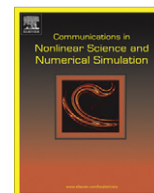




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## New approach for consideration of adsorption/desorption data

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## ABSTRACT

In this paper we proposed a new approach to modify the Langmuir model by considering nonlinear effects such as diffusion of water molecules in/out of an adsorbing film for humidity adsorption and desorption kinetics. The model was tested on the humidity adsorption and desorption data of a spin coated 50 nm thick Ruthenium polyridyl complex (Ru-PC K314) film, measured under relative humidity between 11% and 97% using by Quartz Crystal Microbalance (QCM) technique.

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## 1. Introduction

Quartz Crystal Microbalance (QCM) has been frequently used investigate the kinetics of adsorption/desorption of adsorbate molecules [1,2] for monolayer films. It is a powerful technique to determine humidity sensing properties of materials before designing a sensor device during development stages. It is well known that the Langmuir model has been used successfully for monolayer films to analyze adsorption kinetics. A novel ceramic nanowires of TiO<sub>2</sub> and poly (2-acrylamido-2-methylpropane sulfonate) composite material films coated QCM was prepared as a low humidity sensor [3].

In the literature, the swelling behaviour of a series of hydrophilic random copolymer coatings in controlled humidity environments and in water has been investigated using QCM and spectroscopic ellipsometry by Chen et al. [4]. Thin films of polyaniline base, emeraldine base (EB), coating on the quartz crystal microbalance (QCM) electrode have been used as a sensitive layer for the detection of a number of primary aliphatic alcohols such as ethanol, methanol, 2-propanol and 1-propanol vapours [5]. A QCM coated with Nafion<sup>®</sup> film recast from Nafion<sup>®</sup>(Ag) complex solution has been used to investigate the interaction between methanol, water and Nafion<sup>®</sup>(Ag) and to determine simultaneously the concentration of methanol and water (relative humidity) [6].

In this work, we suggest a generalized Langmuir model to include nonlinear effect such as diffusion and condensation during humidity adsorption/desorption process. The suggested model was used to analyze the humidity adsorption and desorption QCM data of spin coated 50 nm Ruthenium polyridyl complex (Ru-PC K314) obtained under relative humidity between 11 % and 97 %.

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## 2. QCM adsorption and desorption kinetics

QCM has been used frequently to measure the fractional coverage  $\theta$  as a function of time during the adsorption and desorption of water vapor molecules by Calix [4] arene films, while the increase in the frequency shift reflects the molecular mass uptake or loss [7,8]. Hence the difference between the oscillation frequency shift ( $\Delta f$ ) of coated and uncoated QCM is directly proportional to the adsorbed mass of moisture molecules. The simplest relationship between the surface adsorption kinetics and frequency shift ( $\Delta f$ ) of QCM can be expressed as following:

$$\frac{d\Delta f}{dt} = -(K_a C + K_d)\Delta f + K_a C \Delta f_{\max} \quad (2.1)$$

where  $\Delta f$  is the QCM resonance frequency,  $t$  is time,  $K_a$  and  $K_d$  are the adsorption and desorption rate constants and  $C$  is the water vapor concentration in the air. During the adsorption process,  $\Delta f$  is equal to  $\Delta f_{\max}$  for very long time.

