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Liquid / liquid interface-based electrochemical sensing of ractopamine and salbutamol

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Abstract

An electrochemical sensor based on ion transfer across micro- and nano-liquid / liquid interfaces has been developed for the detection of protonated drugs, ractopamine ($RacH^+$) and salbutamol ($SalH^+$) via cyclic voltammetry (CV) and linear sweep stripping voltammetry (LSSV). These voltammetric methods enabled the detection and characterisation of the ionised drugs despite that they transferred at high applied potentials. The drugs' thermodynamic and analytical parameters were determined. The limit of detection in the sub-μM range is suitable for applications to detection in real samples. Electrochemistry at the liquid / liquid interfaces was shown to be a viable technique for drug sensing.

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Keywords: electrochemical sensor; ion transfer; micro- and nano-liquid / liquid interfaces; protonated drugs; voltammetric methods

1. Introduction

Electrochemical sensing based on ion transfer across the interface between two immiscible electrolyte solutions (ITIES), or at liquid / liquid interfaces, has progressed from the transfer of model ions (e.g. tetraalkylammonium ions) to the detection of biologically relevant molecules (e.g. proteins, peptides, amino acids and other small molecules (drugs, neurotransmitters and food additives)) [1].

Ractopamine (Rac) and salbutamol (Sal) (or also known as albuterol) are β-adrenergic agonists with similar chemical structures and functions. These drugs were originally developed as therapeutic drugs in

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human and veterinary medicine for the treatment of pulmonary/respiratory diseases such as asthma. Unfortunately, β-adrenergic agonists are also illegally applied in the livestock industry as growth promoters, where they divert fat deposition to the production of muscle tissue. β-adrenergic agonist-treated animals may pose adverse effects on human health, especially in the cardiovascular and central nervous systems. As a result, this veterinary drug residue issue has recently become a public food safety concern [2, 3]. Therefore, rapid, simple and sensitive analytical methods for the detection and quantification of β-adrenergic agonists are vital.

A number of methods have been reported for the determination of ractopamine and salbutamol including immunoassays, electrochemical methods, spectrophotometry, high performance liquid chromatography, and so forth [3]. Even though spectrophotometry and chromatography are widely employed, these techniques are expensive and time-consuming (for derivatization steps) [4]. Electrochemical methods arise as advantageous due to low instrumental cost, fast analysis and simplicity. However, strong electrode fouling/poisoning reported for salbutamol detection is a drawback for solid / liquid interface based electrochemical sensing [4]. In addition, the ability of liquid / liquid interface-based electrochemical sensing to be implemented for detection of ionised ractopamine and salbutamol remains unexplored.

Herein, the electrochemical behaviour of $RacH^+$ at the micro- and nano-ITIES arrays, and $SalH^+$ at the micro-ITIES array via CV and LSSV is presented. Emphasis is placed on the electrochemical behaviour of the protonated drugs at the micro-ITIES array due to the issue of insufficient potential window for the transfer process. However, protonated drug detection at the micro-ITIES array will provide a basis for future studies at nano-ITIES array. The oxidation behaviour of ractopamine at the solid / liquid interface was also examined. In addition, the thermodynamic parameters for the transfer of ionisable ractopamine, and the influence of the interfering substances, including serum protein, towards $RacH^+$ detection were also studied.

2. Material and Methods

2.1. Materials and reagents

Chemical reagents used were obtained from Sigma-Aldrich Pty. Ltd., Australia. 10 mM lithium chloride (LiCl) prepared in ultrapure water, and 10 mM bis(triphenylphosphoranylidene)ammonium tetrakis(4-chlorophenyl)borate (BTPPATPBCl) dissolved in 1,6-dichlorohexane (DCH), served as the aqueous and organic phase solutions, respectively. In the micro-ITIES study, the organic phase was present as an organogel with incorporation of low molecular weight poly(vinylchloride) (PVC) (10 % w/v). The organic reference solution consisted of 10 mM BTPPACl dissolved in 10 mM LiCl. Ractopamine hydrochloride and salbutamol, and tetrapropylammonium chloride (TPrACl) served as the drugs and model analyte species studied, respectively. The stock solutions of ractopamine hydrochloride and salbutamol were prepared in methanol (MeOH) due to their low solubility in water. In the study of the oxidation of ractopamine, the supporting electrolyte solution of 0.1 M phosphate buffered saline (PBS) (pH 7.4) was prepared in ultrapure water. 5 mM of interferents, prepared in 1 mM PBS solution were used in the interfering substances study. In the effect of artificial serum matrix towards $RacH^+$ detection, artificial serum compositions are as detailed previously [5].

2.2. Preparation of micro- and nano-interface arrays

The silicon micropore arrays used for micro-ITIES patterning were 11.09 ± 0.12 μm radius, r_a, 30 pores in a hexagonal array, and with pore centre-to-centre separation, r_c, of 18.4 ± 2.1 times the pore