Complexation of valinomycin with some univalent organic cations in nitrobenzene saturated with water

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ABSTRACT

From extraction experiments and γ-activity measurements, the exchange extraction constants corresponding to the general equilibrium $C^+(aq) + \mathbf{1} \cdot Cs^+(nb) \Longleftrightarrow \mathbf{1} \cdot C^+(nb) + Cs^+(aq)$ taking place in the two-phase water–nitrobenzene system (C^+ = methylammonium, ethylammonium, propylammonium, ethanolammonium, diethanolammonium, triethanolammonium, protonated tyramine, protonated dopamine, or protonated DL-noradrenaline; $\mathbf{1}$ = valinomycin; aq = aqueous phase, nb = nitrobenzene phase) were evaluated. Furthermore, the stability constants of the $\mathbf{1} \cdot C^+$ complex species in nitrobenzene saturated with water were calculated; they were found to increase in the following cation order: propylammonium < ethylammonium < protonated tyramine < methylammonium < protonated dopamine < triethanolammonium < diethanolammonium < ethanolammonium < protonated DL-noradrenaline.

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1. Introduction

The antibiotic valinomycin (abbrev. **1**; see Scheme 1) was discovered in *Streptomyces fulvissimus* cultures [1]. It is a macrocyclic dodecadepsipeptide composed of 12 alternating amino acids and esters, exhibiting a threefold symmetry [2]. It forms complexes with alkali metal ions, the stability of which shows a pronounced dependence on the ion radius [2–5]. Because of the lipophilic outer envelope of the complex, valinomycin enables univalent cations to be transported across membranes of cells and cell organelles [3], and consequently, it is a powerful uncoupler of oxidative phosphorylation in mitochondria [6]. It also gives rise to ion-selective membrane potentials at bilayer lipid membranes [3]. The very large difference in stability of the potassium and sodium complexes is the cause of the high potassium selectivity of the valinomycin-based ion-selective electrode [7].

The stability and selectivity of the complex formation of natural macrocyclic ionophores (valinomycin, nonactin, monactin, dinactin, and trinactin) with alkali metal ions and monovalent thallium cation have been studied by polarography [8]. With valinomycin, both stability constants and homogenous dissociation rate constants have been determined from polarographic kinetic currents. The macrotetrolides gave diffusion controlled currents. The stability of their complexes increases with the degree of substitution from nonactin to trinactin

[8]. The theoretical structures of the valinomycin complexes with Li^+, Na^+, and NH_4^+ have been solved recently [9–11].

The dicarbollylcobaltate anion (DCC^-) [12] and some of its halogen derivatives are very useful reagents 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 purely theoretical or analytical purposes [13–18], and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste [19–21].

In the current work, the stability constants of the $\mathbf{1} \cdot C^+$ complex species, where **1** denotes the valinomycin ligand and C^+ = methylammonium, ethylammonium, propylammonium, ethanolammonium, diethanolammonium, triethanolammonium, protonated tyramine, protonated dopamine, or protonated DL-noradrenaline (Scheme 2), were determined in the organic phase of the two-phase water–nitrobenzene extraction system.

2. Experimental section

2.1. Chemicals

Compound **1** (see Scheme 1; purum, ≥98%) was purchased from Fluka. Cesium dicarbollylcobaltate (CsDCC) was synthesized by means of the method published by Hawthorne et al. [22]. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The species methylamine hydrochloride (purum, ≥98%), ethylamine hydrochloride (puriss., ≥99%), propylamine hydrochloride (puriss.,
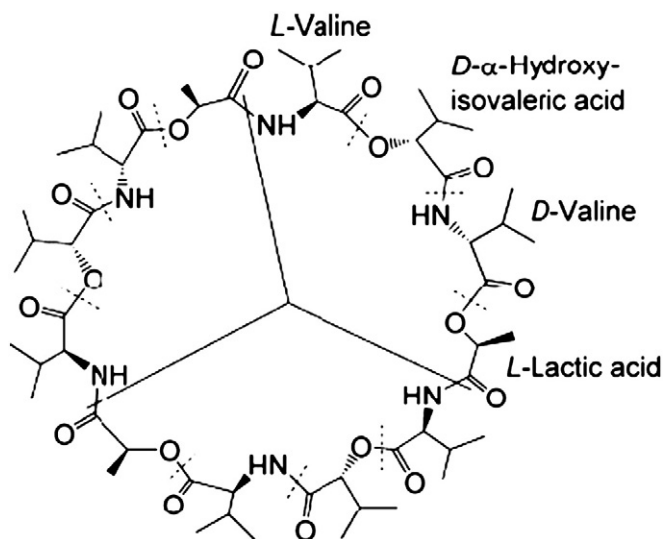
Scheme 1. Structural formula of valinomycin (abbrev. **1**).

