

Experimental and theoretical study on interaction of the potassium cation with antamanide



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ABSTRACT

On the basis of extraction experiments and γ -activity measurements, the extraction constant corresponding to the equilibrium $K^+(aq) + 1 \cdot Na^+(nb) \rightleftharpoons 1 \cdot K^+(nb) + Na^+(aq)$ taking part in the two-phase water–nitrobenzene system (1 = antamanide; aq = aqueous phase, nb = nitrobenzene phase) was evaluated as $\log K_{ex}(K^+, 1 \cdot Na^+) = 0.2 \pm 0.1$. Further, the stability constant of the $1 \cdot K^+$ complex in nitrobenzene saturated with water was calculated for a temperature of 25 °C: $\log \beta_{nb}(1 \cdot K^+) = 4.7 \pm 0.2$. Finally, by using quantum mechanical DFT calculations, the most probable structure of the cationic complex species $1 \cdot K^+$ was derived. In the resulting complex, the “central” cation K^+ is bound by four bond interactions to the corresponding four carbonyl oxygen atoms of the parent ligand 1 . Besides, the whole $1 \cdot K^+$ complex structure is stabilized by two intramolecular hydrogen bonds. The interaction energy of the considered $1 \cdot K^+$ complex was found to be -346.6 kJ/mol, confirming also the formation of this cationic species.

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1. Introduction

The cyclic decapeptide antamanide, *cycl*[-Val(1)-Pro(2)-Pro(3)-Ala(4)-Phe(5)-Phe(6)-Pro(7)-Pro(8)-Phe(9)-Phe(10)-], consisting entirely of *L*-amino acids (see Scheme 1), forms 1:1 complexes with a variety of metal cations [1,2]. Antamanide was isolated from the poisonous mushroom *Amanita phalloides* [3] and it has the unique property of counteracting the toxin phalloidin, produced by the mentioned mushroom. Furthermore, it should be emphasized that antamanide prevents the inhibition of depolymerization of F-actin and G-actin in the liver cell membranes of mammals [4].

The dicarbollylcobaltate anion (DCC^-) [5] and some of its halogen derivatives have been applied very often for the extraction of various metal cations (especially Cs^+ , Sr^{2+} , Ba^{2+} , Eu^{3+} , and Am^{3+}) from aqueous solutions into a polar organic phase, both under laboratory conditions for theoretical or experimental purposes [6–13], and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste [14–16].

In the current work, the solvent extraction of K^+ into nitrobenzene by means of a synergistic mixture of sodium dicarbollylcobaltate (NaDCC) and antamanide (abbrev. 1 ; see Scheme 1) was investigated. Moreover, the stability constant of the proved $1 \cdot K^+$

complex species in the organic phase of the water–nitrobenzene extraction system was evaluated. Finally, applying quantum mechanical DFT calculations, the most probable structure of this cationic complex was predicted on the basis of the thorough conformational analysis (i.e., different initial mutual positions of the ligand 1 and the K^+ cation were considered during the geometry optimization) and the respective vibrational frequency calculations.

2. Experimental

Compound 1 (see Scheme 1) was prepared by the method described in Ref. [17]. Cesium dicarbollylcobaltate (CsDCC) was synthesized by means of the method published by Hawthorne et al. [18]. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. A nitrobenzene solution of hydrogen dicarbollylcobaltate (HDCC) [5] was prepared from CsDCC by the procedure described elsewhere [19]. 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 obtained from DuPont, Belgium; its radionuclidic purity was 99.9%.

