Statistical studies of adsorption isotherms of iron nitrate and iron chloride on a thin layer of porphyrin

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ABSTRACT

The adsorption isotherms achieved at four temperatures of the Iron nitrate and Iron chloride to a biosensor (Porphyrin TPP coated onto Quartz crystal) were simulated using models established through statistical physics formalism. Modeling of experimental isotherms using statistical physics has to offer microscopic interpretations for the mechanism of adsorption. The results showed that the adsorption was exothermic and took place with physisorption. The Iron nitrate adsorption occurred by the formation of multilayer adsorption whereas for Iron chloride the adsorption was monolayer.

The parameters deduced from fitting of the experimental data were discussed and interpreted. The statistical models were also used to investigate thermodynamics functions that govern adsorption mechanism, such as entropy, internal energy, and Gibbs free enthalpy. It is shown that the two systems release energy which confirms that the adsorption is exothermic process.

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1. Introduction

For many years, metalloporphyrines have attracted the attention of authors in electrochemistry for their catalytic properties for the promotion of several electrochemical reactions [1,2]. They are also interesting for their structures and interaction between the central metal and the analyte. Porphyrins, aromatic tetrapyrrole macrocycles, are almost planar molecule and it can easily form stable complexes with charged ions such as magnesium, zinc, iron, cobalt… The specific structures and properties of the metalloporphyrins confirm that they might be useful as probes in analytical chemistry for the molecular recognition [3,4]. The redox activity of both metal center and porphyrin macrocycle improves the ability of these compounds to act as the recognition element of electrochemical sensors. These metalloporphyrin participate at many biological processes [5,6]. They may also provide a solution for cleaning sites contaminated by chlorinated organic pollutants. They have recently gained increasing interest in the fabrication of sensors, electroluminescent, and photovoltaic devices [7,8].

Many porphyrins are naturally occurring; one of the best-known porphyrins is heme [9] (complex iron-porphyrin), the pigment in red blood cells, a cofactor of the protein hemoglobin. They have a big role in biochemistry since complexing porphyrins with iron is very important process in biological environment.

However, the mechanism of the metallization is not yet completely understood. So we will try to examine this phenomenon using a quartz crystal microbalance [10] and statistical physics formalism [11]. Firstly, we started by manufacturing a biosensor [12] (Porphyrin TPP coated onto Quartz crystal) then controlling the adsorbed mass of iron using the microbalance. Secondly, we will try to understand and interpret the phenomenon of metallization [13,14] at microscopic scale. The modeling of adsorption iron on a thin layer of porphyrin constitutes the principal motivation. Throughout the grand canonical ensemble in statistical physics, a treatment of models will be used. Such treatment allows us to better understand the adsorption at the solid liquid interface and interpret this mechanism at the solid-liquid interface at microscopic scale.

2. Materials and methods

The adsorbent used is the Tetraphenylporphyrin, [15] abbreviated TPP or H_2TPP (Fig. 1). The study of naturally occurring porphyrins is complicated by their low symmetry and the presence of polar substituents. Tetraphenylporphyrin is hydrophobic, symmetrically substituted, and easily synthesized. Among the chemical properties we have to

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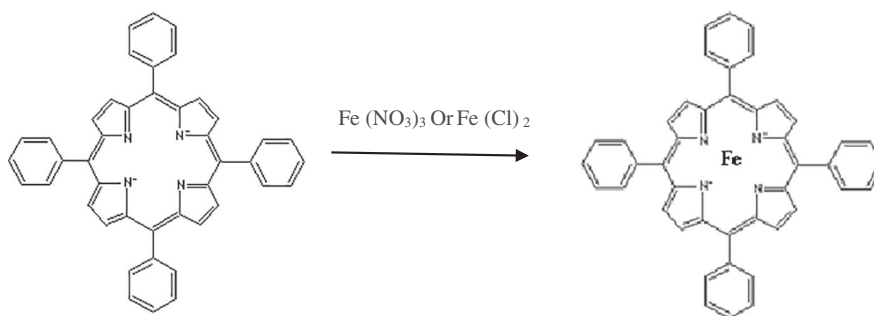
Fig. 1. Metallization of porphyrin (TPP) with Iron.

quote the basic character of porphyrins. The overall structure is quite rigid due to pyrrole rings but it folds to include a small metal atom or becomes dome to accept bigger metal atom [16,17].

A number of features make porphyrins eligible as good sensing materials. Almost all metals have been coordinated to the porphyrins [18]; furthermore, the organic chemistry of these compounds is well developed, and a wide range of different substituents can be introduced at their peripheral positions [19]. The coordinated metal, peripheral substituents, and macrocyclic skeleton influence the related sensing properties of these compounds [20]. All these characteristics increase the versatility of these molecules for porphyrin based sensors [21–23], showing excellent properties in terms of stability, sensitivity, and reproducibility. Some new kinds of metal porphyrin derivatives were synthesized and their multilayer films were used for gas sensing [22].

