A compact device for simultaneous dielectric spectroscopy and microgravimetric analysis under controlled humidity

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Water plays a key role in the functioning of natural and synthetic molecular systems. Despite several hydration studies, different techniques are employed individually for monitoring different physical features such as kinetics, dynamics and absorption. This study describes a compact hydration cell, which enables simultaneous dielectric relaxation spectroscopy (DRS) and mass loss/uptake measurements in thin organic layers under controlled humidity conditions and in a wide temperature range. This approach enabled us to correlate the physical quantities obtained during the same experiment by complementary techniques. To demonstrate the performance of this device, a 200 nm thick Poly(methyl methacrylate) (PMMA) layer was measured at various relative humidity levels (0 – 75%), temperatures (25 – 75°C) and frequencies (DRS: 0.1 Hz – 1MHz) to study how hydration and dehydration processes affect its molecular dynamics. The results show the capability of this setup to study the structural changes upon variation of the water content.

I. INTRODUCTION

Hydration of natural or synthetic macromolecules is responsible for a variety of phenomena, governing both the structure and the stability of such systems. Studying the effect of hydration enhances the understanding of many complex biological mechanisms such as protein folding [1-3], phospholipid hydration, as well as the dynamics and conformation of polymers [4-5]. Especially, the hydration of biomolecules is extensively studied in relation to the dynamics, structure and function [6-8]. These systems exhibit relaxation features typical of polymer systems and glass-forming liquids.

Furthermore, hydration plays a complex functional role in living cells. Since the hydration water determines the membrane stability and regulates its interaction with other molecules such as ions and proteins, several experiments and simulations have been performed. Numerical simulations have been extensively applied for studying a broad range of dynamical properties, including the rotational, translational, and hydrogen-bond dynamics, in the hydration shell that consists of the first water layer surrounding the biomolecules and interacting with them [9]. Moreover, several methods provided information about the organization of the hydration states that is not only restricted to the membrane plane but to a region extending into the cytoplasm, in which polar head groups play a relevant role [10].

Previous studies have characterized the dynamical properties of water confined in phospholipid membranes and show that water dynamics slows down dramatically as the hydration decreases

FIG. 1. Schematic illustration and cross-section of the custom-made hydration cell.

[11]. Another interesting phenomenon that has recently been studied is dehydration in a mixture of phospholipids and zwitterionic surfactants due to the formation of an inner salt layer between the dipoles of phospholipid and surfactant headgroups that reduces potential water binding sites [12].

Previous hydration studies aiming for example at a further refinement of hydration forces theory, largely relied on combining individual measurements of relevant physical quantities under controlled hydration conditions [13]. This procedure is both time-consuming and challenging with respect to the accuracy of hydration control.

In this study, we propose an alternative approach that allows to simultaneously study the dielectric properties, including

relaxation phenomena, and the water uptake/loss of a thin organic (polymer) film. In a compact, single setup providing quasi-equilibrium humidity conditions, dielectric and gravimetric measurements at different temperatures are combined. To achieve this approach, we designed a compact hydration cell based on the following concepts:

- a.** Sealed, small volume hydration cell that contains all sensors, for the dielectric and microgravimetric measurements, together with a reservoir filled with a saturated aqueous salt solution. By choosing a specific salt, a desired relative humidity level (RH) can be maintained over a wide temperature range, which is, for most inorganic salts, almost temperature-independent.
- b.** Thermal insulation of the entire cell along with slow temperature changes allows quasi-equilibrium conditions regarding moisture uptake or desorption by all samples and sensors during heating or cooling protocols.
- c.** Flexible cell design regarding the number of samples and physical parameters being measured. The design, which we discuss here allows measuring three physical phenomena, being kinetics, adsorption and dynamics.

