CHAPTER 1: INTRODUCTION

It can be said that one of main challenges of science is to understand the process underlying the emergence and maintenance of life [1]. Among the different models and available approaches trying to explain that topic, some strategies including chemical reactions were developed in the past. In some of these studies the early atmosphere the earth was simulated [2]. In other studies some compounds found on meteorites [3] and interstellar gases was analyzed by spectroscopy [4]. Strong evidences for the existence of different classes of organic compounds in the prebiotic period, such as derivatives of purine and pyrimidine bases have been provided [5]. Due to the important role of these bases responsible for the replication of the genetic code, it is reasonable to assume the presence of these molecules in any process assigned to being responsible for the origin of life. Several studies have been proposed, which assume that purine and pyrimidine bases can spontaneously self-assemble into a two-dimensional monolayer at the interface between water and crystalline inorganic solids [6-15]. The idea to use inorganic substrates is important because of the widespread idea that they might play a role in processes associated to the origin of life. The formation of peptide bonds between non-coded amino acids on inorganic minerals has been proposed [16] suggesting that it could be the first genetic code system [17]. The suggestion that the purine and pyrimidine might be involved in the formation of self-assemble monolayers in the prebiotic makes the study of this kind of molecules very important to gain a deeper insight into issues that can help to elucidate the origin of life.

In contrast to conventional studies of self-assembling processes in the absence of an electrical field, studies carried out under electrochemical environment can, up to some extent, mimic biological environment. This becomes very transparent when considering that the cells are totally enclosed by a membrane, which encloses the cellular fluid. This fluid, in turn, contains ions such as sodium, potassium and chloride. Additionally, many of the cellular processes are driven by a potential difference across cellular membrane surface [18].

The formation of condensed monolayers of organic molecules on mercury electrodes under electrochemical conditions was first studied by Lorenz [19] followed few years later by Vetterl [20,21], who investigated the monolayer formation of purine and pyrimidine by capacity measurements on Hg electrodes.

Although the first investigations of the behavior of organic molecules on Hg revealed important thermodynamics and kinetic information on the monolayer, studies of two-

dimensional condensation of purine and pyrimidine on solid electrodes has been increased in he last years [22-27]. The advantage of using solid electrodes in electrochemical measurements is that it allows a combination of potential controlled formation of monolayers with other techniques such as scanning tunneling microscopy (STM), which can determine the structural features of surfaces with atomic details [28] and atomic force microscopy (AFM) that resolves these characteristics topographically [29].

STM analyses of adenine on highly oriented pyrolytic graphite (HOPG) and MoS_2 [30] demonstrated that planar orientation of the molecules are stabilized by intermolecular hydrogen bonds and van der Waals interaction. For thymine and uracil on the same surfaces [11] the same hydrogen bonded planar configuration of the molecules seen in the solid state was suggested.

As mentioned above, a relative amount of studies was performed for purine and pyrimidine complementary DNA and RNA bases on different surfaces, but few electrochemical studies were performed to investigate the coadsorption behavior of these bases [31,32].

The DNA molecule is composed by a double strand, which contains purine and pyrimidine bases, a sugar and a phosphate group, making pairs within them by hydrogen bonding. The sequence of the bases in one strand determines the sequence of the bases in the second strand. For example, if one base is adenine in one strand, the opposite base must be thymine; the same is valid for guanine and cytosine (DNA). These are the so- called complementary base pairs (Figure 1.1).

However, if a change in the genetic material occurs, it might lead to cancer and tumor appearance, for instance. A change in the genetic code means that one of the standard base (Figure 1.1) may be replaced by a non-standard base, for example bromouracil (which is a mimic of thymine), resulting in a non-complementary base pair. . On the other hand, the substitution of thymine by bromouracil in the genetic code leads to a greater sensitivity to ionising radiation [33,34], making the use of bromouracil an advantage in cancer therapy.

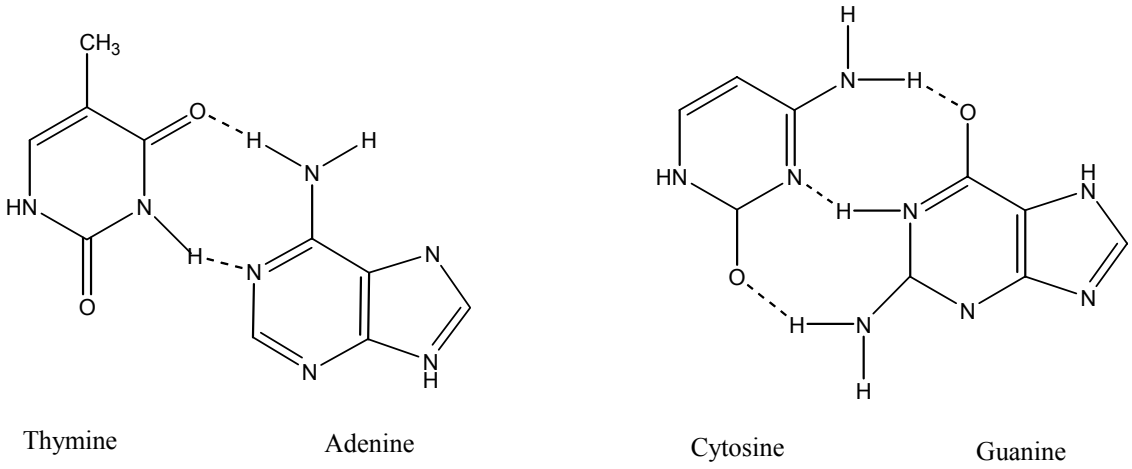

Figure 1.1: Models of the hydrogen bonded complementary base pairs thymine-adenine and cytosine-guanine.

The present thesis is focused on the study of the interaction between DNA bases and the pyrimidine derivative bromouracil in a well-defined gold surface. Specifically, the main goal of this contribution is to investigate if the similar behavior of the base pairs found in the genetic material (DNA) is observed in electrochemical environment. In other words, it aims at understand the interaction between the complementary and non-complementary bases on charged surfaces.

The thesis is structured as follows: in the second chapter some key concepts necessary to understand the discussed results are presented. Chapter 3 describes the experimental aspects involved and includes the instrumentation and techniques employed. In Chapter 4 the adsorption and coadsorption behavior of thymine, adenine and uracil are presented. The adsorption and coadsorption of bromouracil, guanine and adenine are displayed in Chapter 5 and adenosine and thymidine in Chapter 6. In Chapter 7 a summary of the main results is given.