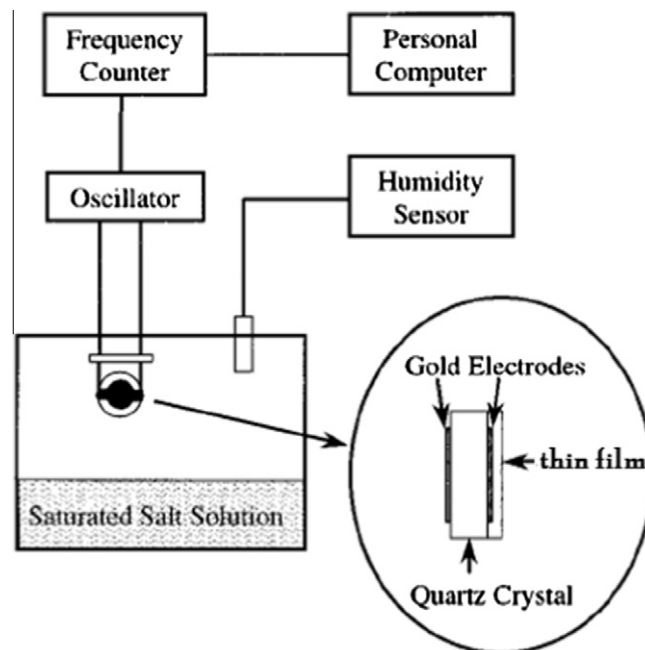
## 3. Experimental

Gold coated QCM 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  $\mu$ l of solution was spin-coated onto quartz crystal with 2000 rpm. After drying at room conditions, it was kept in dessicator at room temperature for 3 h. 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 [9].

A closed box, partly filled with saturated salt solutions, generated a humid environment with good accuracy in the free room above the salt was used to provide a fixed point humidity as shown in Fig. 1. The value of the relative humidity depends on the type of salt given in Ref. [7]. The same experimental setup given in our previous work [7] was used to measure the adsorption kinetics of Ru-PC films above saturated LiCl (11% RH) and K<sub>2</sub>SO<sub>4</sub> (97% RH) aqueous solution level inside a half filled closed container. (Fig. 2) shows the chemical structure of the substance used in measurements.

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 7.995 MHz–7.950 MHz. The density ( $\rho$ ) of the crystal is 2.684 g/cm<sup>3</sup>, and the shear modulus ( $\mu$ ) of quartz is  $2.947 \times 10^{11}$  g/cm · s<sup>2</sup>. 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 0.196cm<sup>2</sup>.

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 during measurements while maintaining the temperature around 23 °C. For this purpose, a EI-1050 selectable digital relative humidity



**Fig. 1.** The experimental setup to measure the adsorption and desorption kinetics of Ru-314 films under fixed point humidity between 25% RH and 80% RH above a saturated salt solution inside a closed container using hybrid system of QCM electrodes and a commercial humidity sensor.

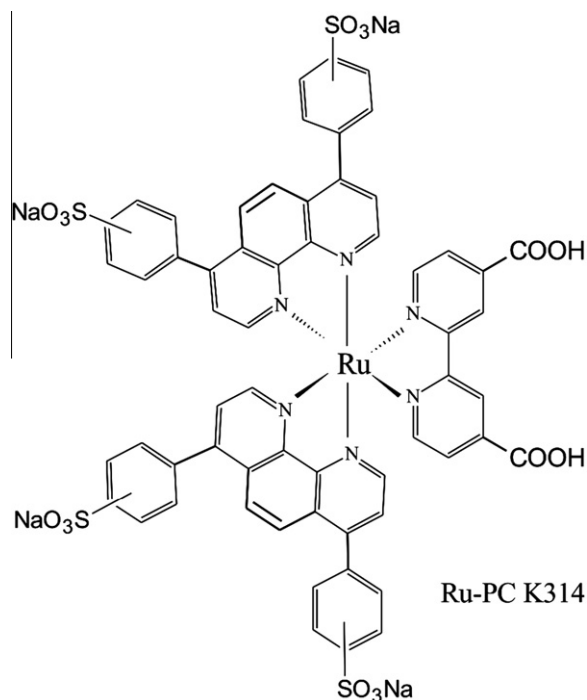


Fig. 2. Chemical structure of ruthenium polyridyl complex.

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 (Staeafa, Switzerland). The detailed information about the synthesis of [RuII (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 et al. [10].

#### 4. Langmuir model and its modification

In this paper, we deal with Langmuir model which was first developed in 1916 by Irving Langmuir, [11] and developed later by others [12,13]. In order to analyze the adsorption and desorption kinetics of gas vapor molecules onto organic or inorganic films, Langmuir adsorption isotherm model is applied by [14–18]. As a result the model describes the rate of surface reaction for forming a monolayer on the surface by using the below equation,

$$\frac{d\theta}{dt} = k_a(1 - \theta)C - k_d\theta \quad (4.1)$$

Here  $\theta$  is a unitless quantity, e.g. fraction of surface coverage,  $K_a$  and  $K_d$  denote the rate constants for the adsorption and desorption processes. In this experiment, the concentration  $C$  is proportional to the relative humidity.

