Complexation of the Ammonium Cation with Dibenzo-18-crown-6: Extraction and DFT Study

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1. Introduction

The observation that macrocyclic polyethers form stable complexes with alkali and alkaline earth metal cations has stimulated a great deal of interest in these compounds for their possible applications in various branches of chemistry and biology.1–3 Extensive thermodynamic data suggest that the stability of macrocyclic complexes depends on the relative cation and ligand cavity size, the number and arrangements of the ligand bonding sites, the substitution on the macrocyclic ring and the solvent effects. In this context it should be noted that several reviews have covered many aspects of the chemistry of the mentioned macrocyclic compounds.3–6

The dicarboxylcobaltate anion (DCC–)7 and some of its halogen derivatives are very useful reagents for the extraction of various metal cations (especially Cs+, Sr2+, Ba2+, Eu3+ and Am3+) from aqueous solutions into a polar organic phase, both under laboratory conditions for purely theoretical or analytical purposes,8–25 and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.26–28

In the current work, the stability constant of the cationic complex species 1-NH4+, where 1 denotes dibenzo-18-crown-6 (see Scheme 1), in nitrobenzene saturated with water was determined. Moreover, applying quantum mechanical DFT calculations, the most probable structure of the mentioned complex species was predicted.

Abstract

From extraction experiments and γ-activity measurements, the extraction constant corresponding to the equilibrium

\[ \text{NH}_4^+(\text{aq}) + \text{Na}^+(\text{nb}) \leftrightarrow \text{NH}_4^+(\text{nb}) + \text{Na}^+(\text{aq}) \]

taking place in the two-phase water - nitrobenzene system (1 = dibenzo-18-crown-6, aq = aqueous phase, nb = nitrobenzene phase) was evaluated as \( \log K_{\text{ex}}(\text{NH}_4^+, \text{Na}^+) = –0.1 \pm 0.1 \). Further, the stability constant of the 1-NH4+ complex species in water-saturated nitrobenzene was calculated for a temperature 25 °C as \( \log \beta (1-\text{NH}_4^+) = 5.7 \pm 0.2 \). Finally, by using quantum mechanical DFT calculations, the most probable structure of the 1-NH4+ cationic complex was derived. In this complex, the “central” cation NH4+ is bound by three strong linear hydrogen bonds to the three corresponding ethereal oxygen atoms of the parent crown ligand 1. The interaction energy of the resulting complex 1-NH4+ was found to be –796.1 kJ/mol, confirming the formation of the considered complex species.

Keywords: Ammonium cation, dibenzo-18-crown-6, complexation, extraction and stability constants, water-nitrobenzene system, DFT, complex structure
2. Experimental

Dibenzo-18-crown-6 (abbrev. I; see Scheme 1) was purchased from Fluka. Cesium dicarbollylcobaltate (CsDCC) was synthesized by means of the method published by Hawthorne et al. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. A nitrobenzene solution of hydrogen dicarbollylcobaltate (HDCC) was prepared from CsDCC by the procedure described elsewhere. The equilibration of the nitrobenzene solution of HDCC with stoichiometric NaOH, which was dissolved in an aqueous solution of NaCl (0.20 mol/L), yielded the corresponding NaDCC solution in nitrobenzene. The radionuclide $^{22}$Na$^+$ was supplied by DuPont, Belgium.

The extraction experiments were carried out in 10 mL glass test-tubes with polyethylene stoppers: 2 mL of an aqueous solution of NH$_4$Cl of a concentration in range from $1 \times 10^{-3}$ to $5 \times 10^{-3}$ mol/L and microamounts of $^{22}$Na$^+$ were added to 2 mL of a nitrobenzene solution of I and NaDCC, whose initial concentrations also varied from $1 \times 10^{-3}$ to $5 \times 10^{-3}$ mol/L (in all experiments, the initial concentration of I in nitrobenzene, $C_{\text{i,nb}}$, was equal to the initial concentration of NaDCC in this medium, $C_{\text{NaDCC}}$). The test-tubes filled with the solutions were shaken for 2 h at 25 °C, using a laboratory shaker. Then the phases were separated by centrifugation. Afterwards, 1 mL samples were taken from each phase and their activities were measured by means of a well-type NaI(Tl) scintillation detector connected to a $\gamma$-analyzer NK 350 (Gamma, Budapest, Hungary).

