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A novel potentiometric sensor for promethazine based on a molecularly imprinted polymer (MIP): The role of MIP structure on the sensor performance

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ABSTRACT

A novel potentiometric sensor based on a molecularly imprinted polymer (MIP) for determination of promethazine (PMZ) was prepared. Promethazine MIP particles were prepared and dispersed in 2-nitrophenyloctyl ether and then embedded in a polyvinyl chloride matrix. The effect of the monomers type on the sensor performance was investigated, and an important role for this parameter was shown. It was shown that the membrane electrode with a MIP prepared by vinylbenzene and divinylbenzene had a better performance in comparison to membrane electrodes containing MIPs prepared with methacrylic acid-ethylene glycol dimethacrylate or vinylbenzene-ethylene glycol dimethacrylate. After optimization, the membrane electrode constructed with a MIP of vinylbenzene-divinylbenzene exhibited a Nernstian response (31.2 ± 1.0 mV decade^{-1}) over a wide concentration range, from 5.0×10^{-7} to 1.0×10^{-1} M, with a low detection limit of 1.0×10^{-7} M and a response time of ~50 s. The method has the requisite accuracy, sensitivity and precision to assay PMZ in syrup samples and biological fluids.

1. Introduction

Molecularly imprinted polymers (MIPs) are promising materials for continual use in sensor fields as the recognition element or modifying agent. An MIP is a synthetic polymer possessing selective molecular recognition properties for the shape and positioning of functional groups because of its recognition sites within the polymer matrix that are complementary to the analyte molecule. These materials are similar to biological specific receptors in some ways because of their high selectivity to the target molecule and their recognition mechanism [1,2]. MIPs have been used for electrochemical sensor development as the highly selective recognition element of the sensor [3–6].

Promethazine is widely used for its antihistaminic, sedative, antipsychotic, analgesic and anticholinergic properties. However, promethazine hydrochloride can cause adverse effects in humans, such as endocrinal, cardiac and reproductive alterations. Therefore, its determination in commercial formulations and biological samples is extremely important [7].

Many analytical techniques such as titrimetric procedures [8–10], spectrophotometric methods [11], spectrofluorometry [12], high performance liquid chromatography [13] and voltammetry [14] have been employed for promethazine (PMZ) determination.

Potentiometry is one of the simplest instrumental techniques that many chemists encounter. Potentiometric sensors provide an exciting and achievable opportunity to perform biomedical, environmental and industrial analyses away from a centralized laboratory because they make it possible to combine the ease of use and portability of potentiometry with simple, inexpensive fabrication techniques. While potentiometry has been used for many years, the advances in the field of ion-selective electrodes make it a valuable technique in the modern laboratory [15,16].

The unique feature of potentiometry with MIP-based sensors is that the species do not have to diffuse through the membrane so there is no size restriction on the template compound. Despite all these advantages, only a few MIP-based sensors have been reported that utilize a potentiometric transducer [17–19]. These studies describe potentiometric sensors created in several different ways: by dispersing MIP particles in plasticizer and embedding them in a polyvinyl chloride (PVC) matrix [20–23], by forming a glassy membrane [24], by assembling the template on the polar surface of an indium tin oxide (ITO) glass plate [25,26], by depositing a MIP polymeric film on the gate surface of an ion-sensitive field-effect transistor [27,28] and by embedding MIPs in the carbon paste electrode [29].

The potentiometric sensor that has already been reported for promethazine determination [30,32] usually uses the ion-pairing agent as the ionophore, which suffers from the main disadvantage of low selectivity toward the target molecule. The use of a MIP as the ionophore in the membrane electrode for promethazine determination would be an interesting development in this field because it would provide improved selectivity in the developed sensor.

