

Anomalous behaviour of the quartz crystal microbalance in the presence of electrolytes

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Received 2nd March 2000, Accepted 14th March 2000

Published on the Web 31st March 2000

Quartz crystal microbalance (QCM) impedance analysis was used as a microgravimetric tool for thiol adsorptions in a flow injection system. The presence of electrolyte was found to interfere with the proper measurement of the deposited mass and resulted in an error of more than 70%. Aqueous solutions of 1:1 electrolytes, of up to 6 mM can cause mass errors as high as 60 ng cm⁻², that is the equivalent of a monolayer of medium sized molecules. 1:2, 1:3, and 2:2 electrolytes yield even higher errors. The interference is mainly due to the mechanical elasticity of the Gouy Chapman diffuse double layer and cannot be excluded even by using sophisticated QCM impedance methods.

Introduction

The quartz crystal microbalance (QCM) has been extensively used as a gravimetric tool. The Sauerbrey equation¹ relates the mass changes on a piezoelectric quartz crystal to the change in its resonance frequency. For this linear frequency to mass relation to hold, the material in contact with the metal covered quartz must be rigid, otherwise viscoelastic changes also contribute to the frequency shift, leading to an erroneous interpretation of the mass.² Even if the material is not entirely rigid, crystals modified with very thin layers usually follow the Sauerbrey equation, and, on this basis, different sensors have been designed.³ When the layer is thick, the viscoelastic properties of the film modify dramatically the QCM measurements.⁴ In these cases, the QCM impedance analysis permits the separation of the mass and the viscoelastic changes by measuring not only the frequency but also the crystal losses.⁵

Since most of the QCM gravimetries are performed in solution, the response of the QCM to the properties of liquids has been profusely investigated. For solutions of non-electrolytes, the Kanazawa equation⁶ predicts a linear relationship between the resonant frequency and the square root of the density–viscosity product. The presence of electrolytes in the solution is known to modify this situation,⁷ but the studies are very limited and the effects remain unclear.

In this work it is demonstrated that the presence of dilute electrolytes during QCM microgravimetry causes strong interferences, that are mainly due to the elastic contribution of the diffuse double layer near the metal covered quartz. This interference cannot be avoided by using impedance techniques, since it does not only affect the changes in frequency but also the losses of the crystal.

Quartz crystal impedance analysis

The mechanical properties of a quartz resonator can be described in terms of an electrical equivalent circuit. The most

widely used is the Butterworth–Van Dyke model,⁸ which consists of a motional impedance in parallel with a parasitic capacitance C_0 , due to the connections, cables and the quartz itself. The motional impedance consists of a series RLC circuit where R represents the damping losses, L the inertia and C the quartz compliance, which is not expected to vary.⁹ The inductance L is directly related to the resonance frequency by $f_r \approx 1/2\pi(LC)^{1/2}$

When non-piezoelectric layers are attached to the quartz resonator, the equivalent parameters L and R change. It is common to refer to these parameters as a complex impedance $Z = R + XL$, where the inductive reactance $XL = i\omega L$, i being the imaginary unit and ω the oscillation frequency of the quartz resonator. If the impedance of the bare quartz resonator $Z_Q = R_Q + XL_Q$ is much higher than the impedance of the non piezoelectric layer $Z_f = R_f + XL_f$, the total impedance of the system can be approximated as $Z = Z_Q + Z_f$.⁹

For a homogeneous viscoelastic film covered with a semi-infinite liquid of a given density and viscosity, Martin's matrix model for multilayers¹⁰ can be used to solve the equivalent impedance as a function of the thickness of the film d_f , its density ρ_f and its complex mechanical modulus $G_f = G'_f + iG''_f$. This complex modulus contains the information about the viscoelasticity of the film material. The elastic modulus G'_f represents the elasticity and the loss modulus G''_f is related to the film viscosity by $G''_f = \omega\eta_f$. If the film properties G_f and ρ_f change with the distance to the quartz crystal, numerical results can also be obtained by using this approach.¹⁰