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

3. Results and Discussion

Previous results indicated that the two-phase water-NH$_4$Cl-nitrobenzene- I (dibenzo-18-crown-6) - sodium dicarbollylcobaltate (NaDCC) extraction system (see Experimental), chosen for determination of the stability constant of the cationic complex I-NH$_4^+$ in water-saturated nitrobenzene, can be characterized by the main chemical equilibrium

$$\text{NH}_4^+(\text{aq}) + \text{I}^+: \text{Na}^+(\text{nb}) \Leftrightarrow \text{I-NH}_4^+(\text{nb}) + \text{Na}^+(\text{aq}); \quad K_{\text{ex}}(\text{NH}_4^+ \cdot \text{I}^+ \cdot \text{Na}^+)$$

with the respective equilibrium extraction constant $K_{\text{ex}}(\text{NH}_4^+ \cdot \text{I}^+ \cdot \text{Na}^+)$:

$$K_{\text{ex}}(\text{NH}_4^+ \cdot \text{I}^+ \cdot \text{Na}^+) = \frac{[\text{I-NH}_4^+(\text{nb})[\text{Na}^+(\text{aq})]}{[\text{NH}_4^+(\text{aq})][\text{I}^+: \text{Na}^+(\text{nb})]} \quad (2)$$

where the subscripts “aq” and “nb” denote the aqueous and nitrobenzene phases, respectively.

It is necessary to emphasize that I is a considerably hydrophobic ligand, practically present in the nitrobenzene phase only, where it forms – with NH$_4^+$ and Na$^+$ – the very stable complexes I-NH$_4^+$ and I-Na$^+$.

Taking into account the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of the univalent cations studied at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratio of sodium, $D_{\text{Na}} = [\text{I-Na}^+\text{nb}]/[\text{Na}^+\text{aq}]$, combined with Eq. (2), we obtain the final expression for $K_{\text{ex}}(\text{NH}_4^+ \cdot \text{I}^+ \cdot \text{Na}^+)$ in the form

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

where $C_{\text{i,aq}}$ is the initial concentration of NH$_4$Cl in the aqueous phase and $C_{\text{i,nb}}$ denotes the initial concentration of NaDCC in the organic phase of the system under consideration.

In this study, from the extraction experiments and $\gamma$ activity measurements (see Experimental) by means of Eq. (3), the following value of the constant $K_{\text{ex}}(\text{NH}_4^+ \cdot \text{I}^+ \cdot \text{Na}^+)$ was determined as $\log K_{\text{ex}}(\text{NH}_4^+ \cdot \text{I}^+ \cdot \text{Na}^+) = -0.1 \pm 0.1$.

Furthermore, with respect to previous results, $33$–$37$ for the exchange extraction constant $K_{\text{ex}}(\text{NH}_4^+ \cdot \text{Na}^+)$ corresponding to the equilibrium $\text{NH}_4^+(\text{aq}) + \text{Na}^+(\text{nb}) \Leftrightarrow \text{I-NH}_4^+(\text{nb}) + \text{Na}^+(\text{aq})$ and for the extraction constant $K_{\text{ex}}(\text{NH}_4^+ \cdot \text{I}^+ \cdot \text{Na}^+)$ defined above, as well as for the stability constants of the complexes I-Na$^+$ and I-NH$_4^+$ in nitrobenzene saturated with water, denoted by $\beta_{\text{nb}}(\text{I-Na}^+)$ and $\beta_{\text{nb}}(\text{I-NH}_4^+)$, respectively, one gets

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

Using the value $\log K_{\text{ex}}(\text{NH}_4^+ \cdot \text{Na}^+) = 1.3$ inferred from Reference 31, the constant $\log K_{\text{ex}}(\text{NH}_4^+ \cdot \text{I}^+ \cdot \text{Na}^+)$ given above, $\log \beta_{\text{nb}}(\text{I-Na}^+) = 7.1 \pm 0.1$ and applying Eq. (4), we gain the stability constant of the I-NH$_4^+$ complex in nitrobenzene saturated with water as $\log \beta_{\text{nb}}(\text{I-NH}_4^+) = 5.7 \pm 0.2$. This means that in the mentioned nitrobenzene medium, the stability of the I-NH$_4^+$ complex under study is somewhat lower than that of the cationic complex species I-Na$^+$.

