

A combined experimental and theoretical study on the complexation of the ammonium ion with benzo-18-crown-6

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Received: 3 November 2009 / Accepted: 20 January 2010 / Published online: 23 February 2010
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Abstract From extraction experiments in the two-phase water/nitrobenzene system and γ -activity measurements, the stability constant of the benzo-18-crown-6–ammonium complex in nitrobenzene saturated with water was determined. Furthermore, the structure of the resulting complex was derived by means of theoretical calculations at the density functional level.

Keywords Crown ethers · Macrocycles · Ab initio calculations · Complex structure · Complexation

Introduction

In 1967, Pedersen published his first papers [1, 2] dealing with cyclic polyether compounds with oxyethylene groups $-\text{CH}_2-\text{CH}_2-\text{O}-$, which are called crowns owing to their structure. These electroneutral crown compounds form relatively stable complexes in nonaqueous solvents, especially with alkali and alkaline-earth metal cations, which are located in the ligand cavities. The ratio of the size of the crown ligand cavity to the ion radius of the central cation is a decisive or at least important factor in the stability of the complex compounds formed [3]. It is the

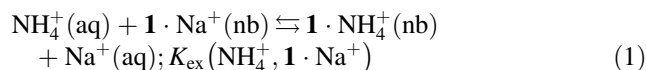
complexing properties of the crowns that have driven the rapid development of the chemistry of these cyclic polyethers witnessed in recent decades.

Recently, protonation of valinomycin, some calix[4]arenes, and dibenzo-18-crown-6 has been investigated [4–12]. On the other hand, in the current work, the stability constant of the benzo-18-crown-6–ammonium ($\mathbf{1}\cdot\text{NH}_4^+$) complex species (Scheme 1) is determined in the organic phase of the water/nitrobenzene extraction system. Moreover, by applying quantum-mechanical density functional level of theory (DFT) calculations, the most probable structure of the above-mentioned cationic complex species is derived.

Results and discussion

Extraction experiments

Based on previous results [4, 13, 14], the two-phase water– NH_4Cl /nitrobenzene– NaDCC-1 (benzo-18-crown-6) extraction system (see “Experimental”), chosen for determination of the stability constant of the cationic complex $\mathbf{1}\cdot\text{NH}_4^+$ in nitrobenzene saturated with water, can be characterized by the main chemical equilibrium (1) to which the equilibrium extraction constant (Eq. 2) corresponds; “aq” and “nb” denote the presence of the species in the aqueous and nitrobenzene phases, respectively.



$$K_{\text{ex}}(\text{NH}_4^+, \mathbf{1} \cdot \text{Na}^+) = \frac{[\mathbf{1} \cdot \text{NH}_4^+]_{\text{nb}} [\text{Na}^+]_{\text{aq}}}{[\text{NH}_4^+]_{\text{aq}} [\mathbf{1} \cdot \text{Na}^+]_{\text{nb}}} \quad (2)$$

It is necessary to emphasize that $\mathbf{1}$ is a considerably hydrophobic ligand, practically present in the nitrobenzene

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phase only, where this ligand forms—with NH_4^+ and Na^+ —the very stable complexes $\mathbf{1}\cdot\text{NH}_4^+$ and $\mathbf{1}\cdot\text{Na}^+$.

