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Ferroceneboronic acid for the electrochemical probing of interactions involving sugars

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ABSTRACT

Ferroceneboronic acid (FcBA) was used as a redox-active probe suitable for monitoring of diol–boronate interactions. Voltammetric and amperometric measurements allowed to detect FcBA forms – free and bound in the boronate complex. In this way, the complexation interaction was studied for a set of saccharide molecules as model diols and the corresponding affinity equilibrium constants were determined. A shift of the peak potential on voltammograms accompanying formation of the boronate complex with FcBA was proposed as a probe for electrochemical characterization of surface-confined diol-containing structures. The model experiments were carried out using sorbitol- and 1,6-hexandiol-modified polyepichlorhydrin conjugates deposited on the electrodes; the former compound was able to form the boronate complex while no change of the peak potential for the latter conjugate was observed. This approach seems promising for artificial bioelectronic affinity receptors and technology of reagentless biosensors where the binding interaction directly stimulates a measurable electrochemical event.

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1. Introduction

The extensive efforts are focused on the development of non-enzymatic chemical sensors for determination of glucose. The suitable detection approaches include boronic acid (BA) which is seriously studied as a specific recognition ligand [1]. Such sensors are based on formation of the boronate complex; the chemical nature of the immobilized ligand provides excellent stability and sufficient sensitivity, however, the wide specificity towards diverse compounds (diols, amino acids, hydroxamic acids) is a problem. These properties are different compared to common enzymatic biosensors (limited stability, high specificity). The principle of recognition of sugars with boronic acid as a ligand is the widely known formation of five- and six-membered cyclic diesters with 1,2- and 1,3-diols, respectively. It is important to emphasize that suitable diols must gather the *cis* configuration [2]; more precisely, the suitable molecule of diol must possess *syn*-periplanar torsion angle between the neighboring hydroxyls for effective complexation interaction [3]. As diol compounds are widespread in the nature, it is not surprising that sensors based on the affinity complexation of target analytes with BA ligands exhibit only limited specificity. Typically, a group of similar compounds possessing the required diol element becomes recognized.

The interaction between diol and BA is mainly governed by the appropriate configuration of the diol moiety; for example, sorbitol with its 2-, 3- and 5-suitably positioned hydroxyl groups [4] provides higher number of possibilities for interaction and forms more stable complexes compared to e.g. glucose. As additional parameters influencing the interaction, the pK_a values of both diol and the BA ligand play significant role. The common mistake in the boronates-related applications is the consideration that more alkaline environment promotes the interaction. It was shown that some derivatives of BA interact even more strongly under neutral conditions; this is due to the fact that the effect of diol as an acid group is frequently forgotten. For this reason it is necessary to optimize pH under which the experiments are performed [5].

The promising approach to enhance affinity or specificity of the interaction between BA and particular analyte is the modification of the binding site or its near environment. The most frequently utilized modification is addition of a nitrogen containing group to close proximity of the boron atom [6–8]. The interaction between B and N atoms stabilizes tetrahedral configuration of boron, which binds diols more firmly then the native trigonal form [6,9]. The B–N intramolecular interaction offers several orders of magnitude faster diol binding than usual BAs [6] and in addition it extends this behavior also to less alkaline near-physiological pH [10].

Reactivity, affinity and chemical behavior of boronic acids are commonly studied by means of optical methods – comprehensive kinetic studies of diverse boronates were performed using the

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fluorescent Alizarin Red S method [11,12]. However, the electrochemistry was applied for studies of selected BA derivatives as well; potentiometric [9,13] and voltammetric [14,15] methods were reported. The voltammetry typically follows formation and changes within the monolayer of BA assembled on the electrode surface; BA becomes either embedded in a thiol-containing molecule or attached through a suitable linker. Afterwards, electrochemical markers (e.g. ferri/ferrocyanide) allow to monitor permeability of such layers after binding of glycated compounds [1,16], typically proteins [14]. Alternatively, the surface modified with boronic acid served for immobilization of antigen which was further detected by peroxidase-labeled antibody [15].

An attractive approach utilized electrochemically-labeled BA; boric acid residuum was directly connected to an electroactive probe, e.g. ferrocene [17–19] and tetrathiafulvalene [20]. The simplest compound with the shortest connection of BA and ferrocene is ferroceneboronic acid (FcBA) [21]. The utilization of FcBA as electrochemical marker for proteins was already published in the literature [22]; so far, FcBA served only as a marker for surface-bound complexes. Although Wayner and colleagues [17] reported comprehensive study on properties of FcBA, surprisingly the electrochemical resolution of free and bound forms of FcBA in solution was not yet widely employed. The principle of the electrochemical resolution of free and bound forms of FcBA stems from its redox potential shift upon diol binding. The shift of the redox potential is due to the change in an electron configuration upon complex formation with another compound not necessarily electrochemically active (inactive diol). In addition to FcBA, the electrochemical properties of several other molecules containing ferrocene and boric acid parts were published [10,18,19]. Norrild and Søtofte [10] reported the derivative consisting of ferrocene and two BA residues linked to each of the cyclopentadienyl rings. Unfortunately, electrochemical properties were not tested. Arimori and colleagues [18] introduced an interesting molecule consisting of ferrocene derivative linked to the structure of two BAs connected through an aliphatic chain and Ori and Shinkai [19] synthesized ferroceneboronic acid with tertiary amine in its structure. Simple electrochemical properties of both compounds were tested on the set of several saccharides. Depending on the structure of the sensoric molecule, the positive [18,23] or negative [17,19] redox shifts were reported.

