Humidity adsorption kinetics of water soluble calix[4]arene derivatives measured using QCM technique

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ARTICLE INFO

Article history:
Accepted 16 November 2009
Available online 22 November 2009

Keywords:
Carboxylated calix[4]arene film
Humidity sensor
QCM
Langmuir model

1. Introduction

Calixarenes are macrocyclic molecules that can be easily functionalize from their upper and lower rims [1]. The cylindrical-shaped calixarenes of varying cavity sizes can form a variety of host–guest types of inclusion complexes. This feature of calixarene is similar to cyclodextrins. However, π–π interaction is observed in calixarenes due to the benzene groups [2]. Calixarenes are generally soluble in organic solvents; however water soluble ones are also synthesized and reported by many authors. Several derivatives of water soluble calixarenes were synthesized and used in many applications [3–8]. Thin films of calixarenes have been widely used in chemical sensors. Due to their zeolite-like capacity and selectivity, calixarenes became promising materials for sensor applications. The functional groups at the upper and lower rims determine their selectivity in host–guest interactions and physical properties [9–10]. These materials are also used in gas or organic solvent vapor sensors [11–13]. Sensor applications of calixarenes have been reported for a few transducer types such as quartz crystal microbalances (QCM) [14–16] and ISFETs [17]. It is also known that especially water soluble calixarene derivatives adsorb water molecules [6]. Nevertheless we have not reached any report on humidity sensing properties or adsorption–desorption kinetics of calixarene based on QCM techniques.

QCM have been widely employed for the determination and investigation of the kinetics of adsorption/desorption of adsorbate molecules. QCM technique is a powerful technique for determining the sensing properties of materials before a sensor device design during development stages.

QCM is based on frequency shift of coated quartz crystal with sensing element due to adsorption of humidity atoms on the surface of the sensing material [18]. The mass change (Δm) on surface of the quartz crystal is calculated by using Sauerbrey equation [18] from the frequency change (Δf):

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\mu \rho}} \times \Delta m = -C \times \Delta m$$ (1)

where \(f_0\) is the resonant frequency of the fundamental mode of the QCM crystal, \(A\) is the area of the gold disk coated onto the crystal, \(\rho\) is the density of the crystal, and \(\mu\) is the shear modulus of quartz. Hence the frequency shift is directly proportional to the adsorbed mass on the calix[4]arene modified gold QCM electrodes.

In this study humidity sensing properties of calix[4]arene films coated onto QCM gold electrodes were investigated. The change of resonance frequency of QCM was monitored with increasing relative humidity (RH) from 29% up to 80%. Calix[4]arene derivatives includes both carboxylate and sulphonate groups which are sen-
sitive to water molecules. The adsorption and desorption kinetic parameters determined by using Langmuir model show that the calix[4]arene films have strong affinity to water vapor between 29% and 80% relative humidity.

2. Experimental

Synthesis and film preparation of calix[4]arene derivative: calix[4]arene derivative was synthesized according to previously published procedure and molecular structure is given in Fig. 1 [3–4,19]. Its structure was confirmed by re-characterizing with spectroscopic methods such as $^1$H NMR and FTIR. $^1$H NMR (400 MHz D$_2$O at 20 °C): $\delta$ 4.12 (br, 8H, Ar–CH$_2$–Ar), 4.36 (s, 8H, OCH$_2$CO), 7.68 (br, 8H, ArH). IR (KBr) cm$^{-1}$: 1612 (C=O), 1210 and 1116 (SO$_3$).

1 mg/ml calix[4]arene was dissolved in de-ionized water and 5 μl of solution was drop casted on to quartz crystal. After the water completely evaporated at room temperature, it was kept in dessicator at room temperature for 3 h. The thickness of films were measured with a Dektak profilometer from Veeco and found to be 300 nm.

2.1. Humidity measurement technique

The images of film surface were taken with an optical microscopy (Olympus) with a digital camera under 45% and 95% RH. A Time-Resolved Electrochemical Quartz Crystal Microbalance (EQCMB) with the model of CH4000A 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 and 7.950 MHz. The density ($\rho$) of the crystal is 2.684 g/cm$^3$, and the shear modulus ($\mu$) 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$^2$.

Gold coated quartz crystal electrodes were placed into ethanol and ultrasonically cleaned, then rinsed by de-ionized water. After dried with argon gas, quartz crystal was placed into the Teflon housing and the reference frequency was recorded.

Fig. 2 shows the experimental setup to measure the adsorption and desorption kinetics of calix[4]arene films above saturated salt solution inside a closed container using hybrid system of QCM electrodes and a commercial humidity sensor.

A E1-1050 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).

3. Results and discussion

Fig. 3a and b shows the optical microscopy image of the calix[4]arene film under 45% and 95% RH, respectively. The optical images were taken simultaneously with increasing RH from 45% to 95% in approximately 15 min. While a smooth structure of calix[4]arene film is optically observed at 45% RH condition, a rough surface structure is observed at 95% RH, showing a fast condensation of water film. By increasing RH, calix[4]arene film swelled due to water uptake. However, the humidity sensing experiments have been done between 29% and 80% RH to observe adsorption process rather than condensation.