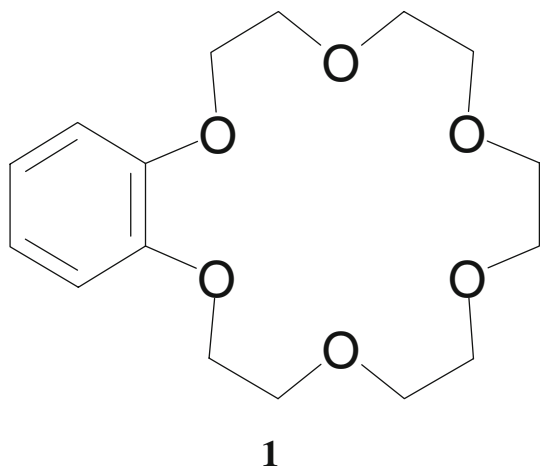
Taking into account the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of NH_4^+ and Na^+ ions at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratio of sodium, $D_{\text{Na}} = [\mathbf{1}\cdot\text{Na}^+]_{\text{nb}}/[\text{Na}^+]_{\text{aq}}$, combined with Eq. 2, we obtain the final expression for the above-mentioned extraction constant (Eq. 3); $C_{\text{NH}_4\text{Cl}}^{\text{in, aq}}$ is the initial concentration of NH_4Cl in the aqueous phase and $C_{\text{NaDCC}}^{\text{in, nb}}$ denotes the initial concentration of NaDCC in the organic phase of the system under consideration.

$$K_{\text{ex}}(\text{NH}_4^+, \mathbf{1}\cdot\text{Na}^+) = \frac{1}{D_{\text{Na}}(1 + D_{\text{Na}})} \frac{C_{\text{NaDCC}}^{\text{in, nb}}}{C_{\text{NH}_4\text{Cl}}^{\text{in, aq}} - C_{\text{NaDCC}}^{\text{in, nb}}} \quad (3)$$

From the extraction experiments and γ -activity measurements, and by using Eq. 3, the following value of the constant $K_{\text{ex}}(\text{NH}_4^+, \mathbf{1}\cdot\text{Na}^+)$ was evaluated as $\log K_{\text{ex}}(\text{NH}_4^+, \mathbf{1}\cdot\text{Na}^+) = 1.0$. Furthermore, with respect to Refs. [4, 13, 14], for the exchange extraction constant $K_{\text{ex}}(\text{NH}_4^+, \text{Na}^+)$ corresponding to the equilibrium $\text{NH}_4^+(\text{aq}) + \text{Na}^+(\text{nb}) \rightleftharpoons \text{NH}_4^+(\text{nb}) + \text{Na}^+(\text{aq})$ and for the extraction constant $K_{\text{ex}}(\text{NH}_4^+, \mathbf{1}\cdot\text{Na}^+)$ defined above, as well as for the stability constants of the complexes $\mathbf{1}\cdot\text{Na}^+$ and $\mathbf{1}\cdot\text{NH}_4^+$ in nitrobenzene saturated with water, denoted by $\beta_{\text{nb}}(\mathbf{1}\cdot\text{Na}^+)$ and $\beta_{\text{nb}}(\mathbf{1}\cdot\text{NH}_4^+)$, one obtains Eq. 4.

$$\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{NH}_4^+) = \log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Na}^+) + \log K_{\text{ex}}(\text{NH}_4^+, \mathbf{1}\cdot\text{Na}^+) - \log K_{\text{ex}}(\text{NH}_4^+, \text{Na}^+) \quad (4)$$

Using the value $\log K_{\text{ex}}(\text{NH}_4^+, \text{Na}^+) = 1.3$ inferred from [13], the constant $K_{\text{ex}}(\text{NH}_4^+, \mathbf{1}\cdot\text{Na}^+)$ given above, $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Na}^+) = 7.4$ [15], and applying Eq. 4, we obtain the



Scheme 1

stability constant of the $\mathbf{1}\cdot\text{NH}_4^+$ complex in water-saturated nitrobenzene as $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{NH}_4^+) = 7.1$. Besides this, Table 1 summarizes the stability constants of the cationic complexes $\mathbf{1}\cdot\text{M}^+$, where $\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$, or NH_4^+ , in nitrobenzene saturated with water at 25 °C. Thus, from the data reviewed in this table it follows that the stability of the considered complexes $\mathbf{1}\cdot\text{M}^+$ in the mentioned nitrobenzene medium increases in the order: $\text{Cs}^+ < \text{Rb}^+ < \text{Li}^+ < \text{NH}_4^+ < \text{Na}^+ < \text{K}^+$.