In this contribution the most suitable measuring procedure was developed and kinetic parameters were calculated for set of different types of *cis*-diols (polyols, mono- and disaccharides) with an important physiological role. The obtained results were used for evaluating FcBA as an electrochemical marker for amperometric determination. The probing of electrode confined *cis*-diol containing compounds was tested with the emphasis of resolution between free and bound forms of FcBA. To achieve this goal, the electrode was modified with a (poly)diol moiety as a model glycoprotein and interactions of FcBA with such layer were examined.

2. Experimental

2.1. Chemicals

Ferroceneboronic acid (FcBA) was provided by Sigma, its stock solution (100 mol dm^{-3}) was prepared in dimethylsulfoxide (DMSO). Galactose, sorbitol and maltose were provided by Merck, glucose, cellobiose, mannitol and lactose by Lachema (Brno, Czech Rep.), sucrose by Penta (Prague, Czech Rep.), fructose by Duchefa and mannose by Alchimica. Phosphate buffer (50 mmol dm^{-3}, pH 8.0, 100 mmol dm^{-3} KCl) was used for all experiments and all stock solutions of diols, especially saccharides, were prepared in phosphate buffer at least 2 h before use to assure equilibration between α-/β-anomers. Polyepichlorhydrin (PECH) was from Aldrich, 1,6-hexanediamine, 1,6-hexanediol and glutaraldehyde (GA) were supplied by Fluka and used as received.

2.2. Electrochemical measurements

The adopted set-up employed the PalmSens detector (Palm Instruments) and PalmSens PC software ver. 2.11 (Ivium). Cyclic (CV) and differential pulse (DPV) voltammetric measurements were performed in the potential range from −0.3 to 0.5 V (vs. Ag/AgCl reference electrode) with the potential step of 0.005 V and scan rate of 0.1 V/s and 0.05 V/s for CV and DPV (pulse time 0.05 s), respectively.

The screen-printed electrode (SPE; type AC1.W1.R1 from BVT Technologies) was used; both working and auxiliary electrode were gold and Ag/AgCl was used as reference electrode. Cleaning of the working electrode was always realized by cycling potential in range from −1.5 to 1.5 V in chromosulphuric acid followed by rinsing with distilled water. Prior to measurements, twenty CV scans in the presence of 1 mM FcBA were performed to stabilize electrochemical signal.

Measurements were carried out with SPE dipped into 1 mmol dm^{-3} FcBA solution in the 50 mmol dm^{-3} phosphate buffer pH 8.0, 100 mmol dm^{-3} KCl containing 1% DMSO in the absence of any diol, using 5 ml of the solution. Next, the concentration of the tested diol compound was gradually increased by sequential additions followed by brief stirring (the 30 s intervals assured time for quantitative interaction between diol and boronic acid [11]) and CV and DPV measurements were eventually performed. Data were processed and evaluated in Origin 7.0 (Microcal).

To compensate for minor production fluctuations among individual SPEs used (geometric area, roughness), normalization of the recorded signals was carried out; the measured DPV curves were divided by the height of a peak obtained with the electrode in the solution where only FcBA was present. This peak was taken as reference and represents normalized value of current equal to 1. The normalized data was further processed as follows:

$$I(c) = (I_{free,0} - I_{bound,0}) \left(\frac{I_{free,c}}{I_{free,c} + I_{bound,c}} \right) \quad (1)$$

Here $I(c)$ represents the processed current originating from the free form of FcBA at the particular concentration of diol c, I_{free} and I_{bound} are currents measured at the potential of free and bound forms of FcBA, respectively. Such processing of the raw data eliminated the influence of viscosity, which affects mobility of the FcBA–diol complex [18,19] especially at higher concentrations of sugars.

Amperometric data were recorded at the fixed potentials of 0.075, 0.0 and −0.075 V. Measurement procedure was the same as in the case of voltammetry measurements except stirring through whole experiment. The experiment in absence of FcBA served as reference.

2.3. Calculation of kinetic constants

Interaction of FcBA with diol represented by the peak current I for the given concentration c of diol was approximated by the common saturation kinetics, as the limited amount of the binding sites of FcBA was one of the principal conditions for this simple model. Absolute values of decrease of the peak current determined at potential corresponding to free FcBA was used for evaluation and represented the sites occupied by the bound diol. The resulting processed values of current were plotted against the corresponding concentration of particular diol and the interactions were

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