Chapter 7
Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D)

Kenichi Sakai

Abstract Quartz crystal microbalance with dissipation monitoring (QCM-D) can detect changes in oscillating frequency of a quartz crystal as well as in energy dissipation of adsorption material. For example, a decreased frequency results from an increased adsorption amount, while an increased dissipation results from an increased viscoelasticity of the adsorption layer. The QCM-D can monitor the frequency and dissipation changes with less than 1 s intervals. This enables us to analyse non-equilibrium adsorption or reaction system in solution. Various sensors such as gold, silica, titania, iron oxide or polystyrene are available for the QCM-D instrument, which enables QCM-D measurement possible for a wide range of applications. Special attention should be paid to the solvation effect of the adsorption material; the amount obtained by QCM-D is expressed as "wet mass", while that of other methods such as ellipsometry or optical reflectometry is called "dry mass". Another important point in QCM-D measurement is the effect of viscosity and density of bulk solution because these properties also contribute to the frequency change.

Keywords Quartz crystal microbalance with dissipation monitoring (QCM-D) · Frequency · Energy dissipation · Adsorption

7.1 Introduction

Measuring adsorption isotherms is indispensable for evaluating the adsorption behaviour of surfactants at solid/liquid interfaces. Adsorption isotherm measurement has been practiced for many years, and the depletion method is one of the most common procedures. This method consists of adding surfactants into a dispersed solid particle system and then measuring the equilibrium concentration of the

K. Sakai (✉)
Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, Tokyo, Japan
e-mail: k-sakai@rs.noda.tus.ac.jp

M. Abe (ed.), *Measurement Techniques and Practices of Colloid and Interface Phenomena*, https://doi.org/10.1007/978-981-13-5931-6_7

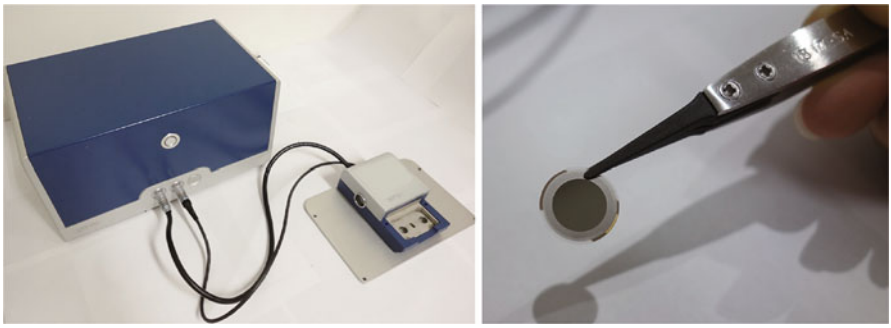

Fig. 7.1 Q-Sense QCM-D instrument

surfactant in the bulk solution after a certain time period. The adsorption amount per unit mass or area of the solid particle can be calculated by the concentration difference of the surfactant before and after adsorption. Although requiring multiple steps is a drawback, the depletion method has advantages for the adsorption isotherm measurement as it requires only common analytical instruments and procedures such as high-performance liquid chromatography (HPLC) analysis or solvent extraction of surfactant complex formed with dye.

In recent years new methods of evaluating adsorption onto flat solid surfaces have been developed, such as quartz crystal microbalance with dissipation monitoring (QCM-D), optical reflectometry (OR), ellipsometry and surface plasmon resonance (SPR) techniques. Although these new instrumentations are rather expensive and not easily available at the time needed, useful information can be obtained with the appropriate knowledge of their advantages and limitations as well as their well-designed experimental preparation. The principle of QCM-D is to measure the change (reduction) in oscillating frequency of a quartz crystal corresponding to the adsorption amount of material based on the Sauerbrey equation (Eq. 7.1) [1]. Energy dissipation can also be measured (Eq. 7.2) along with the frequency change oscillator using QCM-D (Fig. 7.1) by Q-Sense corporation. The amplitude of oscillation decays by cutting off the electric current for the oscillator. Abrupt decay of amplitude will be found for adsorbed soft viscoelastic materials, while hard adsorbed materials with lower viscoelasticity keep oscillation with slow decay. Namely, dissipation is a useful indicator to represent rheological properties of the adsorbed material, i.e. higher viscoelasticity is larger in dissipation (Fig. 7.2) [2]. As such, QCM-D is a highly sensitive instrument capable of detecting tiny amounts of adsorption, but it should be noted that results could be easily interfered due to additional factors. Those points will be discussed further in the following sections based on the author's experience with Q-Sense QCM-D.