Quantum-mechanical calculations

Quantum-mechanical calculations were carried out at the density functional level of theory (DFT, B3LYP functional) using the Gaussian 03 suite of programs [16]. Although a possible influence of a polar solvent on the detailed structures of **1** and $\mathbf{1}\cdot\text{NH}_4^+$ can be imagined, our quantum-chemical calculations in similar cases, performed in an analogous way, showed very good agreement of experiment with theory [17–22].

In the model calculations, we optimized the molecular geometries of the parent crown ligand **1** and its complex with NH_4^+ . The optimized structure of a free ligand **1** is illustrated in Fig. 1. In Fig. 2, the structure obtained by DFT optimization of the $\mathbf{1}\cdot\text{NH}_4^+$ complex is depicted together with the lengths of the corresponding hydrogen bonds (in Å). In the $\mathbf{1}\cdot\text{NH}_4^+$ cationic complex species, which is energetically most favored, there are three strong linear hydrogen bonds directed to one (Ar–O–CH₂) ethereal oxygen (1.85 Å) and two (CH₂–O–CH₂) ethereal oxygen atoms (1.80 and 1.77 Å) of the parent ligand **1**.

Finally, the interaction energy, $E(\text{int})$, of the $\mathbf{1}\cdot\text{NH}_4^+$ complex [calculated as the difference between electronic energies of the complex $\mathbf{1}\cdot\text{NH}_4^+$ and isolated **1** and NH_4^+ species, $E(\text{int}) = E(\mathbf{1}\cdot\text{NH}_4^+) - E(\mathbf{1}) - E(\text{NH}_4^+)$] was found to be $-807.2 \text{ kJ mol}^{-1}$, which confirms quite unambiguously the formation of the considered cationic complex $\mathbf{1}\cdot\text{NH}_4^+$.

Experimental

Cesium dicarbollylcobaltate (CsDCC) was purchased from Katchem (Řež, Czech Republic). A nitrobenzene solution

Table 1 Stability constants of the $\mathbf{1}\cdot\text{M}^+$ complexes (**1** = benzo-18-crown-6; $\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$, or NH_4^+) in nitrobenzene saturated with water at 25 °C

| M^+ | Li^+ | Na^+ | K^+ | Rb^+ | Cs^+ | NH_4^+ |
|---|------------------|------------------|------------------|------------------|------------------|------------------|
| $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{M}^+)$ | 7.0 ^a | 7.4 ^a | 7.6 ^a | 6.3 ^a | 5.5 ^a | 7.1 ^b |

^a Ref. [15]

^b This work

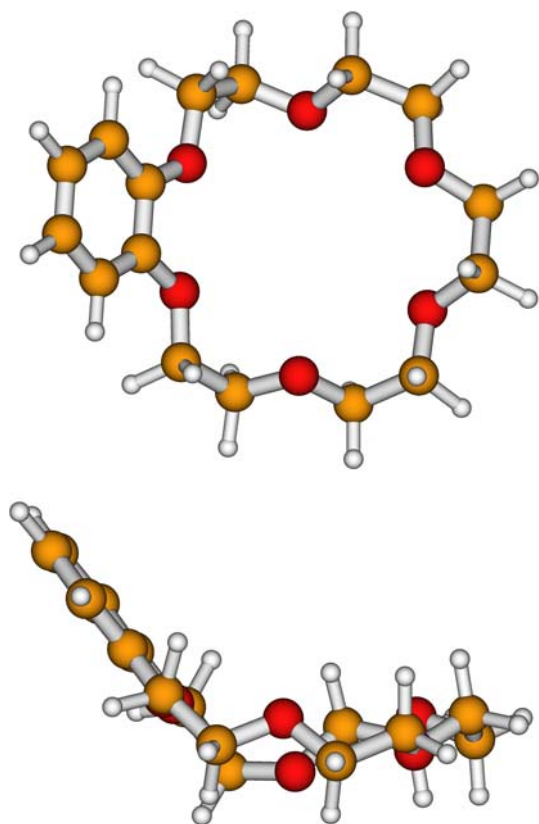


Fig. 1 Two projections of the DFT-optimized structure of free **1** [B3LYP/6-31G(d)]