water used for the extraction experiments was double distilled and it was deionized as well. The radionuclide $^{137}Cs^+$ was obtained from Techsnaveksport, Russia.
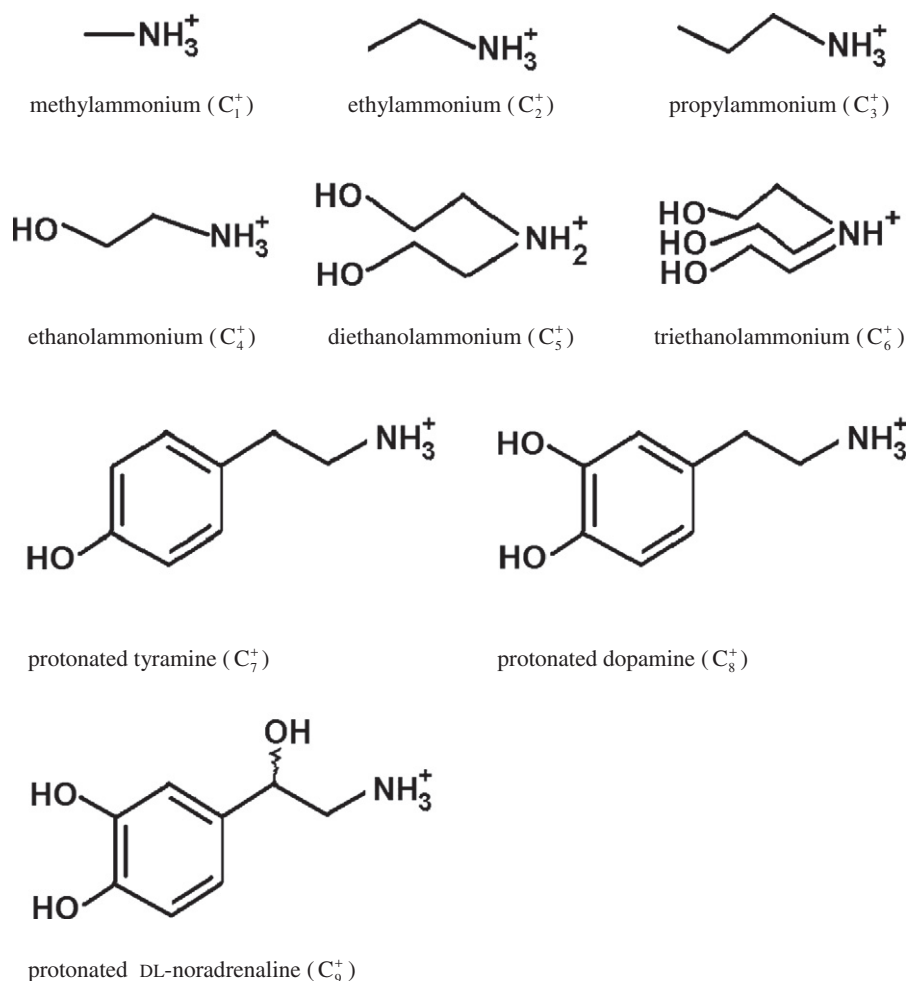
2.2. Extraction

The extraction experiments were carried out in 10 mL polypropylene test-tubes with polypropylene stoppers: 2 mL of an aqueous solution of C^+Cl^- ($C^+ = C_1^+, C_2^+, ..., C_9^+$; see Scheme 2) of the concentration in the range from 1×10^{-3} to 5×10^{-3} mol/L and microamounts of $^{137}Cs^+$ were added to 2 mL of a nitrobenzene solution of **1** and CsDCC, whose initial concentrations varied also from 1×10^{-3} to 5×10^{-3} mol/L (in all experiments, the initial concentration of **1** in nitrobenzene, $C_1^{in,nb}$, was equal to the initial concentration of CsDCC in this medium, $C_{CsDCC}^{in,nb}$). 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 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 NK 350 (Gamma, Budapest, Hungary).

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

3. Results and discussion

Regarding the results of previous papers [12,23–25], the two-phase water–C^+Cl^- ($C^+ = C_1^+, C_2^+, ..., C_9^+$; see Scheme 2)–nitrobenzene–

≥99%), ethanolamine hydrochloride (purum, ≥98%), diethanolamine hydrochloride (purum, ≥98%), triethanolamine hydrochloride (puriss., ≥99%), tyramine hydrochloride (purum, ≥98%), dopamine hydrochloride (purum, ≥98%), and DL-noradrenaline hydrochloride (purum, ≥98%) were supplied by Aldrich and were employed as received. The

methylammonium (C_1^+)

ethylammonium (C_2^+)

propylammonium (C_3^+)

ethanolammonium (C_4^+)

diethanolammonium (C_5^+)

triethanolammonium (C_6^+)

protonated tyramine (C_7^+)

protonated dopamine (C_8^+)

protonated DL-noradrenaline (C_9^+)

Scheme 2. Structural formulas of the 9 organic cations (abbrev. $C_1^+, C_2^+, ..., C_9^+$).