Parameters identification for the Langmuir model

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Abstract: In this paper, we model the adsorption and desorption kinetic data of Ruthenium polypridyl complex film. In our model, we use the nonlinear regression methodology. We measure the data by the technique so-called Quartz Crystal Microbalance. In the end, we reported that adsorption rate k_a is same for both adsorption and desorption of Ruthenium polypridyl complex film.

Keywords: Langmuir model, adsorption, desorption, Quartz Crystal Microbalance, nonlinear regression.

1. INTRODUCTION

The humidity adsorption and desorption kinetic data of spin coated 50 nm Ruthenium polypridyl complex (Ru-PC K314) film has been measured under relative humidity between 11 % and 97 % using by Quartz Crystal Microbalance (QCM) technique. QCM have been extensively used for the determination and investigation of the kinetics of adsorption/desorption of adsorbate molecules Hartmann et al. (1996); Kalchenko et al. (2002); I. A. Koshets (2005) for monolayer films. QCM technique denotes a powerful approach for determining the sensing properties of materials before a sensor device design during development stages.

Langmuir model has been used successfully for monolayer films to analyze adsorption kinetics. For multilayer films, the Langmuir model can not be used due to the diffusion of adsorbed molecules between layers. Therefore it should be modified to determine the adsorption and desorption rates for the diffusion effect.

The manuscript is organized as follows. In section 1, we will give more information about the experiment. In section 2, we briefly discuss about celebrated Langmuir model which was first introduced in Langmuir (1916). In section 3, we will introduce the models that we propose for humidity adsorption and desorption kinetic data of spin coated 50 nm Ruthenium polypridyl complex (Ru-PC K314) film. In section 4, we briefly mention about nonlinear regression analysis. In section 5, we introduce our model and estimate the parameters of the model for the measured data. The last section constitutes a brief conclusion of the paper.

2. EXPERIMENTAL

For the preparation of QCM electrodes, gold coated quartz crystal electrodes were placed into ethanol and ultrasonically cleaned, then rinsed by de-ionized water. 1 mg/ml Ru-PC was dissolved in deionized water. 5 μl of solution was spin-coated on to quartz crystal with 2000 rpm. After drying at room conditions, it was kept in dessicator at room temperature for 3 hours. Then the quartz crystal coated with Ru-PC film was used to record both the reference frequency at 11 % and the frequency changes up to 97 % relative humidity. The thicknesses of films were measured using a Dektak profilometer from Veeco and found to be 50 nm.

A Time-Resolved Electrochemical Quartz Crystal Microbalance (EQCM) with the model of CHI400A Series from CH Instruments (Austin, USA) has been used to measure the change in the resonance frequency of quartz crystals between gold electrodes via both serial and usb interface connected to a computer. The QCM works with oscillation frequencies between 7.995MHz - 7.950MHz. The density (ρ) of the crystal is 2.684 g/cm^3, and the shear modulus (μ) of quartz is 2.947×10^{11} $g/cm.s^2$. Around oscillation frequency of 7.995-MHz, a net change of 1 Hz corresponds to 1.34 ng of materials adsorbed or desorbed onto the crystal surface of an area of 0.196 cm^2.

The signals coming from a QCM electrode and a commercial RH humidity sensor were simultaneously measured during the adsorption and desorption process. Both the relative humidity and temperature were also recorded

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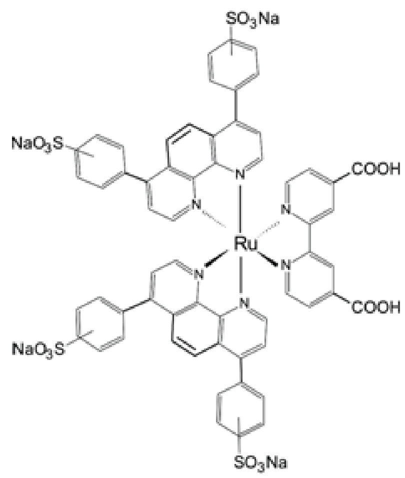

Ru-PC K314

Fig. 1. Chemical structure of ruthenium polypridyl complex

during measurements while maintaining the temperature around 23°C. For this purpose, a EI-1050 selectable digital relative humidity and temperature probe with a response time of 4 s and a resolution of 0.03 % RH was used with a USB controlled LabJack U12 ADC system combined with a single chip sensor module (SHT11) manufactured by Sensirion (Staefa, Switzerland).

The detailed information about the synthesis of $[Ru^{II}($ bis$(4,7$-diphenyl-$1,10-$phenanthroline-disulfonic acid disodium salt) $(4,4'$-dicarboxy-$2,2'$-bipyridine)], (Ru-PC K314) can be found in Ocakoglu and Okur (2010). For further information, see the reference.