In the present work, we will use two adsorbates; The first is the Iron (III) nitrate ($Fe(NO_3)_3$) which called also ferric nitrate. Since it is deliquescent, it is commonly found in its nonahydrate form $Fe(NO_3)_3.9H_2O$ in which it forms colorless to pale violet crystals. The second is the Iron (II) chloride, also known as ferrous chloride. It has the formula $FeCl_2$ and it is usually obtained as an off-white solid.

The quartz microbalance (QCM) [24,25] is one of the most methods used to achieve adsorption isotherms for thin layers. So, we will devote to the achievement of adsorption isotherms of Iron nitrate and ferrous chloride on a thin layer of Porphyrin with the quartz crystal microbalance.

For film deposition, a volume of 30 μL of TPP was spin coated at 3000 rpm for 1 min onto the larger gold electrode to cover the overlapping electrodes portion. The coated crystals were then dried at 100 °C for at least 2 h. After drying, we started our measurements.

The experimental setup for the adsorption measurements with the quartz crystal microbalance is depicted in Fig. 2.

The QCM [10,24] used for experiment is composed of coated electrode, frequency-meter instrument (model PM 700), a crystal holder, and adsorption cell. In the calculation of the adsorbed amount of Iron nitrate or Iron chloride, a linear relationship between the change of the areal mass density and the frequency shift was assumed. Such relation is known as Sauerbrey equation which is given as [26]:

$$\Delta F = -\frac{2F_0^2}{A\sqrt{\rho\mu}}\Delta m \qquad (1)$$

Where ΔF is the frequency shift (Hz), F_0 is the resonant frequency of the crystal (Hz), Δm is the adsorbed amount (μg), A is the active electrode area (cm^2), ρ is the density of quartz (2.648 g.cm^{-3}), and μ is the shear modulus of quartz (2.947×10^{11} g.cm^{-1}.s^{-2}).

This relation can be also written by combining the constants to give a specific constant relative to a crystal called crystal sensitivity constant C [27–29]:

$$\Delta m = -\frac{\Delta F_m}{C} \qquad (2)$$

where $C \approx 56.6$ μg^{-1}.cm^2.Hz for a 5 MHz AT-cut quartz crystal, i.e., when 56.6 μg of mass is deposited on 1cm^2 of area, it will produce a shift of negative 1 Hz in the resonant frequency of the crystal.

The QCM crystal holder was immersed in the adsorption cell filled with $V_s = 100$ mL of pure water. After stabilization of the QCM frequency change (took around 2 h), 100 μL of concentrated Iron nitrate or Iron chloride solution (10^{-4} M) was injected with syringe while the solution was stirred with a magnetic stirrer. The reported concentration of adsorbate was the final concentration in the adsorption cell (10^{-7} M).

The quartz microbalance displays the change in the frequency for this concentration. Using the Sauerbrey relationship, the adsorbed amount per unit of area expressed in μg.cm^{-2} is derived from the measured frequency. We proceed in the same way to get the adsorbed amounts for the increasing concentration solutions. We give in Fig. 3 the mass of Iron adsorbed per unit of mass adsorbant with the error bar.

In the following, we use a statistical physics treatment to establish the expression of statistical model giving the adsorbed quantity versus the concentration. Then, we apply the adequate analytical expression to fit experimental isotherms.

3. Theoretical background of studies

Adsorption properties and equilibrium data, commonly known as adsorption isotherms, describe how adsorbates interact with adsorbent materials. Theoretical modeling of adsorption isotherms is a powerful method used for surface characterization. Thus, the correlation of equilibrium data by either theoretical or empirical equations is essential to the practical design and operation of adsorption systems. Moreover, in contrast to the empirical methods, the use of statistical physics development gives a physical meaning to the model parameters and allows the
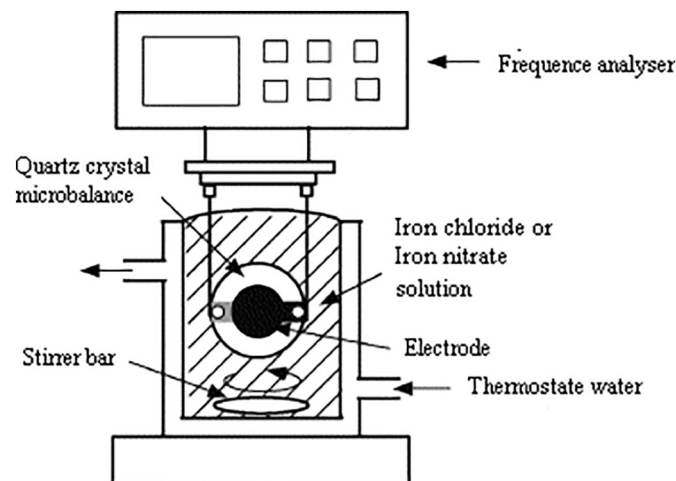

Fig. 2. Experimental setup for adsorption measurements with QCM.