To demonstrate the capabilities of the hydration cell, we have studied the dielectric properties of Poly(methyl methacrylate) (PMMA) as a well-documented reference material [14-15]. Among the variety of polymers that have been examined as a function of water content by dielectric relaxation spectroscopy (DRS), e.g. Poly(2-methoxyethyl acrylate) PMEA [16, 17] and poly(ethylene glycol) PEG [18], PMMA was chosen for its capability to absorb water and its significant sensitivity to humidity. Despite its hydrophobic nature, it can absorb ~2% w/w (weight percent) of water. Moreover, it is low-cost and it shows long-term stability and resilience to aqueous salt solutions [19-21]. It has been widely used as an active polymer, for example in optical humidity sensors [22-24], in chemical sensor for detecting analytes in both liquid and gaseous media, in molecular separation and in drug delivery as a microparticles matrix [25].

The compact device presented in this work enables real-time to follow water absorption and desorption in function of time and temperature. Furthermore, it allows monitoring changes in the sample thickness.

DRS measurements were employed to study the molecular dynamics, the physical network morphology changes and the interfacial effects due to the loss and uptake of water molecules [26]. In addition, the absorption and with it the absolute layer thickness is monitored with monolayer sensitivity via a quartz crystal microbalance (QCM) that consist of a thin quartz crystal plate with metal electrodes deposited on both the front and back sides. The QCM technique is versatile. It has been widely employed in biosensors for biodetection [27,28], for the study of interactions between molecules and lipids [29] and for monitoring phase transition in biomimetic membranes [30,31]. Among other applications it is also used in soft matter characterization for the determination of materials sensing properties [32].

II. EXPERIMENT

A. Experimental setup

The main components of the hydration cell are displayed in Figure 1. The device consists of three major parts: two metal blocks in brass and a sensing head with pins to connect the system to the analyzers. These parts combine to form a cylindrical

FIG 2. Photograph of the sensing head that includes a QCM chip, an IDE (interdigitated comb electrode) and a Pt100 resistor as temperature sensor.

humidity chamber, which is 7 cm deep with a 4 cm inner diameter. Moreover, in the bottom block a small bucket in polyether ether ketone (PEEK) is placed, which is filled with a saturated salt solution to control the relative humidity inside the chamber. It is a benefit that the bottom block can be mounted or dismantled separately to quickly change the salt solution without moving the sensing head. To control the inside temperature, a Thermocoax wire is coiled around the metal middle block and fixed with cement. The temperature range is between 21°C and 200°C at the current stage of development. All sensors in the system (QCM, interdigitated comb electrode IDE and Pt100) are mounted onto the brass cover plate as shown in Figure 2.

A conventional QCM sensor measures mass changes per unit area by measuring the change in frequency of the quartz crystal oscillator. The frequency increases or decreases respectively by the removal or addition of a small amount of mass from/onto the surface of the quartz sensing crystal. The Sauerbrey equation allows to convert the change of the resonance frequency in the mass change per unit area [33]:

$$\Delta f = - \frac{2f_0^2}{A\sqrt{\mu_q\rho_q}} \cdot \Delta m \quad (1)$$

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, μ_q is the density of the crystal (2.648 g cm^{-3}), ρ_q is the shear modulus of the quartz ($1.67 \times 10^5 \text{ g cm}^{-1} \text{ s}^{-2}$) and Δm the change of the mass on the surface. For a given temperature and in the limit of a small sample mass, the frequency shift is directly proportional to the adsorbed mass on the QCM chip according to Eq.1.

In our setup the QCM chip is connected to a thickness counter (Tectra GmbH, Frankfurt, Germany). The raw data from the QCM chip are based on a constant water mass density of 1 g/cm^3 from which we obtained the apparent thickness variation due to water uptake and desorption. The mass change was calculated afterwards by multiplying the measured thickness by the water density. However, this density is temperature dependent, therefore the mass change has to be corrected using the water density values as tabulated by the NIST (National Institute of Standards and Technology) [34]. Once the mass variation has been determined,

FIG. 3. (a) Frequency response calculated from the acquired apparent thickness of a PMMA coated QCM chip at constant relative humidity conditions between 0% and 75% RH using the Sauerbray model. (b) Water uptake kinetics at 25° C of a PMMA coated QCM chip, including fits based on the kinetic Langmuir adsorption isotherm model.

the frequency shift can be extracted by using Eq. 1. Hence it is possible to measure the film swelling and shrinking according to its moisture content.