The extraction experiments were carried out in 10 mL polypropylene test-tubes with polypropylene stoppers: 2 mL of an aqueous solution of KCl of a concentration in the range from 1×10^{-3} to 3×10^{-3} mol/L and 10 kBq of $^{22}Na^+$ were added to 2 mL of a

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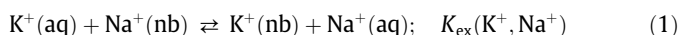
nitrobenzene solution of **1** and NaDCC, whose initial concentrations varied also from 1×10^{-3} to 3×10^{-3} mol/L (in all experiments, the initial concentration of **1** in nitrobenzene, $C_1^{\text{in,nb}}$, was equal to the initial concentration of NaDCC in this medium, $C_{\text{NaDCC}}^{\text{in,nb}}$). The test-tubes filled with the solutions were shaken for 3 h at 25 ± 1 °C, using a laboratory shaker. Then the phases were separated by 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 sodium, D_{Na} , were determined as the ratios of the corresponding measured radioactivities of $^{22}\text{Na}^+$ in the nitrobenzene and aqueous samples.

3. Results and discussion

3.1. Extraction experiments

In terms of previous papers [5,20,21], the two-phase water–KCl–nitrobenzene–**1** (antamanide)–sodium dicarbollycobaltate (NaDCC) extraction system, can be described by the following equilibrium

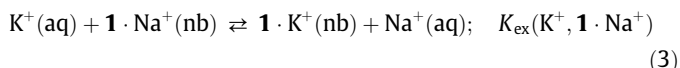


with the corresponding exchange extraction constant $K_{\text{ex}}(\text{K}^+, \text{Na}^+)$; aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively. For the constant $K_{\text{ex}}(\text{K}^+, \text{Na}^+)$ one can write [5,20]

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

where $K_{\text{K}^+}^i$ and $K_{\text{Na}^+}^i$ are the individual extraction constants for K^+ and Na^+ , respectively, in the water–nitrobenzene system [20]. Knowing the values $\log K_{\text{K}^+}^i = -4.1$ [20] and $\log K_{\text{Na}^+}^i = -6.0$ [20], the exchange extraction constant $K_{\text{ex}}(\text{K}^+, \text{Na}^+)$ was simply calculated from Eq. (2) as $\log K_{\text{ex}}(\text{K}^+, \text{Na}^+) = 1.9$.

Our previous results [22,23] indicated that the two-phase water–KCl–nitrobenzene–**1** (antamanide)–NaDCC extraction system (see Section 2), chosen for determination of the stability constant of the complex $\mathbf{1} \cdot \text{K}^+$ in water-saturated nitrobenzene, can be characterized by the main chemical equilibrium



with the respective equilibrium extraction constant $K_{\text{ex}}(\text{K}^+, \mathbf{1} \cdot \text{Na}^+)$:

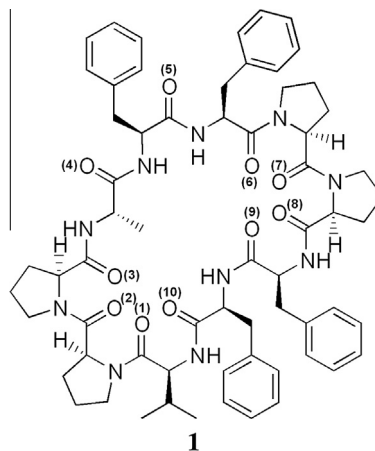
$$K_{\text{ex}}(\text{K}^+, \mathbf{1} \cdot \text{Na}^+) = \frac{[\mathbf{1} \cdot \text{K}^+]_{\text{nb}} [\text{Na}^+]_{\text{aq}}}{[\text{K}^+]_{\text{aq}} [\mathbf{1} \cdot \text{Na}^+]_{\text{nb}}} \quad (4)$$

At this point it should be noted that **1** is a considerably lipophilic ligand, practically present in the nitrobenzene phase only, where this ligand forms – with K^+ and Na^+ – the relatively stable complexes $\mathbf{1} \cdot \text{K}^+$ and $\mathbf{1} \cdot \text{Na}^+$, as given below.

