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Adsorption of pesticide benfluralin at the electrochemical interface

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ABSTRACT

The adsorption behaviour of a dinitroaniline herbicide benfluralin was studied by means of electrochemical as well as scanning probe techniques. The double layer capacitance reflects very sensitively changes of the interfacial structure at the surfaces. This allows discrimination between a simple adsorption process and a slow transition of adsorbed film structure controlled by the mechanism of nucleation. The information about nucleation kinetics and growth mechanism of the film on the electrode was obtained from the time dependence of the double layer capacitance employing the mercury drop electrode. The phase transition may lead to the reorientation of the molecules within the adsorbed layer. These findings were supported by scanning tunneling microscopy.

1. Introduction

Benfluralin (*N*-butyl, *N*-ethyl, 2,6-dinitro, 4-(trifluoromethylaniline) (Scheme 1) is a dinitroaniline herbicide registered for use on lettuce. The mechanism of its action is based on the microtubule assembly inhibition. Since its chemical structure contains alkyl chains, it can be predicted, that the adsorption of this herbicide at various interfaces would be significant. Most of pesticides and their metabolites are very stable in soil. Their accumulation at the natural interfaces plays an important role in the contamination of environment. They can remain in the surface layers of soil, where they are exposed to the activity of microorganisms and photoprocesses. Alternatively, they may penetrate to the ground water and contaminate sources of drinking water. Such behaviour was found in the case of herbicides atrazine and terbutylazine, the molecules of which are structurally very similar, differing only in the presence of *iso*-propyl and *tert*-butyl substituents on their 6-amino- groups [1]. However, this minor structural alteration causes profound differences in the decomposition rates in the environment leading to a ban of atrazine in the European Union. We reported the study on their formation of compact film and its transition on mercury electrode, which is markedly different for both pesticides [1,2].

Processes taking place at the electrochemical interface often involve an adsorption. The adsorbate–surface and adsorbate–adsorbate interactions participate in the formation of physically adsorbed ‘compact’ layers. The double layer capacitance of the electrode/electrolyte interface sensitively reflects changes of the interfacial structure at the surfaces. This allows discrimination between a simple adsorption process and a slow transition of adsorption film structure controlled by the nucleation and growth mechanism. Strong adsorbate–adsorbate interactions support the formation of compact two-dimensional layers [3–7]. The desorption of the compact surface film involves a process inverse to the nucleation (the hole formation). The change of molecular orientation in an adsorbed layer is another process that can take place at the interface. The molecular orientation dependence on the electrode potential was observed in the case of nitrogen heterocompounds purines, pyrimidines and pyridines, 2,2′-bipyridine, adenine, adenosine [8–12].

Since these dinitroaniline pesticides and their metabolites exhibit toxicity to wildlife, the study of their adsorption at the interface is highly demanding. The aim of this contribution is to explore the nucleation kinetics and elucidate the mechanism of the film growth formation on the mercury electrode employing time resolved double layer capacitance measurements. Hanging mercury drop electrode was chosen as a model interface in this study as it offers a fresh, atomically flat and reproducible surface. The adsorbate–adsorbate interaction study is supported by STM topography images on Au(1 1 1).

2. Experimental

Benfluralin (*N*-butyl, *N*-ethyl, 2,6-dinitro, 4-(trifluoromethylaniline) was purchased as a pesticides reference material from Sigma–Aldrich (Riedel-de Haën, Sigma–Aldrich). Potassium fluoride was of analytical grade (Merck). Water was distilled and subsequently de-ionized by means of Millipore system (Milli-Q, Millipore Co., USA). Electrochemical measurements were carried out using an electrochemical system for cyclic voltammetry, phase-sensitive AC and DC polarography. It consisted of a fast

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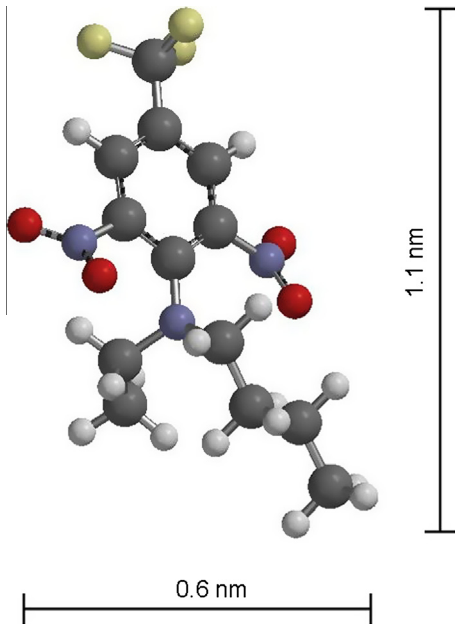

Scheme 1. The chemical structure of benfluralin **1**.

rise-time potentiostat, a lock-in amplifier (Stanford Research, model SRS830) and a frequency response analyzer (Stanford Research, model SRS760). The instruments were interfaced to a personal computer via an IEEE-interface card (PC-Lab, AdvanTech Model PCL-848) and a data acquisition card (PCL-818) using 12-bit precision. Sine-wave frequency and peak-to-peak amplitude for the phase-sensitive AC polarography and capacitance-time measurements were 320 Hz and 5 mV, respectively. A three-electrode electrochemical cell was thermostated using Ministat CC (Huber, Germany). The reference electrode, Ag|AgCl|1 M LiCl, was separated from the test solution by a salt bridge. The working electrode was a valve-operated static mercury electrode (SMDE2, Laboratorní Přístroje, Prague) with an area 1.13×10^{-2} cm^2 and mechanically controlled drop time. The auxiliary electrode was a cylindrical platinum net. Oxygen was removed from the solution by passing a stream of argon.