Experimental

Polished 14 mm gold coated AT cut quartz crystals (ICM Company Inc. Oklahoma City, USA) with an active area of 0.196 cm² and a thickness of 0.168 mm were mounted on a 50 μ L flow injection QCM cell with only one face in contact with the carrier. A flow of 24 μ L s⁻¹ was accomplished by a 200 mL water reservoir placed 30 cm over the level of the QCM cell and its drain. The temperature of the carrier was stabilized by means of an 80 cm tubing coil immersed in a room temperature equilibrated water bath (24 °C), placed directly at the entry of the QCM cell. Injections in the mainstream were done manually, using a 500 μ L syringe. An automatic syringe was used to inject definite amounts of electrolyte solution in the carrier reservoir to vary the electrolyte concentration. The QCM setup and the transfer function method to measure QCM impedance have been described elsewhere.¹¹ Potentials are quoted against saturated calomel electrode (SCE). The chemicals used were of analytical grade.

Results and discussion

Fig. 1a shows the result of a characteristic experiment in which the QCM impedance parameters were measured in real time in a flow injection system. At $t = 150$ s, 100 μ L of a 200 mM

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aqueous solution of aminoethanethiol chlorohydrate (AET) were injected into the feedstream. After about 30 s, the thiol arrives at the bare gold coated crystal and the adsorption process begins. Both components of the impedance, R and XL increase to a maximum value and then decrease until a stationary value is reached. In a first approximation, ΔXL (or Δf) should represent the mass of the adsorbed layer. If the thiol adsorption was the only process taking place, only an increase in XL would be expected. The XL plot, however, looks like the one corresponding to an initial adsorption of more than one monolayer, followed by a partial desorption. On the other hand, the variation of R along the peak is unexpectedly high. For a molecular sized layer, Martin's equation¹⁰ predicts negligible dumping, even for a soft layer. In our case, ΔR is comparable with ΔXL , and the Sauerbrey equation should not be used.^{2,11} A second injection of thiol produces the same anomalous behaviour, but the final value of XL is equal to its initial value, indicating that no further adsorption took place. Fig. 1b shows the corresponding parametric polar plot of R vs. XL , with the time as the parameter. The curve shows a fast shift to the left-upper part (increase in XL and R), that corresponds to the first peak. After this point (point 1), the R vs. XL plot describes a quarter of a circle, going counterclockwise until point 2. The second peak produces a fast recovery clockwise towards point 1, followed by a slower quarter of a circle back until point 2. At point 2, the crystal is in contact with pure water, and the change in XL (2.1 Ω) corresponds to a mass increase of $m_r = 88$ ng cm⁻² (1.15 nmole cm⁻²). Note that the increase in R at this point is much lower than the increase in XL , and allows us to use the Sauerbrey equation to calculate the mass.

If the adsorption had been carried out in a batch cell, the final value would be that of point 1 in the parametric plot, which corresponds to an apparent mass increase of $m_{app} = 151$ ng cm⁻², that is, more than 70% excess error. Similar results would be obtained for reversible gravimetries (*i.e.* specific sensors), even if measured in flow systems. To determine the source of this error, some side experiments were performed. Other charged thiols, sodium mercaptoacetate (MA) and sodium mercaptopropanesulfonate (MPS), yielded similar anomalous adsorption curves. However, the injection of a non-charged thiol (dithiothreitol) or a zwitterion (cysteine) produced simple adsorption curves. On the other hand, if these thiols were mixed with equimolar amounts of KCl just before the injection, the anomalous behaviour appeared again. If the pure water carrier is replaced by 1M KCl solution, all the adsorption

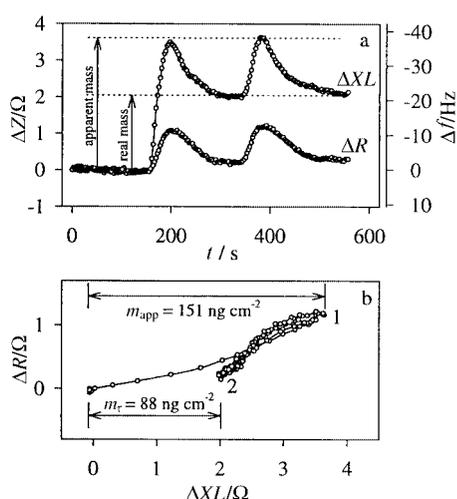


Fig. 1 a: Adsorption gravimetry of aminoethanethiol chlorohydrate (AET) on gold. 100 μ L of aqueous 200 mM AET solution was injected directly into the flow system at $t = 150$ s. A second injection is also shown. Both components of the QCM impedance, XL and R were measured in real time during the gravimetry. b: Parametric polar plot for R vs. XL for the data of Fig. 1a. The real mass of the adsorption process is shown. A wrong estimate of the mass, due to the electrolyte concentration change during injection, is also shown.