The quantum mechanical calculations were carried out at the density functional level of theory (DFT, B3LYP functional) using the Gaussian 03 suite of programs. The 6-31G(d) basis set was used and the optimizations were unconstrained. In order to increase the numerical ac-
accuracy and to reduce oscillations during the molecular geometry optimization, two-electron integrals and their derivatives were calculated by using the pruned (99,590) integration grid, having 99 radial shells and 590 angular points per shell, which was requested by means of the Gaussian 03 keyword “Int = UltraFine”.

Although a possible influence of a polar solvent on the detailed structures of 1 and its complex with NH$_4^+$ could be imagined, our quantum mechanical calculations in similar cases, performed in an analogous way, showed very good agreement of experiment with theory.$^{42-49}$

In the model calculations, we optimized the molecular geometries of the parent crown ligand 1 and the 1·NH$_4^+$ complex species. The optimized structure of the free ligand 1 is illustrated in Figure 1.

In Figure 2, the structure obtained by the full DFT optimization of the 1·NH$_4^+$ complex is depicted, together with the lengths of the corresponding hydrogen bonds (in Å; 1 Å = 0.1 nm). In the 1·NH$_4^+$ cationic complex species, which is most energetically favoured, the “central” cation NH$_4^+$ is bound by three strong linear hydrogen bond interactions to the two (Ar-O-CH$_2$) ethereal oxygens (1.83 and 1.83 Å) and to one (CH$_2$-O-CH$_2$) ethereal oxygen atom (1.84 Å) of the parent crown ligand 1.

Finally, the interaction energy, E(int), of the 1·NH$_4^+$ complex [calculated as the difference between the pure electronic energies of the complex 1·NH$_4^+$ and isolated 1 and NH$_4^+$ species: $E\text{(int)} = E(1·NH_4^+) - E(1) - E(NH_4^+)$] was found to be −796.1 kJ/mol, which confirms the formation of the considered cationic complex species 1·NH$_4^+$.

4. Acknowledgements

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5. References

Povzetek

Iz eksperimentov ektrakcije in meritev $\gamma$-aktivnosti smo določili konstante ektrakcije za ravnotežja $\text{NH}_4^+(\text{aq}) + \text{I-Na}^+(\text{nb}) \Leftrightarrow \text{I-NH}_4^+(\text{nb}) + \text{Na}^+(\text{aq})$ v dvo faznem sistemu voda-nitrobenzen ($\text{I} = \text{dibenzo-18-crown-6}$, $\text{aq} = \text{vodna faza}$, $\text{nb} = \text{faza nitrobenzene}$), log $K_{eX}(\text{NH}_4^+,\text{I-Na}^+) = -0.1 \pm 0.1$. Pri 25 °C smo določili konstanto stabilnosti kompleksa $\text{I-NH}_4^+$ v nitrobenzeni, nasičenem z vodo, ki znaša log $\beta(\text{I-NH}_4^+) = 5.7 \pm 0.2$. Z uporabo kvantno mehanskih DFT izračunov smo določili najbolj verjetno strukturo $\text{I-NH}_4^+$ kationskega kompleksa. Ugotovili smo, da je »centralni« kation $\text{NH}_4^+$ s tremi močnimi linearnimi vodikovimi vezmi vezan na tri eterske kisikove atome crownskega liganda $\text{I}$. Energija interakcije kompleksa $\text{I-NH}_4^+$ znaša $-796.1 \text{kJ/mol}$, kar potrjuje strukture privzete konformacije kompleksa.