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Electrocatalytic properties of vitamin B_{12} towards oxidation and reduction of nitric oxide

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Abstract

This paper reports on the catalytic behaviour of cyanocobalamin (VB_{12}) towards the reduction and oxidation of nitric oxide. When VB_{12} is adsorbed on glassy carbon electrodes, it catalyses the reduction of nitric oxide (NO) in pH 4 and 9 buffers. In the absence of NO, cyclic voltammetry shows that VB_{12} is reduced by a one-step two-electron reduction from Co^{III} to the Co^{I} species. Addition of NO at pH 9 to solutions of VB_{12} resulted in the splitting of the cyclic voltammetry peaks as a result of a consecutive one-electron reduction of the central Co^{III} metal in VB_{12} to Co^{II} and finally to Co^{I}. The catalytic peak for oxidation of NO on a glassy carbon electrode modified with VB_{12} was observed at 1.21 V versus Ag|AgCl, at pH 9. The products of the catalytic reduction of nitric oxide include ammonia and hydroxylamine. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Cyanocobalamin; Nitric oxide; Electrocatalysis; Oxidation; Reduction

1. Introduction

Nitric oxide (NO) has a number of significant roles in physiology, microbiology and atmospheric chemistry. For example NO has been shown to be involved in physiological processes such as vasodilation and neurotransmission in the brain [1,2]. NO plays a role in the immune system's ability to kill tumor cells and intracellular parasites. Elevated levels of NO have been shown to indicate human organ transplant failure [3]. Excess concentrations of NO have been implicated as a factor in septic shock [4], Parkinson's and Alzheimer's diseases [5].

The ability to measure NO accurately is crucial for further understanding of its numerous biological roles. Measuring NO in biological media is very difficult because of its low concentrations and short life time. Most methods for measuring NO are indirect since they rely on measurements of secondary species such as nitrite, the oxidation product of NO. For direct determination, nitrite interferes with the detection of NO. Nitric oxide can be oxidized to nitrite at about 0.9 V versus saturated calomel electrode on platinum electrodes [6].

Direct electrochemical reduction of NO is favoured thermodynamically but is kinetically slow. The use of porphyrin and phthalocyanine complexes for the electrocatalytic oxidation or reduction of NO has gained momentum [7–18]. The metallophthalocyanine (MPc) and metalloporphyrin (MP) complexes have been shown to lower the potential and increase the currents for the reduction and oxidation of NO [8,14,16–19]. The use of electrodes modified with nickel(II) tetrakis(3-methoxy-4-hydroxy phenyl) porphyrin (NiTMHPP) and covered with Nafion®, prevented the interference of nitrite in NO detection [7]. Metalloproteins such as cytochrome *c* [20], hemoglobin and myoglobin [21–23] have been studied for their use as electrocatalytic sensors for NO.

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