Simultaneous dielectric spectra are acquired using μm -spaced interdigitated comb electrodes in combination with a high resolution impedance analyzer (Alpha analyzer, Novocontrol Technologies). In the present work, IDEs have been designed using Clewin software and subsequently fabricated using optical lithography. Laser Writer LW405 (MICROTECH S.r.l., Palermo, Italy) was used for patterning planar structures in situ directly on the wafer. First, the glass substrate was coated with 100 nm Al layer by sputter coating and then with the photoresist by spin coating. After development, the photoresist was removed by etching to make the exposed region transparent. The obtained IDEs have 100 pairs of comb-like shape electrodes 5 μm -spaced with a width of 5 μm and a length of 3600 μm .

After soldering the sample to the pins, the sensing head is placed on top of the device to seal the humidity chamber. For this purpose, four screws are used to get a good seal by tightening an O-ring between the sensing head and the main body of the device. Furthermore, thermal convection effects caused by ambient air turbulence are minimized by putting the whole setup inside an insulating box.

Such IDE configurations have various advantages over the classical parallel-plate configuration [35,36]. As the electric field is planar, the total capacitance of the IDE can be easily decomposed into a background part related to the empty IDE having an intrinsic capacitance C_0 and a variable component that depends on the film thickness. Conductive epoxy resin is used to glue silver wires onto the connect pads of the IDE.

B. Sample preparation

As a proof-of-concept, syndiotactic PMMA was used as the sensing layer. PMMA layers were synthesized by dissolving 0.1 mg of s-PMMA in 2 g of Chloroform. All reagents were used as received from Sigma-Aldrich N.V. (Diegem, Belgium) and had a purity of minimally 99.9%. This mixture was stirred at 65 °C for 60 min to completely dissolve the polymer. In a next step, the

solution was spin-coated (60 s at 1000 rpm) onto a 1 cm^2 aluminum-coated glass substrate and onto the QCM chip. This resulted in PMMA layers with an average thickness of 200 nm as measured using atomic force microscopy. Subsequently the samples were placed in the hydration cell and exposed to P_2O_5 (0% RH) until equilibrium.

Four different saturated salt solutions were used to control the RH: LiCl (13% RH), MgCl_2 (33% RH), NaBr (58.2% RH) and NaCl (75% RH) [37]. Before each measurement the samples were equilibrated in P_2O_5 thus the dried state was the reference condition.

C. QCM gravimetric measurements

The QCM technique was used to analyse the absorption-desorption kinetics of water on the PMMA film. The corresponding variation in the frequency shift reflects the mass uptake or loss. A gold quartz crystal (Inficon No. 008-010-G10) with a fundamental frequency of 6 MHz in air was used as a mass sensor. When operating in its fundamental mode, the theoretical sensitivity factor is 16.02 ng Hz^{-1} (12.05 $\text{ng Hz}^{-1} \text{cm}^{-2}$) [38].

Isothermal measurements at 25 °C were performed for studying the water uptake/desorption kinetics after a step-like change in RH. Moreover, the effect of the temperature on the PMMA kinetics was monitored by implementing temperature ramps.

D. Dielectric measurements

Dielectric relaxation spectra in the frequency range from 0.1 to 10⁶ Hz were obtained by performing a heating and cooling cycle between 25°C and 75°C at a rate of 1 K/min. Generally, the complex dielectric permittivity, ϵ^* , contains information about the electronic, atomic and orientational polarizability of a dielectric material. While the fast, electronic contribution represents the permittivity at optical frequencies via the Maxwell relation $\epsilon \approx n^2$ (n is the refractive index), the orientational polarization gives access to molecular relaxation processes, which occur on time-

FIG. 4. (a) Mass uptake obtained from PMMA coated QCM resonance frequency shifts using the Sauerbrey model for adsorption as a function of RH. (b) Mass uptake and loss as a function of temperature during heating and cooling at constant RH with hysteresis effect due to changes in the structure of PMMA. (c) Corrected mass uptake and loss during heating and (d) cooling. The temperature dependence was removed by subtracting the reference curves acquired in the dried state.

scales larger than 10^{-12} s and are due to orientational fluctuations of permanent dipoles at various length scales (from bond rotations up to polymer segmental dynamics) [39].