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

Hence the difference between the oscillation frequency shifts  $\Delta f$  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 ( $\Delta f$ ) of QCM can be expressed by expression (2.1).

As one can notice from comparison of expressions (2.1) and (4.1), the frequency shift  $\Delta f$  is directly proportional to  $\theta$ . The fitting of experimental data realized with accordance of expression (4.1) by the Eigen-Coordinates (ECs) method gives unsatisfactory results [19]. We see at least two possible reasons: (a) experimental data are not so clean and always contains some uncontrollable factors; (b) the experimental data contains more than one exponential function and so the simplest model (4.1) should be modified and generalized. In order to see possible modifications let us present Eq. (4.1) in the form of the finite difference equation:

$$\theta(t + T) \cong TK_a + [1 - T(K_a + K_d)]\theta \quad (4.2)$$

Eq. (2.1) can be rewritten in complete analogy with Eq. (4.2).

Eq. (4.2) expresses in the simplest form the linear principle of the strongly-correlated variables. Eq. (4.2) can be easily generalized if we present this equation in the form:

$$F(t + kT) = \sum_{n=0}^{k-1} a_n F(t + nT) + c_0 \quad (4.3)$$

This equation has a simple physical meaning. It signifies that the adsorption/desorption phenomenon can be divided on some stages related on a structure of a surface (which in the most cases represents a random fractal surface) and the geometrical configuration of the adsorbed/desorbed molecules. The physical meaning of the constants  $a_n$  should be related with relative concentrations of the molecules and character of the surface that participate in this phenomenon. Their exact dependence on concentration and fractal dimension of the surface considered will be a subject of the further research. In this paper we only verify this general relationship on available data. The solution of the functional equation was considered in paper [20]. It is expressed in the form of linear combination of exponential functions:

$$F(t) = \sum_{n=1}^k E_n(t) \exp(\lambda_n t) + b \quad (4.4)$$

Here the constant  $b$  is expressed in the form

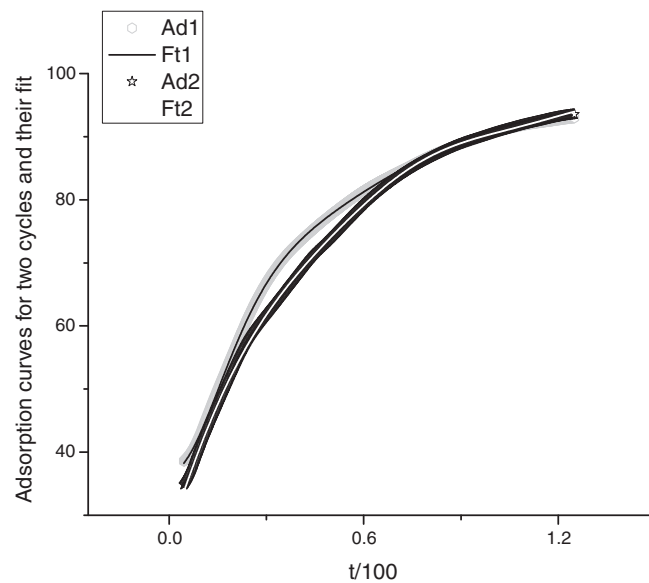


Fig. 3. The fit of the adsorption curves realized for two cycles with function (4.8).

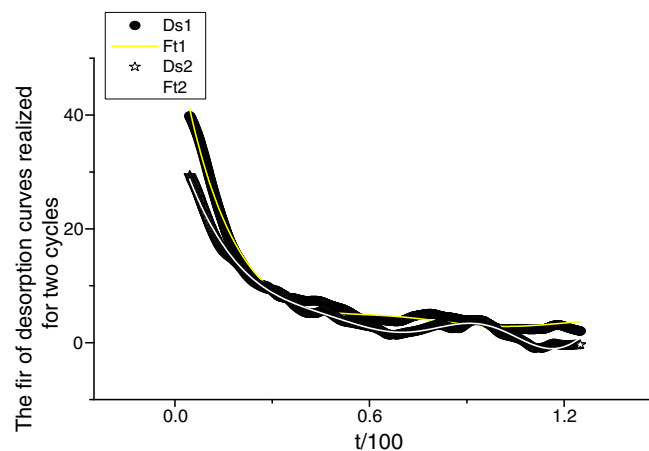


Fig. 4. The fit of desorption curves realized for two cycles with function (4.8).