gravimetries are normal, even for charged thiols. Thus, it appears that the anomalous gravimetries correlate with the relative change of concentration of charged species in the bulk during the process.

Fig. 2 shows a second experiment, in which the carrier is enriched with KCl up to 6 mM. The sensor is a bare gold covered crystal. Note that R and XL show maxima when plotted as a function of the electrolyte concentration. The parametric plot (inset) shows a circular shape that is similar to the one described by the anomalous adsorption process. For a semi-infinite liquid any change in its bulk properties should produce monotonic curves of R vs. XL .² It is known that the response of the QCM to thin layers of variable viscosity and/or elasticity is characterized by a curvature of the R vs. XL plot.² For low values of G , the layer does not move in-phase with the crystal, and the response is characterized by the losses ($R \approx XL$). For high moduli, the layer is hard enough to move in-phase with the surface, and the impedance is characterized mainly by the inertia, with $XL \gg R$.^{2,12} Therefore, we assume that a thin viscoelastic layer is effectively formed between the quartz crystal and the bulk solution. Since the solution in contact with the QCM consists exclusively of solvent and electrolyte, this thin layer can only be identified with the Gouy Chapman diffuse electric double layer (DDL).

We have calculated the viscoelastic properties of the DDL, using the multilayer model proposed by Martin.¹⁰ For the calculations, the viscous moduli G'' and the elastic moduli G' were assumed to change exponentially from G''_{max} and G'_{max} in the vicinity of the crystal, to $G''_{bulk} = 60$ kPa and $G'_{bulk} = 0$ for regions far away from the crystal. The characteristic length in which the changes take place is the Debye length¹³ $d_D = 0.307 \times 10^{-9} \text{m} (c_{KCl}/M)^{-1/2}$. For KCl solutions, the density changes less than 20% even for saturation concentration.¹⁴ We have approximated the density of the DDL as the density of pure water. The DDL was modelled as being composed of 99 layers, each one of constant ρ , G'' and G' . The thickness of each layer is $0.03 d_D$. In this form, the layers occupy a region of $3 d_D$ from the quartz surface. After this point, a semi-infinite layer with the properties of water is considered. To calculate the impedance corresponding to a given set of G''_{max} and G'_{max} and d_D , Martin's matrix propagation method¹⁰ was employed. For each experimental point, the values G''_{max} and G'_{max} that satisfy the R and XL measurements were found by means of a simplex algorithm and iterated until the error between the experimental data and the model was less than 0.01Ω , which is less than the experimental error (0.05 Ω).

The results are shown in Fig. 3. Note that the viscosity $G''_{max} = 123$ kPa in the vicinity of the gold can double the value for the bulk solution $G''_{sol} \approx 60$ kPa. Furthermore, the elasticity G'_{max} near the crystal is almost 36 kPa, while for dilute solutions it is usually zero. We consider this elasticity to be the

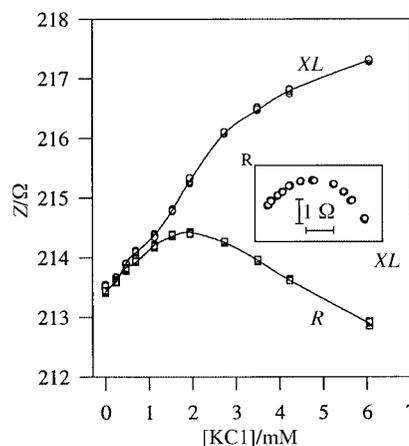


Fig. 2 QCM impedance components R and XL vs. KCl concentration. Each point is the mean value of 30 measurements. Inset: parametric plot of R vs. XL , [KCl] is the parameter and increases clockwise.

main contribution to the increase of R in the anomalous gravimetries. If no elasticity was present, Martin's multilayer model predicts negligible values for R , even for large changes in G''_{\max} .