Scanning tunneling microscopy (STM) measurements were carried out in the air at room temperature employing Agilent 5500 SPM (Agilent Technologies), scanner N9501A-US06310232. The STM probes were prepared by mechanical cutting of platinum/iridium (80/20% m/m) wire (GoodFellow, Great Britain) by scissors. The vertical movement of the probe was referenced to the average step height differences (0.25 nm) between two atomically smooth terraces of Au(1 1 1) surface (evaporated on mica substrate followed by hydrogen annealing, the substrates purchased from Agilent and used as received). STM images were recorded in the constant current mode with tunneling current setpoint of 50 pA, scan speed was between 0.54 and 0.76 μm s^{-1}, the bias voltage was −0.1 V. The adsorbed layers of benfluralin on Au(1 1 1) surface were prepared as follows. The Au(1 1 1) surface was exposed to the freshly prepared solution of benfluralin (0.2 mM in 0.1 M KF containing 20% ethanol) for 330 s. Subsequently, the surface was dried under the stream of argon and immediately subjected to the STM imaging.

3. Results and discussion

Adsorption properties of benfluralin **1** were investigated by AC polarography. The imaginary admittance component $Y'' \sim 2\pi fC$ was recorded as a function of the electrode potential, with C being the double layer capacity. The quantity f is the perturbation frequency. All experiments were performed in the presence of potassium fluoride as a supporting electrolyte in order to avoid a specific adsorption of electrolyte anions at the electrode/electrolyte interface. It is known that chloride, bromide and iodine anions specifically adsorb at mercury electrodes at positive potentials, whereas fluoride is one of few anions that does not adsorb specifically at all [13]. Fig. 1 shows the change of double layer capacity as a function of the bulk concentration of **1**. A decrease of the double layer capacity indicates a strong adsorption of the compound **1**. The shape of AC voltammogram in the range of potentials between −0.05 V and −0.50 V reflects interesting adsorption behaviour of the compound **1**. A typical "capacitance pit" is a signature of the adsorbed layer caused by strong adsorbate–adsorbate interactions, which leads to the formation of compact two-dimensional physically adsorbed layers. A further increase of benfluralin concentration was found to lead to its precipitation in the aqueous solution, as expected in cases of compounds with a limited solubility [1].

The double layer capacitance of the hanging mercury drop electrode/aqueous 1 M KF containing 50% ethanol (v/v) in the presence of **1** in the solution bulk as a function of the electrode potential is shown in Fig. 2. The AC voltammogram shows two peaks on both real (not shown) and imaginary admittance component at −0.62 V and −0.78 V corresponding to the reduction of nitro group in the molecule of **1** (Scheme 1) [14,15].

The time dependence of the double layer capacitance C at a constant electrode potential allows the distinction between the mass transfer and nucleation-controlled processes. The measurements were done purposely within the range of electrode potentials, at which no faradaic processes were observed. The experiments are technically rather challenging as one needs to form a reproducible hanging mercury drop electrode/electrolyte interface of a constant area for an extended time period (typically 10^3–10^4 s). Any mechanical vibrations or imperfections at the capillary orifice would cause a loss of the contact or a fall of the mercury drop. A sigmoidal shape of the capacitance time (C–t) transients may be easily translated into the dependence of the relative surface coverage θ as a function of time. The measurements are carried out at a constant bulk concentration and temperature, allowing time to be the only variable in the parameter space. The surface coverage θ is given by the Eq. (1) assuming the adsorption model of two parallel capacitors:

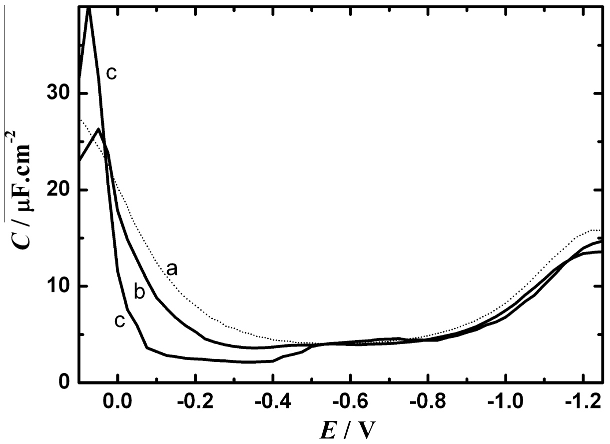

Fig. 1. The double layer capacitance of the mercury drop electrode in aqueous 1 M KF/20% ethanol (v/v) in the presence of benfluralin at concentrations: (a) 0.00 mM, (b) 0.29 mM and (c) 0.70 mM as a function of the electrode potential. The data was obtained at the frequency 320 Hz with the amplitude of 5 mV.