Employing 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, $D_{\text{Na}} = [\mathbf{1} \cdot \text{Na}^+]_{\text{nb}} / [\text{Na}^+]_{\text{aq}}$, combined with Eq. (4), we gain the final expression for $K_{\text{ex}}(\text{K}^+, \mathbf{1} \cdot \text{Na}^+)$ in the form:

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

where $C_{\text{KCl}}^{\text{in,aq}}$ is the initial concentration of KCl 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.



Scheme 1. Structural formula of antamanide (abbrev. **1**).

In this work, from the extraction experiments and γ -activity measurements (see Section 2) by means of Eq. (5), the following value of the constant $K_{\text{ex}}(\text{K}^+, \mathbf{1} \cdot \text{Na}^+)$ was determined as $\log K_{\text{ex}}(\text{K}^+, \mathbf{1} \cdot \text{Na}^+) = 0.2 \pm 0.1$ (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).

Furthermore, with respect to previous results [22,23], for the extraction constants $K_{\text{ex}}(\text{K}^+, \text{Na}^+)$ and $\log K_{\text{ex}}(\text{K}^+, \mathbf{1} \cdot \text{Na}^+)$ defined above, as well as for the stability constants of the complexes $\mathbf{1} \cdot \text{K}^+$ and $\mathbf{1} \cdot \text{Na}^+$ in nitrobenzene saturated with water, denoted by $\beta_{\text{nb}}(\mathbf{1} \cdot \text{K}^+)$ and $\beta_{\text{nb}}(\mathbf{1} \cdot \text{Na}^+)$, respectively, one gets

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

Using the constants $\log K_{\text{ex}}(\text{K}^+, \text{Na}^+)$ and $\log K_{\text{ex}}(\text{K}^+, \mathbf{1} \cdot \text{Na}^+)$ given above, the value $\log \beta_{\text{nb}}(\mathbf{1} \cdot \text{Na}^+) = 6.4 \pm 0.1$ [24], determined from the distribution of sodium picrate in the water–nitrobenzene extraction system containing the antamanide ligand **1**, and applying Eq. (6), we obtain the stability constant of the $\mathbf{1} \cdot \text{K}^+$ complex in water-saturated nitrobenzene as $\log \beta_{\text{nb}}(\mathbf{1} \cdot \text{K}^+) = 4.7 \pm 0.2$. This means that in the mentioned nitrobenzene medium, the stability constant of the complex $\mathbf{1} \cdot \text{K}^+$ is substantially lower than that of $\mathbf{1} \cdot \text{Na}^+$. In this context it should be noted that the stability constant of the cationic complex species $\mathbf{2} \cdot \text{K}^+$, where **2** denotes a hexaarylbenzene – based receptor (see Scheme 2), in nitrobenzene saturated with water is $\log \beta_{\text{nb}}(\mathbf{2} \cdot \text{K}^+) = 5.1$ [25]. Thus, in this medium, the stability of the species $\mathbf{1} \cdot \text{K}^+$ is somewhat lower than that of the cationic complex $\mathbf{2} \cdot \text{K}^+$.

3.2. DFT calculations

The theoretical calculations were performed at the density functional level of theory (DFT, B3LYP functional) [26,27], employing the Gaussian 09 suite of programs [28]. The 6-31G(d,p) basis

Table 1
Experimental data concerning determination of $\log K_{\text{ex}}(\text{K}^+, \mathbf{1} \cdot \text{Na}^+)$ on the basis of Eq. (5).

$C_{\text{KCl}}^{\text{in,aq}}$ (mol/L)	$C_{\text{NaDCC}}^{\text{in,nb}}$ (mol/L)	D_{Na}	$\log K_{\text{ex}}(\text{K}^+, \mathbf{1} \cdot \text{Na}^+)$
1.0×10^{-3}	1.0×10^{-3}	0.73	0.3
1.5×10^{-3}	1.5×10^{-3}	0.76	0.2
2.0×10^{-3}	2.0×10^{-3}	0.74	0.3
2.5×10^{-3}	2.5×10^{-3}	0.78	0.2
3.0×10^{-3}	3.0×10^{-3}	0.85	0.1

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