**Table 1**

The fitting parameters presented by (4.8)

Cycle	$A_0, A_1$	$A_2, A_3$	$\lambda_1, \lambda_2$	$\omega$
Ad1	96.971, -0.9397	-13.247, -59.227	-6.8904, -2.2149	10.709
Ad2	98.647, 0.2634	0.69817, -71.822	-0.54768, -2.1982	10.206
Ad3	97.677, 3.1639	8.325, -93.886	-5.5395, -2.6999	12.668
Des1	3.4147, 0.86231	-0.33054, 50.218	-0.41477, -6.7359	8.8866
Des2	1.664, 0.05576	-0.12518, 34.386	2.6103, -5.2821	12.703
Des3	2.0239, 3.2448	2.3631 58.115	-0.09221, -11.461	2.3575

Ad = Adsorption, Des = Desorption.

$$b = c_0 \left( 1 - \sum_{n=0}^{k-1} a_n \right)^{-1} \quad (4.5)$$

The unknown exponential constants  $\lambda_n$  are found as roots of the characteristic polynomial

$$x^k - \sum_{n=0}^{k-1} a_n x^n = 0, \quad \lambda_m = \frac{\ln(x_m)}{T}, \quad m = 1, 2, \dots, k \quad (4.6)$$

 $E_n(t)$  in (4.4) can be expressed approximately in the form of periodical functions with period  $T$ .

$$E_n(t) \cong a_n + b_n \cos \left( 2\pi \langle m \rangle \frac{t}{T} - \varphi_n \right) \quad (4.7)$$

Here  $a_n$ ,  $b_n$  and  $\varphi_n$  are some fitting constants. The value  $\langle m \rangle$  defines the leading mode. The fitting to function (4.4) can be realized with the help of the ECs method [19] that helps to reduce the non-linear fitting procedure to the conventional linear least square method (LLSM). For verification of the hypothesis (4.3) we chose the minimal number of components (items)  $k = 3$ . The fitting function identified by the ECs method is written as:

$$\theta(t) = A_0 + A_1 \cos(\omega t) e^{\lambda_1 t} + A_2 \sin(\omega t) e^{\lambda_1 t} + A_3 e^{\lambda_2 t} \quad (4.8)$$

This fitting function (4.8) contains 6 fitting parameters and describes all available data with acceptable accuracy. Figs. 3 and 4. Show the fit to the adsorption and desorption data for two different cycles, respectively.

The set of the fitting parameters are given in Table 1. Notations are taken from expression (4.8). The accuracy of adsorption data is located in the interval:  $[0.04\% < \text{RelErr} (\%) < 0.07\%]$  as for the desorption data the accuracy is in the interval.  $[0.15\% < \text{RelErr} (\%) < 0.34\%]$ .

## 5. Conclusions

Finding new generalization of the Langmuir model is an interesting problem. In this work, a generalized Langmuir model including nonlinear effect such as diffusion and condensation during humidity adsorption/desorption process was used to analyze the humidity adsorption and desorption QCM data of spin coated 50 nm Ruthenium polyridyl complex (Ru-PC K314) obtained under relative humidity between 11% and 97%. The obtained results definitely show that the Langmuir equations can be generalized by making use of the ECs method. The experimental confirmation of the hypothesis (4.8) that follows from solution of the functional Eq. (4.3) implies that some important factors participating in adsorption/desorption phenomena can be taken into account. This is the first and serious generalization attempt of such kind that received the experimental confirmation. The analysis of the physical meaning of the parameters  $a_n$  that figuring in Eq. (4.3) and the proper explanation of oscillating solutions merits a special research.

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