3. LANGMUIR MODEL

In this paper, we deal with Langmuir model which was first developed by Irving Langmuir in 1916 Langmuir (1916); Kankare and Vinokurov (1999); Kapoor et al. (1990). In order to analyze the adsorption and desorption kinetics of gas vapor molecules onto organic or inorganic films, Langmuir adsorption isotherm model is applied Sauerbrey (1959); Karpovich and Blanchard (1994); Gregg and Sing (1967); Sun et al. (2007); Su and Chang (2008). As a result the model describes the rate of surface reaction for forming a monolayer on the surface by using the below equation,

$$\frac{d\theta}{dt} = k_a(1-\theta) - k_d\theta. \qquad (1)$$

Here θ is a unitless quantity, which means the fraction of surface coverage, k_a and k_d denote the rate constants for the adsorption and desorption processes.

In this study QCM has been used to measure the fractional coverage θ a function of time during the adsorption and desorption of water vapor molecules.

Hence the difference between the oscillation frequency shift Δf of coated and uncoated QCM is directly proportional to the adsorbed mass of moisture molecules. The relationship between the surface adsorption kinetics and frequency shift (Δf) of QCM can be expressed as below

$$\frac{\Delta f}{dt} = (k_aC + k_d)\Delta f + k_aC\Delta f_{max}. \qquad (2)$$

where C is the water vapor concentration in the air. Moreover, note that during adsorption process, (Δf) is equal to max Δf_{max} for a very long time period.

4. NONLINEAR REGRESSION

The classical regression model assumes that the population regression function is the linear function of n independent variables, say x_i for $i = 1, \ldots, n$ and the linear regression model can be written as in the following general matrix form:

$$y = \beta X + u,$$

where β is the vector of parameters, X is the vector of independent variables $x_1, \ldots, x_n$ and u is the stochastic error term. The reason that we add a stochastic term is there are many unexpected and unobservable cases that will affect us to do some errors in modeling. The measurement error in calculations, missing variables in the model are the examples for such kind of unobservable errors. In order to have a realistic model, we must add a stochastic term to the model, so called disturbance term.

When we fit a model to our data, we obtain best-fit values that we interpret in the context of the model. In many cases the conditional expectation of the dependent variable is not a linear function of independent variables. Because of this reason, it is more practical to model with nonlinear systems to have more realistic models. For further information about nonlinear regression analysis, see Seber and Wild (2003) and Motulsky and Christopoulos (2004).

5. THE MAIN RESULT

The aim of this paper is to fit the measured data of spin coated 50 nm Ruthenium polypridyl complex (Ru-PC K314) film to a curve by an appropriate methodology. Polynomial fitting, cubic spline, linear regression are some fundamental techniques for this procedure. However, most of them ignore the theoretical part of the study and just focus on curve fitting. We use nonlinear regression methodology to fit a curve regarding fundamentals of the theory. Moreover, it is showed that many type of the data are best analyzed by using nonlinear least squares Motulsky and Ransnas (1987).

We assume that the difference between the oscillation frequency shift $y := \triangle f$ of coated and uncoated QCM can be modeled by a nonlinear regression function as follows

$$y_t = f(t, y, k_a, k_d) + \varepsilon_t,$$

for all $t \in [0, T]$. Here, f is a nonlinear function of time and the process itself with parameters k_a and k_d. Indeed,

$$f(t, y, k_a, k_d) = \frac{k_a\,C y_{max}}{k_a\,C + k_d} + (y_0 - \frac{k_a\,C y_{max}}{k_a\,C + k_d} e^{-(k_a\,C + k_d)(t - t_0)}),$$

where t_0 and y_0 are the initial values for t and y respectively. Therefore, for the adsorption data we use the following model:

$$y_t = \frac{k_a\,C y_{max}}{k_a\,C + k_d} + (y_0 - \frac{k_a\,C y_{max}}{k_a\,C + k_d} e^{-(k_a\,C + k_d)(t - t_0)}) + \varepsilon_t, \qquad (3)$$

where the expectation and the variance of ε is zero and a constant number respectively, i.e.,

$$E[\varepsilon_t] = 0$$

and

$$Var(\varepsilon_t) = \sigma^2$$

for a positive constant σ.

