethylacetamide)); aq = aqueous phase, nb = nitrobenzene phase) was evaluated as  $\log K_{\text{ex}}(\text{H}^+, \mathbf{1}\cdot\text{Na}^+) = -1.4 \pm 0.1$ . Further, the stability constant of the *p*-tert-butylcalix[4]arene-tetrakis(*N,N*-diethylacetamide)- $\text{H}^+$  complex in water saturated nitrobenzene was calculated for a temperature of 25°C as  $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{H}^+) = 8.1 \pm 0.1$ .

**Keywords.** Calixarenes; Macrocycles; Protonation; Stability constant; *p*-tert-Butylcalix[4]arene-tetrakis(*N,N*-diethylacetamide).

## Introduction

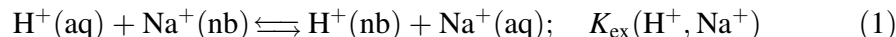
Calixarenes are macrocyclic compounds, which are not only easily available on a large scale, but also offer nearly boundless possibilities for chemical modification [1]. This makes them highly attractive as building blocks for more sophisticated and elaborate host molecules. Among the numerous ‘tailor made’ ligands for a large variety of metal cations, crown ether derivatives of calixarenes (calixcrowns) represent not only some of the earliest complexes [2], but also elegantly demonstrate the potential of these compounds [3]. Calixarenes find applications as selective binders and carriers, as analytical sensors, as catalysts, and model structures for biomimetic studies [4].

Up to now, a complex species of the proton with any calixarene has not been experimentally proved. In the present communication, the stability constant of the *p*-tert-butylcalix[4]arene-tetrakis(*N,N*-diethylacetamide)- $\text{H}^+$  ( $\mathbf{1}\cdot\text{H}^+$ ) complex in the organic phase of the water-nitrobenzene extraction system was determined.

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## Results and Discussion

Regarding previous results [7, 8], the two-phase water-HCl/nitrobenzene-NaDCC extraction system can be described by equilibrium (1)

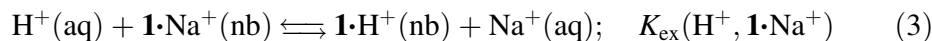


with the corresponding exchange extraction constant  $K_{\text{ex}}(\text{H}^+, \text{Na}^+)$ ; aq and nb denote the presence of the species in the aqueous and nitrobenzene phases. The constant  $K_{\text{ex}}(\text{H}^+, \text{Na}^+)$  can also be written as Eq. (2) [7] where  $K_{\text{H}^+}^i$  and  $K_{\text{Na}^+}^i$  are the individual extraction constants for  $\text{H}^+$  and  $\text{Na}^+$  in the water-nitrobenzene system.

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

Knowing  $\log K_{\text{H}^+}^i = -5.7$  and  $\log K_{\text{Na}^+}^i = -6.0$  [7], the exchange extraction constant  $K_{\text{ex}}(\text{H}^+, \text{Na}^+)$  was simply calculated from Eq. (2) as  $\log K_{\text{ex}}(\text{H}^+, \text{Na}^+) = 0.3$ .

In terms of previous papers [7–10], the two-phase water-HCl/nitrobenzene-NaDCC-1 extraction system, chosen for determination of the stability of the complex  $\mathbf{1}\cdot\text{H}^+$  in water saturated nitrobenzene, can be characterized by the main chemical equilibrium (3) to which the equilibrium extraction constant (Eq. (4)) corresponds.



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

It is necessary to emphasize that  $\mathbf{1}$  is a considerably hydrophobic ligand, practically present in the nitrobenzene phase only, where this ligand forms – with  $\text{H}^+$  and  $\text{Na}^+$  – the very stable complexes  $\mathbf{1}\cdot\text{H}^+$  and  $\mathbf{1}\cdot\text{Na}^+$ .

Taking into account the conditions of electroneutrality in the organic and aqueous phases (Eqs. (5) and (6)), the mass balances of proton and sodium ion at equal volumes of the nitrobenzene and aqueous phases (Eqs. (7) and (8)), and the measured equilibrium distribution ratio of sodium (Eq. (9)) combined with Eq. (4) to yield the final expression for the extraction constant (Eq. (10)).