In this work, a molecularly imprinted polymer with recognition sites for promethazine was prepared and then used to fabricate the

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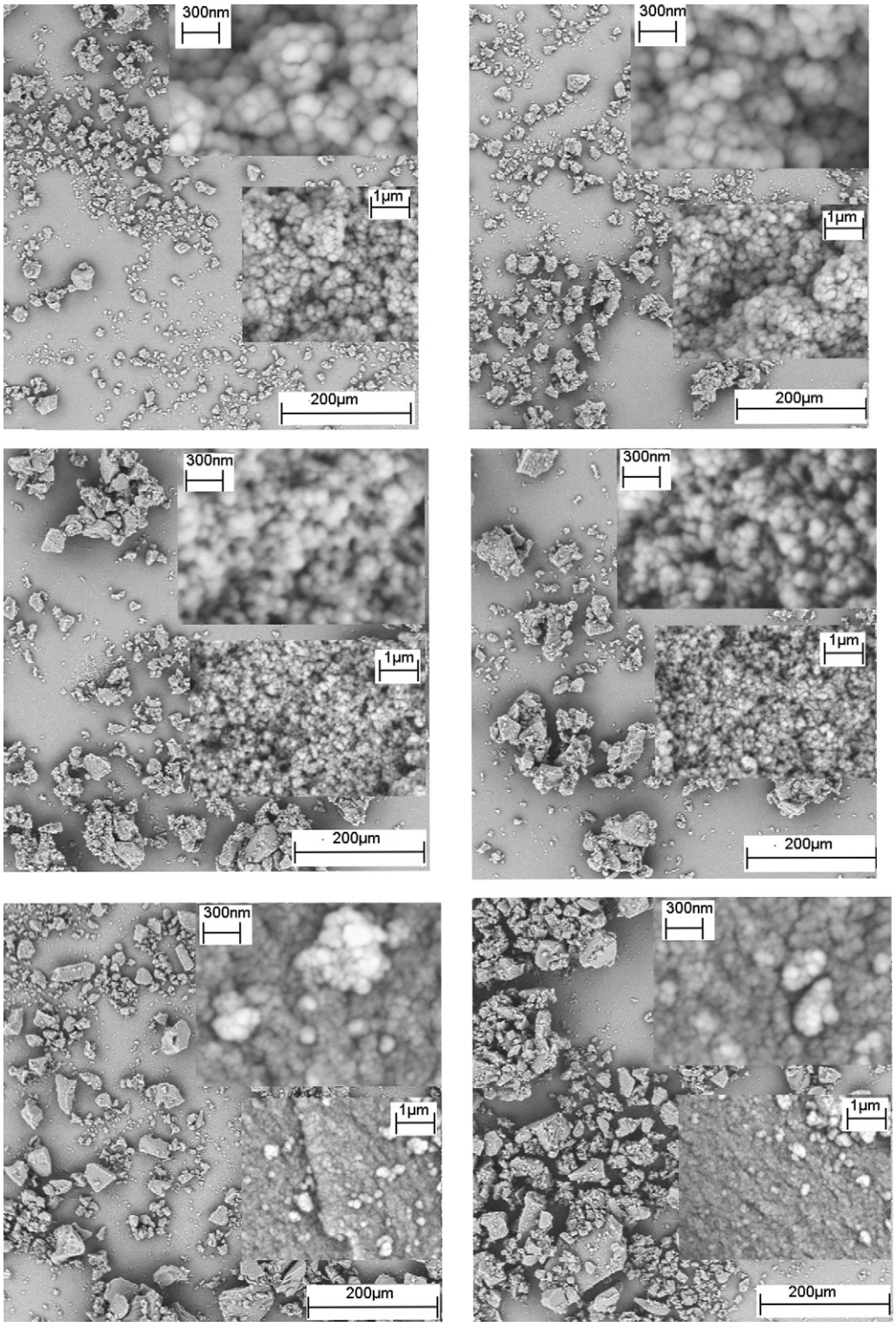

Fig. 1. Scanning electron microscopy images of MIPs (left side) and NIPs (right side) for different structures, including MAA-EGDMA (top), VB-EGDMA (middle) and VB-DVB (bottom).

promethazine-selective potentiometric sensor, creating the first MIP-based promethazine sensor. It was found that the MIP composition as determined by the nature of the monomers used for the MIP preparation had a considerable effect on the final sensor performance. After optimization of the parameters influencing the sensor performance, the sensor was successively used for promethazine determination in pharmaceutical products and serum samples.

2. Experimental

2.1. Reagents

Promethazine hydrochloride and clozapine were obtained from Fluka (Switzerland). Methacrylic acid (MAA), 4-vinylpyridine (VB), divinylbenzene (DVB), ethylene glycol dimethacrylate (EGDMA),