Note that for modeling adsorption data Langmuir is convenient since

$$\lim_{t \to t_0} y_t = A_0,$$

$$\lim_{t \to \infty} y_t = \frac{k_a C_1 \triangle f_{max}}{k_a C_1 + k_d}.$$

However, for desorption data Langmuir model is not a good candidate because we have to guarantee that

$$\lim_{t \to t_0} y_t = y_{max},$$

$$\lim_{t \to \infty} y_t = M,$$

for a constant M which sufficiently small number and close to the minimum of the data series. Regarding all of these properties, we suggest an homogeneous exponential model for the desorption data instead of Langmuir model. We proposed the following one:

$$y_t = y_0 \exp(-(k_a C_2 + k_d)(t - t_0)) + noise. \qquad (4)$$

5.1 Data Analysis

We have 3 adsorption and desorption cycles of data of Ruthenium polypridyl complex film which is measured by QCM technique. The starting nodes, the maximum values and the length of the time series are summarized by the following tables. Here are the details of the data of Ruthenium polypridyl complex film:

Table 1. Cycle 1

Properties	Adsorption	Desorption
Start	-3.81×10^{-7}	94.65
End	96.07	-0.63
Max	96.14	94.65
Length	1532	1482

Table 2. Cycle 2

Properties	Adsorption	Desorption
Start	0.18	96.57
End	96.67	0.75
Max	96.74	96.60
Length	1499	1468

Table 3. Cycle 3

Properties	Adsorption	Desorption
Start	0.81	97.56
End	97.43	-1.01
Max	97.53	98.33
Length	1479	1528

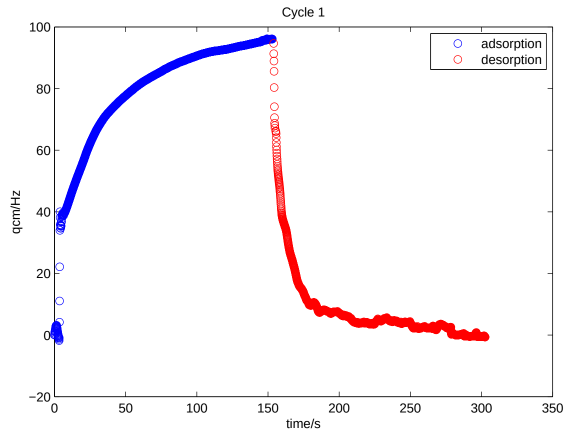

Fig. 2. Plot of observed data for adsorption and desorption

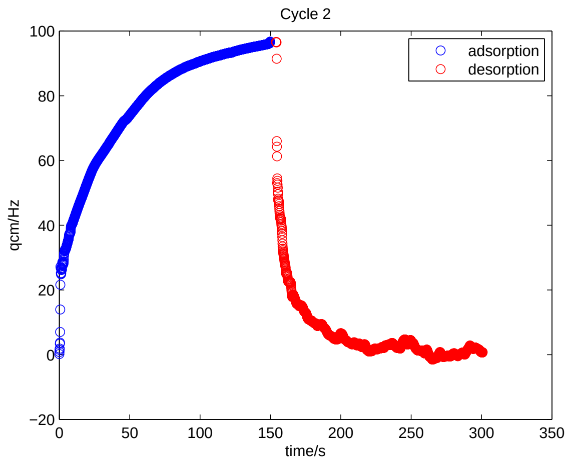

Fig. 3. Plot of observed data for adsorption and desorption

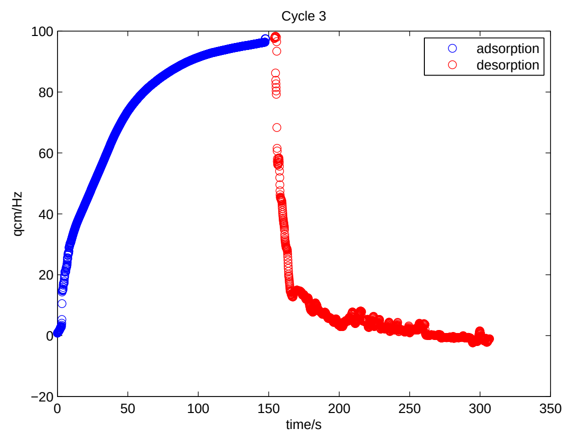

Fig. 4. Plot of observed data for adsorption and desorption

5.2 Parameter Estimation

Parameter estimation is the crucial part of mathematical modeling. An estimator attempts to approximate the unknown parameters using the measurements. In this paper, we use nonlinear least squares methodology to find the parameters of adsorption and desorption concentration rate. The parameters describe the physical setting such that it represents the distribution of the data.

However, we have realized two facts. First, the initial values of the original data does not satisfy the usual conditions of a function. Because of this reason we cut some initial points from the measured data in each cycle before estimating the parameters of the nonlinear least squares. Moreover, we realized that the desorption data series are noisy. So, first we denoise the original desorption series by wavelet methodology. For each cycle we have found the most appropriate wavelet family to denoise. It is explicitly specified at each table below. Every calculation is done by MATLAB® program.