$$[\mathbf{1}\cdot\text{H}^+]_{\text{nb}} + [\mathbf{1}\cdot\text{Na}^+]_{\text{nb}} = C_{\text{NaDCC}}^{\text{in,nb}} \quad (5)$$

$$[\text{H}^+]_{\text{aq}} + [\text{Na}^+]_{\text{aq}} = C_{\text{HCl}}^{\text{in,aq}} \quad (6)$$

$$[\text{H}^+]_{\text{aq}} + [\mathbf{1}\cdot\text{H}^+]_{\text{nb}} = C_{\text{HCl}}^{\text{in,aq}} \quad (7)$$

$$[\text{Na}^+]_{\text{aq}} + [\mathbf{1}\cdot\text{Na}^+]_{\text{nb}} = C_{\text{NaDCC}}^{\text{in,nb}} \quad (8)$$

$$D_{\text{Na}} = [\mathbf{1}\cdot\text{Na}^+]_{\text{nb}}/[\text{Na}^+]_{\text{aq}} \quad (9)$$

$$K_{\text{ex}}(\text{H}^+, \mathbf{1}\cdot\text{Na}^+) = \frac{1}{D_{\text{Na}}(1 + D_{\text{Na}})} \frac{C_{\text{NaDCC}}^{\text{in,nb}}}{C_{\text{HCl}}^{\text{in,aq}} - C_{\text{NaDCC}}^{\text{in,nb}}} \quad (10)$$

From the extraction experiments and  $\gamma$ -activity measurements by using Eq. (10), the following value of the constant  $K_{\text{ex}}(\text{H}^+, \mathbf{1}\cdot\text{Na}^+)$  was evaluated as  $\log K_{\text{ex}}(\text{H}^+, \mathbf{1}\cdot\text{Na}^+) = -1.4 \pm 0.1$ . Moreover, with respect to Refs. [9] and [10], for the extraction constants  $K_{\text{ex}}(\text{H}^+, \text{Na}^+)$  and  $K_{\text{ex}}(\text{H}^+, \mathbf{1}\cdot\text{Na}^+)$  defined above, as well as for the stability constants of the complexes  $\mathbf{1}\cdot\text{Na}^+$  and  $\mathbf{1}\cdot\text{H}^+$  in nitrobenzene saturated with water, denoted by  $\beta_{\text{nb}}(\mathbf{1}\cdot\text{Na}^+)$  and  $\beta_{\text{nb}}(\mathbf{1}\cdot\text{H}^+)$ , one gets Eq. (11).

$$\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{H}^+) = \log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Na}^+) + \log K_{\text{ex}}(\text{H}^+, \mathbf{1}\cdot\text{Na}^+) - \log K_{\text{ex}}(\text{H}^+, \text{Na}^+) \quad (11)$$

Using the constants  $\log K_{\text{ex}}(\text{H}^+, \text{Na}^+)$  and  $\log K_{\text{ex}}(\text{H}^+, \mathbf{1}\cdot\text{Na}^+)$  given above, the value  $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Na}^+) = 9.8$  [11], and applying Eq. (11), we obtain the stability constant of the  $\mathbf{1}\cdot\text{H}^+$  complex in water saturated nitrobenzene at 25°C as  $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{H}^+) = 8.1 \pm 0.1$ .

By means of an ion-transfer polarographic method, *Kudo et al.* [12] determined the stability constant of the complex dicyclohexyl-24-crown-8- $\text{H}^+$  in water saturated nitrobenzene as  $\log \beta_{\text{nb}} = 7.98$ . This means that the stability constants of  $\mathbf{1}\cdot\text{H}^+$  and the dicyclohexyl-24-crown-8-proton complex in the mentioned medium are comparable.

## Experimental

Cesium dicarbollylcolobaltate (*CsDCC*) was supplied by Katchem, Řež, Czech Republic. A nitrobenzene solution of *HDCC* was prepared from *CsDCC* by the procedure described in Ref. [5]. The 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 **1** was synthesized in the Institute of Macromolecular Chemistry, Prague, Czech Republic, according to Ref. [6]. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclide  $^{22}\text{Na}^+$  (DuPont, Belgium) was of standard radiochemical purity.

The extraction experiments were carried out in 10 cm<sup>3</sup> glass test-tubes covered with polyethylene stoppers: 2 cm<sup>3</sup> of the aqueous solution of HCl of a concentration in the range from  $1 \times 10^{-4}$  to  $1 \times 10^{-3}$  M and microamounts of  $^{22}\text{Na}^+$  were added to 2 cm<sup>3</sup> of the nitrobenzene solution of **1** and *NaDCC*, whose initial concentrations varied also from  $1 \times 10^{-4}$  to  $1 \times 10^{-3}$  M (in all experiments, the initial concentration of **1** in nitrobenzene,  $C_1^{\text{in,nb}}$ , was equal to the initial concentration of *NaDCC* in this medium,  $C_{\text{NaDCC}}^{\text{in,nb}}$ ). The test-tubes filled with the solutions were shaken for 24 h, using a laboratory shaker. Then the phases were separated by centrifugation. Afterwards, 1 cm<sup>3</sup> samples were taken from each phase and their  $\gamma$ -activities were measured using a well-type NaI(Tl) scintillation detector connected to a  $\gamma$ -analyzer NK 350 (Gamma, Budapest, Hungary). The equilibrium distribution ratio of sodium,  $D_{\text{Na}}$ , was determined as the ratio of the measured radioactivities of  $^{22}\text{Na}^+$  in the nitrobenzene and aqueous samples.

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