Calix[4]arene films shows extremely fast adsorption and desorption response against to humidity changes for short time periods. This feature is most probably sourced from both carboxylate and sulphonate groups. Water molecules can easily make strong complex with calix[4]arene from both upper and lower rims which are functionalized eight carboxylate and sulphonate groups. In case of aliphatic functionalized calix[4]arene molecule, water uptake would not be expected.

Fig. 4 shows the frequency responses of an empty and calix[4]arene film covered QCM comparing with relative humidity values of a commercial sensor for four moisture adsorption–desorption cycles between 29% and 80% RH. There is a remarkable frequency response change on the QCM with calix[4]arene film.

Fig. 5a and b shows the frequency response of calix[4]arene film covered QCM adsorption–desorption process at fixed point relative humidity conditions between 22% and 75% RH. The adsorption and desorption between 22% and 75% RH are nearly linear,
but at higher RH values the frequency is increasing quickly leaving a resident absorbed water mass on the film corresponding 25 Hz frequency change between before and after adsorption and desorption process. This is indication of slower desorption rate compare to adsorption rate of the film. To describe the adsorption and desorption kinetics of gas vapor molecules onto organic or inorganic films, Langmuir adsorption isotherm model is frequently used [18,20–23]. This model describes the rate of surface reaction for forming a monolayer on the surface by following equation:
\[
\frac{d\theta}{dt} = k_a(1 - \theta)C - k_d\theta \quad (2)
\]
where \(\theta\) is a unitless quantity, which express the fraction of surface coverage, \(C\) is the water vapor concentration in the air, \(k_a\) and \(k_d\) are the rate constants for the adsorption and desorption processes, respectively. Since the temperature was constant during measurements (23°C), the standard steam tables were used to determine the partial pressure of water vapor at related temperature [24]. The vapor molar concentration \(C\) (M) was calculated from the ideal gas equation at the corresponding partial pressure for the relative humidity measured at the equilibrium point.

In this study, QCM has been used to measure the fractional coverage \(\theta\) as a function of time during the adsorption and desorption of water vapor molecules by calix[4]arene film, while the increase in the frequency shift reflects the molecular mass uptake or loss. 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 relationship between the surface adsorption kinetics and frequency shift \(\Delta f\) of QCM can be expressed as following:
\[
\frac{d\Delta f}{dt} = -(k_aC + k_d) \Delta f + k_aC \Delta f_{\text{max}} \quad (3)
\]
During adsorption process, \(\Delta f\) starts with \(\Delta f_{\text{max}}\) initially and then drops to \(\Delta f_{\text{min}} = \Delta f_{\text{max}}(k_aC_{\text{min}}/k_aC_{\text{max}} + k_d)\) for very long time periods. In this case, the solution of the differential equation for
desorption process is obtained as
\[
\Delta f = \frac{\Delta f_{\text{max}}}{k_d C_{\text{min}} + k_a} \left[ k_d C_{\text{min}} + k_a e^{-(k_a C_{\text{min}} + k_d)t} \right],
\]
(5)
where \( \Delta f \), \( \Delta f_{\text{min}} \) and \( \Delta f_{\text{max}} \) are the QCM resonance frequency shifts, \( t \) is the time, \( C_{\text{max}} \) and \( C_{\text{min}} \) are the concentrations of water molecules in high and low relative humidity conditions, \( k_a \) and \( k_d \) are the adsorption and desorption rate constants, respectively. The experimental data are compared with the data obtained from adsorption and desorption isotherm given in Eqs. (4) and (5) with \( k_a \) and \( k_d \) values obtained from the nonlinear least square fit for each cycle versus time.

The data given in Table 1 allows us to determine the equilibrium constant, \( K_{\text{equ}} \), for calix[4]arene film as following:
\[
K_{\text{equ}} = \frac{k_a}{k_d}
\]
(6)

The Gibbs free energy \( \Delta G \) of adsorption/desorption process in terms of \( K_{\text{equ}} \) at a given temperature is defined as [25]:
\[
\Delta G = -RT \ln K_{\text{equ}}
\]
(7)

The Gibbs free energy for both adsorption and desorption process are calculated using Eq. (7) for each cycle and results are given in Table 1. The average Gibbs free energy for adsorption and desorption of three cycles are obtained as −27.20 and −10.51 kJ/mol, respectively. Under humidity exposure, water molecules are condensed at the calix[4]arene film surface during adsorption process, therefore there is an energy loss for water molecules on calix[4]arene film surface.

4. Conclusion
Calix[4]arene films with 300 nm thickness were obtained by droop-cast technique. The relative humidity response of calix[4]arene film was investigated by QCM technique. The adsorption and desorption kinetics under constant relative humidity around 80% and 23 °C QCM electrode temperature was explained using Langmuir isotherm adsorption model. The average values of adsorption rate, desorption rate and equilibrium constant were obtained as 31.13 M⁻¹ s⁻¹, 0.59 s⁻¹ and 52461.7 M⁻¹, respectively. An average Gibbs free energy for adsorption and desorption of three cycles are obtained as −27.20 and −10.51 kJ/mol, respectively. This shows that the films made of calix[4]arene derivatives with carboxylate and sulphonate groups has an adsorption dominant process against water vapor molecules.

Acknowledgements
This research was partially supported by DPT (State Planning Organization of Turkey) under project number DPT2003K120390 and Selcuk University Scientific Research Council (BAP).

References


Biographies

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