$$\Delta m = -C\frac{\Delta f_n}{n} \tag{7.1}$$

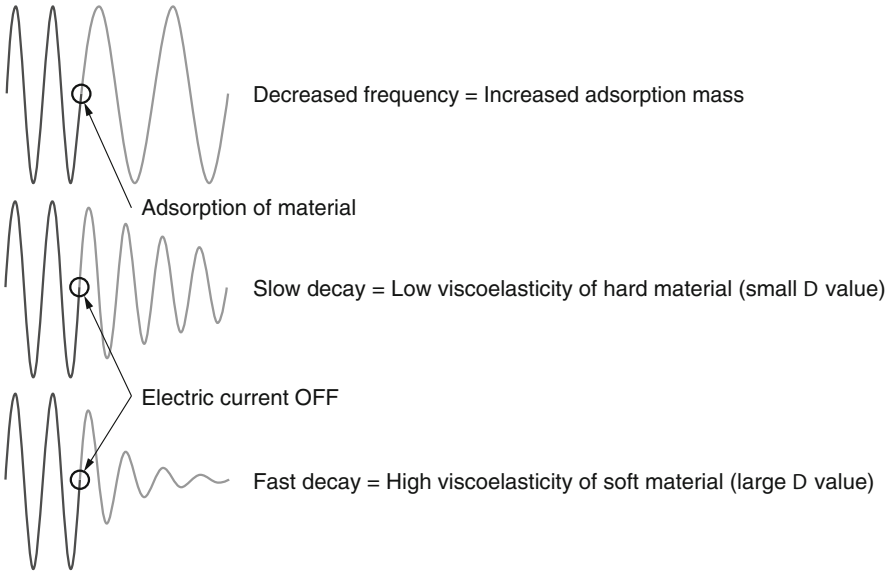

Fig. 7.2 Schematic representation of QCM-D measurements: frequency change and dissipation change

Δm: Mass change
Δf_n: Frequency change observed at the overtone number n
n: Overtone number
C: Constant

$$D = \frac{E_{\text{lost}}}{2\pi E_{\text{stored}}} \tag{7.2}$$

E_{lost}: Lost or dissipated energy
E_{stored}: Stored energy

7.2 What You Get

1. A highly sensitive detection of adsorption amount, e.g. 1 Hz deviation in the resonance frequency for a quartz oscillator with a 5 MHz fundamental frequency corresponds to 17.7 ng/cm^2 = 0.177 mg/m^2 of the mass change.
2. The viscoelastic property of the adsorbed layer can be detected by monitoring energy dissipation, along with the adsorption mass.
3. Adsorption and reaction in both solutions and in gases, along with frequency and dissipation changes in 0.3–0.5 s intervals, can be analysed. This means that non-equilibrium analysis can also be performed as shown in Figs. 7.3 and 7.4, which is difficult to conduct by the depletion method.

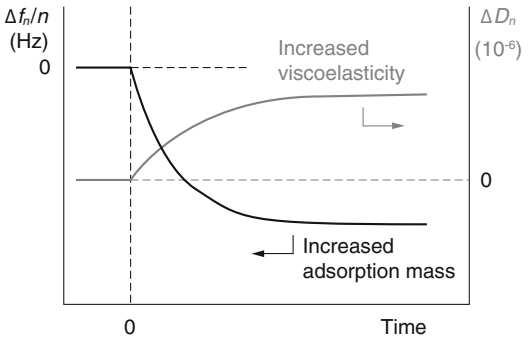

Fig. 7.3 Schematic representation of QCM-D data

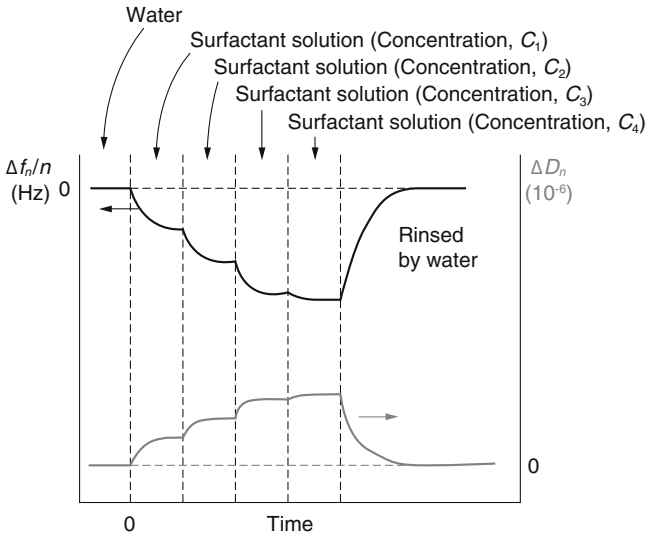

Fig. 7.4 Schematic representation of adsorption isotherm data through QCM-D measurements