In case of a single relaxation process, the dielectric response is well described by the Havriliak-Negami (HN) equation [40]:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{[1 + (i\omega\tau_{HN})^\alpha]^\gamma} \quad (3)$$

with $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$

Here, ε_s and ε_∞ respectively denote the static and high frequency limiting values of the electric permittivity. The equation also contains two shape parameters α and γ as well as the relaxation time τ_{HN} . The parameter $\Delta\varepsilon$ is the dielectric relaxation strength or intensity, which is a relevant quantity as it describes the magnitudes of the effective dipole moment. Typically, in DRS spectra, the slowest process (α -relaxation) is associated to the segmental motions, i.e. the dynamic glass transition T_g . On the other hand, the β and γ relaxations reflect secondary processes, which are usually attributed to side groups rotations. The

Arrhenius equation is common for describing such local dynamics relaxation time [41]:

$$\tau = \tau_0 \exp \left[\frac{E_a}{k_b T} \right] \quad (4)$$

Here, E_a is the activation energy of the relaxation and k_b Boltzmann's constant.

The relaxation processes were studied at different humidity conditions. The results were analyzed for each RH value in terms of water absorption and desorption as determined by the QCM data on the mass change.

III. RESULTS

A. Kinetic QCM experiments

Kinetics studies were carried out in the humidity and temperature-controlled chamber using the QCM sensor. As explained, from the acquired thickness variation, the variation of mass was calculated.

FIG. 5. (a) 3D plot of ‘the conduction-free’ loss $\epsilon''(f)$ of PMMA at room condition showing the α -relaxation process due to the motion of the main polymer chain and the β -relaxation process (b) fitted using the Arrhenius model. (c) Experimental isothermal spectra of the dielectric constant $\epsilon'(f)$ at $f = 10$ Hz and $f = 110$ kHz for different humidity conditions as a function of temperature. At low frequency the secondary β -relaxation process is affected by the water content and an increase in dipole strength is observed due to a change in the mass density.

Regarding the frequency responses the Sauerbrey equation was applied. As shown in Figure 3a, Δf changes significantly as a function of humidity. The first data acquired at 0% and 11% RH reveal a slower desorption rate compared to the adsorption rate of the film. Between each measurement the hydration cell was opened to change the salt solution and the sample was exposed to the ambient air. This caused water uptake from the ambient air as we can see in the frequency steps for each RH condition. According to the Sauerbrey model, the frequency shift is directly proportional to the change in the adsorbed mass. Such change in the mass due to humidity adsorption was fitted using the kinetic Langmuir adsorption isotherm model as shown in Figure 3b. This model describes the rate of surface reaction for forming a monolayer on the surface [38]. The time dependence of the amount of water molecules onto the film surface Δm can be described as following:

$$\Delta m_t = \Delta m_0 + \Delta m_\infty(1 - e^{-t/\tau}) \quad (5)$$

$$\text{with } \tau^{-1} = k_a + k_d$$

Here, τ is the relaxation time, m_∞ the maximum amount of water molecules adsorbed onto the surface at $t \rightarrow \infty$ and k_a and k_d are the rate constants for the adsorption and desorption processes, respectively.

B. QCM adsorption studies in quasi-equilibrium

Figure 4a shows that the mass uptake obtained from QCM resonance frequency shifts for adsorption for different RH (between 0 and 75 %) values at different temperatures. Once the sample was dried and equilibrated in P_2O_5 , the QCM sensor was set to zero. To ensure the system is in equilibrium, the samples were allowed to stabilize overnight at each respective RH condition.