Table 4. Cycle 1 Estimation

Properties	Adsorption	Desorption
k_a	32.499	32.499
k_d	1.02e-004	0.103
# cut points	50	-
wavelet family	-	"haar"

Table 5. Cycle 2 Estimation

Properties	Adsorption	Desorption
k_a	32.331	32.331
k_d	1.074e-004	0.155
# cut points	9	-
wavelet family	-	"db3"

Table 6. Cycle 3 Estimation

Properties	Adsorption	Desorption
k_a	34.554	34.554
k_d	8.441e-005	0.131
# cut points	34	-
wavelet family	-	"rbio1.5"

For each cycle, we calculate the error terms (which are exact values minus estimated values) and show that they have zero expectation with a constant variance. We also check for the heteroscedasticity of the error terms in order to guarantee that the error terms have constant variance. We found that no ARCH effects exist.

Indeed, in each cycle of data, we observe that in the first cycle, the error terms has a mean of -1.1×10^{-15} and variance 0.0051. In the second cycle of data, the error terms has a mean of -0.9×10^{-15} and variance 0.0271. In the last cycle of data, their mean and variance are -0.9×10^{-15} and 0.05 respectively.

Let us show our results by plotting the estimated and observed data over time period. Note that for each cycle at the following graph, the blue circles show the original data of spin coated 50 nm Ruthenium polypridyl complex (Ru-PC K314) film which was measured by QCM technique and the red line shows the estimated data by using the mathematical model introduced in the previous section.

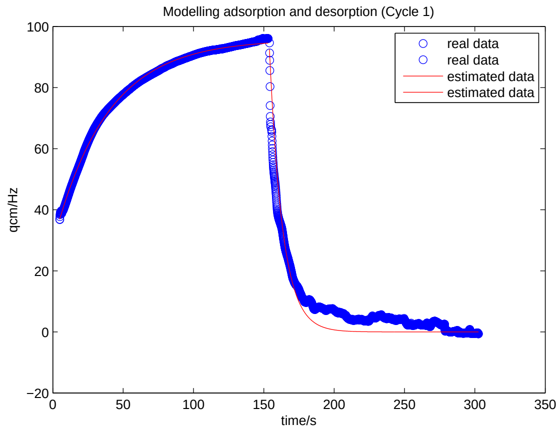

Fig. 5. Plot of estimated and observed data for cycle 1

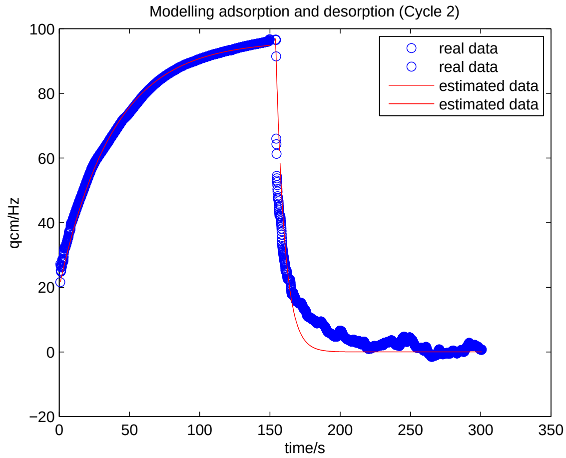

Fig. 6. Plot of estimated and observed data for cycle 2

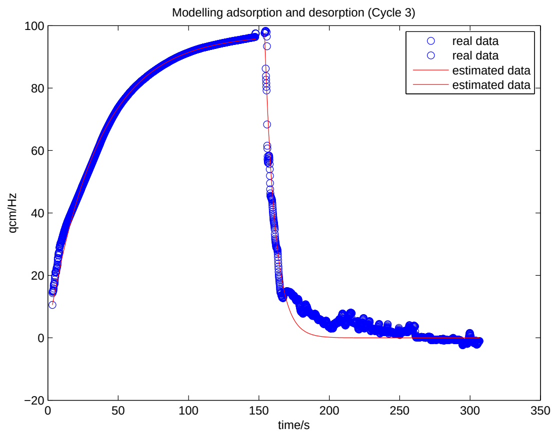

Fig. 7. Plot of estimated and observed data for cycle 3

6. CONCLUSION

In this paper, our aim is to find the parameters k_a and k_d of our models for given 3 cycles of data of Ruthenium polypridyl complex film which is measured by QCM technique. We realized that the humidity desorption data of Ruthenium polyprid complex film is noisy so we denoise the original data by appropriate wavelet families by using

MATLAB® program. For each cycle 1, 2 and 3, we use haar, db3 and rbio1.5 wavelet families respectively. We realized that adsorption concentration rate is in between 32.5 and 34.5. Moreover, the desorption concentration rate is found in between 0.1 and 0.2. We also conclude that the humidity adsorption data of spin coated 50 nm Ruthenium polypridyl complex film is smooth and the Langmuir model with disturbance term is appropriate to model.

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