4. Viscoelasticity and thickness of adsorbed layer can be estimated based on the rheological modelling by utilizing attached analytical software provided with the instrument.

7.3 Essentials and Tips

1. External vibration such as opening and closing of the door and walking alongside or nearby instrument could be a source of noise, so the instrument placement should be chosen carefully.

2. Frequency and dissipation changes using QCM-D measurement are very sensitive to temperature change. For the Q-Sense QCM-D, temperature control is set to be ±0.02 °C. Temperature monitoring and recording is useful to investigate the data with noise.
3. Sensor surface cleansing is an inviolable rule to obtain accurate data, and the cleansing method is different depending on the sensor material. For silica sensors, UV-ozone cleansing followed by repeated ultrasonic cleansing in weakly alkaline-surfactant solution and rinsing by pouring pure water and then drying by nitrogen gas flow is a common practice to decompose and remove organic contaminants on the sensor. Clean tweezers should be used as it could be a source of contamination.
4. The resonance frequency and dissipation values in both air and pure water must be recorded before each measurement. This record is a useful indicator to monitor sensor deterioration.
5. Avoid formation and contamination of air bubbles during the measurement. Special care should be paid for the surfactant solution as its foamability. Degassing the sample solution is desirable for measurements at higher temperatures than an injection temperature into the cell to avoid bubble formation due to the solubility reduction of gas by temperature.
6. The cell module's O-ring should be changed regularly as its deterioration can cause distortion due to loss of elasticity, which can be a source of noise.

7.4 Understanding Your Data

By using QCM-D measurement, the amount of material adsorbed on the sensor can be estimated using the Sauerbrey equation. However, the differences in mass obtained by the measurement should not be confused with the actual adsorption amount, and special attention should be paid to the solvation effect. The estimated adsorption amount measured using QCM-D tends to be larger than that obtained by other methods such as OR, ellipsometry or SPR, and such differences between the results from QCM-D and other methods correspond to the solvation effect [3]. Therefore, the amount obtained by QCM-D is expressed as "wet mass", while that of other methods such as OR is called "dry mass". When the solvation is significant for the adsorption mass, the energy dissipation value also becomes large, corresponding to the increase in viscoelasticity of the adsorbed layer. There is an article reporting that the difference between wet and dry masses becomes insignificant under the consideration of surface roughness of the sensor [4].

Another important point in QCM-D measurement is the effect of viscosity and density of the bulk solution. Frequency will decrease from adsorption on the sensor surface (mass increase), but also increased bulk viscosity and density will reduce the frequency further. It is known that the degree of frequency reduction is in proportion to the square root of the product of bulk viscosity and density of the Newtonian fluid, as shown by the Kanazawa-Gordon equation [5] (Eq. 7.3). In order to evaluate the

adsorption amount of surfactant using QCM-D measurement, solution viscosity and density are assumed to be constant under the experimental condition. For accurate frequency determination, predictable frequency change must be subtracted from the Kanazawa-Gordon equation, or effect of solution viscosity and density experimentally obtained with non-adsorbable sensor must be subtracted [6].

$$\Delta f = -{f_0}^{\frac{3}{2}} \left(\frac{\rho_L \eta_L}{\pi \rho \mu} \right)^{\frac{1}{2}} \tag{7.3}$$

Δf: Frequency change
ρ: Density of oscillator
ρ_L: Density of solution
f_0: Fundamental frequency
μ: Shear modulus of oscillator
η_L: Viscosity of solution

7.5 Useful Hints

Various sensors such as gold, silica, titania, alumina, hydroxyapatite, iron oxide or polystyrene are available for the Q-Sense QCM-D, which enables QCM-D measurement possible for a wide range of applications. A gold sensor is mandatory for the SPR method, and for OR and ellipsometry, the choice of sensors is limited since reflectivity of incident light is required for these methods.

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