The results show that the calculated mass changes as a function of the relative humidity and water uptake at higher RH is up to 10 ng. This curve represents an absorption isotherm showing an initial strong increase in the mass of the film, followed by a weaker linear step up to 60°C where the water uptake seems to be influenced by the temperature. This non-linear behavior from 0 to 10% RH might be explained by the difficult formation of polymer-water hydrogen bonds. To overcome this negative entropy effect a certain amount of favorable initial bonds needs to be formed [42]. Figure 4b shows first of all that the mass upon desorption returns back to its original value. Secondly, a region of hysteresis suggests changes in the solid state structure especially at higher RH.

Even at 0% RH some solvent seems to be trapped inside the polymer structure. This phenomenon is due to thermal lag in the temperature equilibration and to the kinetics of hydration. A temperature dependence is observed in Figure 4b in the constant

slope of the curves because it reflects the temperature effect on the resonance frequency of the crystal. The data have been then corrected and the T dependence removed by subtracting to each data set the reference data got at the dried state (P_2O_5). As a result, we obtain the mass variation curves as function of RH shown in Figure 4c-d, which are no longer affected by heating and cooling. Regarding the measurement in NaBr (58% RH), the graph 4c shows a mass decrease around 50°C due to its humidity fixed points that change dramatically at higher temperature. A previous study confirms such hypothesis, in fact it reveals that despite having the same relative humidity, water content varies considerably with temperature [43]. All the relative humidity curves show the same trend and the saturation vapor pressure, thus the moisture content, is highly nonlinear as it increases rapidly with increasing temperature.

C. Dynamics experiments

Simultaneously, the dielectric data were acquired using IDEs. The experimental setup was validated against a conventional Novocontrol high resolution dielectric spectrometer in dry N_2 atmosphere, where the sample is supposed to be water-free.

Figure 5a shows the data obtained by the conventional spectrometer, measuring in a wide temperature range from 0°C to 150°C. Two processes are observed, the α and the β relaxation process. Concerning the first process, it was detected, as expected, at high temperature, since the T_g of s- PMMA is around 120 °C. In the new setup, due to the use of saturated salt solution we could not reach such elevated temperature therefore we focus on the secondary process that occurs between 25°C and 75°C. The β relaxation process was observed at each humidity condition and follows the Arrhenius behavior below T_g with an activation energy of 76 kJ/mol, which is in good agreement with the reported value [44, 45] (Figure 5b). Such relaxation is symmetric in log frequency and is attributed to the side chain motion of PMMA e.g. the rotation of carboxyl side group is involved.

Therefore, the water uptake in weight is less than 5% of the polymer and up to 33% RH it does not affect the PMMA dynamics since the glass transition temperature is higher than the conditioning temperature of 25°C. It also does not play a role in the activation energy of the process as shown in Figure 5c.

Important features are revealed in Figure 5d. First, at 10 Hz the curves reproduce the trend and the increase shown in the reference data points acquired in the dry N_2 atmosphere using the conventional dielectric spectroscopy setup. Second, the dielectric constant increases in function of the adsorbed moisture content thus it is humidity dependent. Moreover, such adsorption is unaffected by temperature.

Finally, it is possible to approximate the behavior of the dielectric constant at high and low frequency to the infinite and static electric permittivity, ϵ_∞ and the ϵ_s , respectively. The difference between both values corresponds to the relaxation strength of the β process $\Delta\epsilon_\beta$. Note that at low frequency the dielectric constant is much more influenced by the water content as its value increases. Therefore, the process appears stronger due to an increase of dipoles in the structure. As confirmed by the QCM sensor, a mass change occurs due to the water-polymer coupling.

IV. CONCLUSION

The response of a PMMA film to changes in relative humidity was analyzed using the developed and tested compact device. The combination of simultaneous DRS and gravimetric measurements allows monitoring the film dynamics upon variation of the sample mass, which is directly related to the moisture uptake/loss.

The new equipment has a great potential thanks to its capability to simultaneously obtain several parameters from different sensors. It can bring an additional value to a variety of applications including the study of polymers and complex systems such as lipid vesicles. In addition, the setup will be improved for better controlling the humidity condition inside the chamber.

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