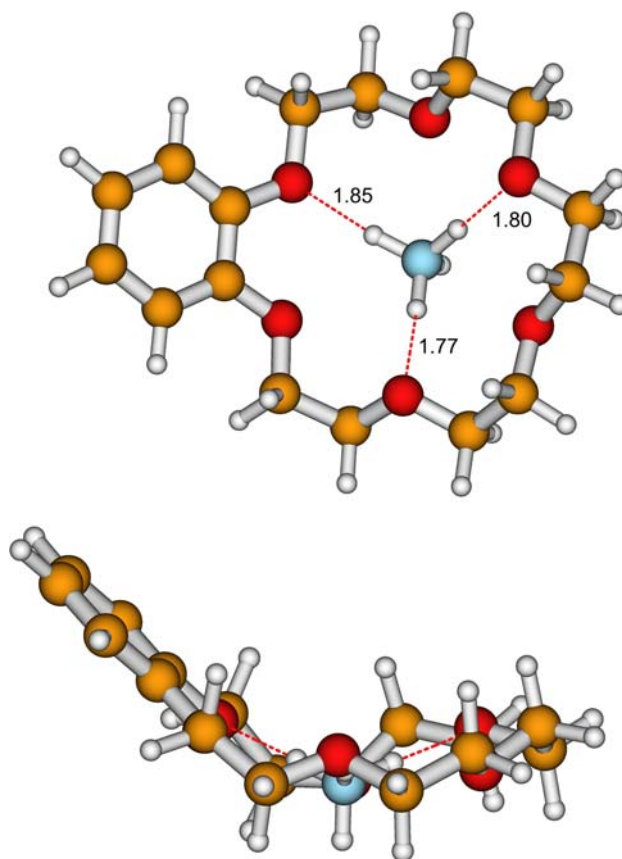


Fig. 2 Two projections of the DFT-optimized structure of the **1**·NH₄⁺ complex [B3LYP/6-31G(d)]

of HDCC [23] was prepared from CsDCC by the procedure described elsewhere [24]. 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. Benzo-18-crown-6 (**1**) was supplied by Fluka, Buchs, Switzerland. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent-grade purity. The radionuclide ²²Na⁺ (DuPont, Belgium) was of standard radiochemical purity.

Extraction experiments were carried out in 10-cm³ glass test-tubes with polyethylene stoppers: 2 cm³ of an aqueous solution of NH₄Cl with concentration in the range from 1 × 10⁻³ to 1 × 10⁻² M and microamounts of ²²Na⁺ were added to 2 cm³ of a nitrobenzene solution of **1** and NaDCC, whose initial concentrations also varied from 1 × 10⁻³ to 1 × 10⁻² M (in all experiments, the initial concentration of **1** in nitrobenzene, C₁^{in,nb}, was equal to the initial concentration of NaDCC in this medium, C_{NaDCC}^{in,nb}). The test-tubes filled with the solutions were shaken for 2 h at 25 ± 1 °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 ratios of sodium, *D*_{Na}, were determined as the ratios of the measured radioactivities of ²²Na⁺ in the nitrobenzene and aqueous samples.

Acknowledgments This work was supported by the Czech Ministry of Education, Youth, and Sports, projects MSM 4977751303 and MSM 6046137307. The computer time at the MetaCentrum (project MSM 6383917201), as well as at the Institute of Physics (computer Luna/Apollo), Academy of Sciences of the Czech Republic, is gratefully acknowledged.

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