Several experiments were performed in order to determine the role of the charged surface on the double layer viscoelasticity. In potentiostatic experiments, the values for G''_{\max} and G'_{\max} were found to be functions of the applied potential. A potential of minimum G was found at about -40 mV vs. SCE, which is close to the potential of zero charge for gold in KCl solutions.¹⁵ When the bare gold was modified with thiols with charged groups directed to the solution (AET and MPS), the viscoelastic properties became a function of the pH. For AET, higher G''_{\max} and G'_{\max} corresponded to lower pH, as expected from the increase of surface charge due to the protonation of the amino groups. An opposite trend was found for MPS derivatised gold, in which the surface charge is expected to increase by increasing the pH. These experiments show clearly that the interference is due to surface charge, and allow us to identify the viscoelastic layer with the electric double layer.

Conclusions

The QCM exhibits anomalous behaviour during microgravimetric analyses in the presence of an electrolyte. The interference in the gravimetric analysis, that can be up to 70% in mass, is directly related to the change in electrolyte concentration. All the studied electrolytes (NaCl, CaCl₂, BaCl₂, ZnSO₄, AlCl₃, KCl, NaClO₄, NaOH, HClO₄ and H₂SO₄) were found to produce similar effects. The data for the first five electrolytes are given as electronic supplementary information[†]. In particular, double and triple charged ions were found to produce the same effects at a lower concentration. The change in the concentration of charged species yields errors not only in the determinations of the frequency (mass), but also in the dumping

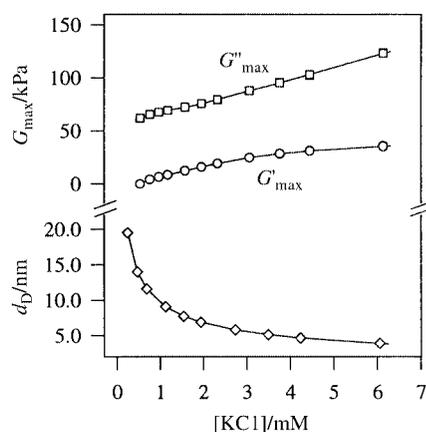


Fig. 3 Rheological properties of the diffuse double layer in the innermost region as function of the bulk concentration. From top to bottom: loss modulus G''_{\max} ; elastic modulus G'_{\max} ; and Debye length d_D . The values were obtained from data in Fig. 2, by using Martin's multilayer model (see text).

[†] Available as electronic supplementary information. See <http://www.rsc.org/suppdata/an/b0/b001725f>

factor of the crystal. Therefore, impedance analysis will always show this interference. It is important to note that thiol chemisorption is a complex process, which is still under study, but these results apply to any microgravimetric analysis, and are not related to the nature of the electrode surface, with the exception of its charge.

The QCM impedance analysis using Martin's multilayer model indicates the presence of a viscoelastic nanometric sized layer close to the crystal. This layer can only be identified with the Gouy Chapman diffuse double layer (DDL). The dependence of the properties of this elastic layer on the surface charge supports this conclusion. We suppose that the origin of this elasticity is the relaxation of the ionic atmosphere, which is much slower than the movement of the charges at the oscillation frequency of 10 MHz.

In order to avoid errors due to the change in electrolyte concentration, a high concentration of support electrolyte should be used when the gravimetric analysis of a charged analyte is performed. For irreversible adsorptions, the flow injection QCM enables the gravimetric data to be recovered once the electrolyte injection has passed.

A solution that contains no other charged species will show the highest error for the gravimetry of a charged analyte, since the presence of the analyte in the bulk solution will form the DDL and will introduce an error. This effect should be taken into account for any microgravimetric technique such as antigen-antibody, template recognition, ion trap or any other technique in which the ionic strength of the solution may vary. Further investigations on these effects are being carried out.

Acknowledgements

This work was supported by Fundacion Antorchas and PROMEP.

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