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Historical perspective

About different types of water in swollen polyelectrolyte multilayers

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ABSTRACT

The review addresses swelling of polyelectrolyte multilayers in water. Different models for the determination of the water content are compared. It is clearly shown that voids under dry conditions present cavities for water which contribute to the water content of the multilayer in the swollen state. This so-called "void water" does not lead to any changes in thickness but in scattering length density during swelling. The "swelling water" leads to both changes in scattering length density and in thickness. Depending on the preparation conditions like the type polymers, polymer charge density, ionic strength and type of salt the ratio of "void water" differs between 1 and 15 vol.% while the amount of "swelling water" is of several ten's of vol.%.

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1. Introduction

Due to miniaturization of devices ultrathin coatings become more and more important. One challenge of the design of thin coating films is that they serve to modify surface properties in an easy way. Suitable films can be prepared by the layer-by-layer (LbL) method where polyanions and polycations are alternately adsorbed from aqueous solutions [1,2]. The main features are that the thickness can be easily tuned with nanometer precision by the numbers of deposited layers or the ionic strength and the macroscopic properties can be controlled by the types of polyelectrolyte used for preparation. During the alternating adsorption process complexes between oppositely charged groups of the polyelectrolytes are formed [3] driven by entropy due to the release of small counterions [4]. The mutual charge compensation of oppositely charged polyelectrolytes is called intrinsic charge compensation, while extrinsic charge compensation refers to charge compensation of polyelectrolytes by counterions. In general, a strong extrinsic charge compensation is related to a lower density of complexation sites than the intrinsic one. The density of complexation sites can be easily controlled by preparation conditions like the type polymers, polymer charge density, ionic strength and type of salt.

Polyelectrolyte multilayer assemblies (e.g., planar films or walls of hollow capsules) are well-known to be sensitive to external parameters such as ionic strength and pH [5–8] temperature [9] or humidity [10]. These features make them particularly attractive for technical applications like sensors and containers for drugs.

The review addresses especially the response of polyelectrolyte multilayer (PEM) to the exposure of different relative humidities and liquid water. Different methods to measure and to calculate the water content are compared.

The water mobility within the multilayers was studied by NMR [11,12] and the swelling behavior mainly by scanning force microscopy (SFM) [13] and ellipsometry [5,10,14]. The disadvantage of SFM and ellipsometry is that the swelling ratio can be only determined by the differences in thickness, since the multilayers are too thin for getting

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information about e.g. the refractive index. In order to get more information about the internal structure and the water distribution neutron reflectivity is used [15–19]. Often not all information of the neutron reflectivity data is used, and the water content is calculated only by the change in thickness. The review shows the importance and the power of the full analysis of neutron reflectivity data using a combination of change in thickness and scattering length density.

Another promising technique for measuring the total amount of incorporated water within PEM is transmission X-ray microscopy (TXM) [20]. TXM allows studying the water content of PEM in microcapsules, which is compared to the one of PEM at planar surfaces.

2. Determination of water content: models and techniques

Polyelectrolyte multilayers are very sensitive to the exposure to water vapor with respect to changes in their structure. A common problem is to compare the water content between different studies, since for long time and even nowadays the relative humidity of the environment is often not properly controlled. This problem is discussed in details in [21]. In the following the suffix "dry" refers to a relative humidity close to 0%. Usually 1% r.h. can be reached. The suffix "swollen" addresses experiments in a certain relative humidity or against liquid water.

In order to calculate the water content within the multilayers three different models are applied in literature:

(1) The simplest model (*thickness model*) calculates the amount of incorporated water ϕ due to changes in thickness before (d_{dry}) and after swelling in water or different relative humidities ($d_{swollen}$):

$$\phi_{swell} = \frac{d_{swollen} - d_{dry}}{d_{swollen}}. \quad (1)$$

This model assumes that the whole water penetrating into the PEM leads to swelling of the polyelectrolyte multilayer. It is the most common model, since it can be applied to data obtained by many simple lab methods like ellipsometry and SFM. In contrast, the two models described in the following, can be only applied to neutron reflectometry (NR). In 2000, first NR measurements at PEMs against liquid water were performed [16]. Generally, a flow cell is used, where the neutron beam is irradiated through the Silicon wafer side, which presents both substrate of the polyelectrolyte multilayer and the top of the flow cell.

(2) The *density model* takes into account that the change in scattering length density of the PEM $Nb_{swollen} - Nb_{dry}$ originates from the incorporation of water [16,22]:

$$\phi'_{swell} = \frac{Nb_{swollen} - Nb_{dry}}{Nb_{water} - Nb_{dry}}. \quad (2)$$

Nb_{water} is the scattering length density of water which is known (D_2O: $6.37 \cdot 10^{-6}$ Å^{-2}, H_2O: $-0.56 \cdot 10^{-6}$ Å^{-2}). If only two compounds would have been taken into account, i.e. water and polymer, the water content determined via the change in thickness or density due to exposure to water (or vapor) should be the same. This is not the case. For instance, a polystyrene sulfonate (PSS)/polyallylamin hydrochloride (PAH) multilayer exposed to liquid water gives a ϕ_{swell} of 0.29, but a ϕ_{swell}' of 0.46 [23]. Hence, a more complex model is needed solving this paradox.

(3) The third model assumes that there are vacuum *voids* in the dry PEM (see Fig. 1a). During exposure to water, the volume fraction of voids is filled with water, which contributes to the change in scattering length but not to the change in PEM thickness (see Fig. 1b). This water fraction is called *void water* ϕ_{void}. The larger amount of water contributes to both swelling and change in scattering length density and is called *swelling water*, ϕ_{swell}, and corresponds to the relative change in thickness in Eq. (1) (see Fig. 1c).

The total amount of water ϕ_{total} is the sum of both water fractions [14,23]:

$$\phi_{total} = (1-x)(1-\phi_{swell}) + \phi_{swell} = \phi_{void} + \phi_{swell} \quad (3)$$

where x the fraction of polymer is given by

$$x = \frac{Nb_{dry}}{Nb_{water}} - \frac{Nb_{swollen} - \phi_{swell} Nb_{water}}{(1-\phi_{swell}) Nb_{water}} + 1. \quad (4)$$

For instance for PSS/PAH multilayers, ϕ_{void} is about 0.12 and therefore the total amount of water (ϕ_{total}) is equal to 0.41 with ϕ_{swell} equal to 0.29 as mentioned above [23]. The two latter values are in good agreement with measurements in saturated water vapor (100% r.h.) [15]. The total amount of water (0.41) is similar but not equal to the water content, calculated by the change in density (0.46). There is a small difference:

$$\phi_{total} - \phi'_{swell} = \phi_{void}\left(1 - \frac{Nb_{water}}{Nb_{water} - Nb_{dry}}\right). \quad (5)$$

That means $\phi_{total} < \phi_{swell}'$ for exposure to D_2O and $\phi_{total} > \phi_{swell}'$ for exposure to H_2O [23]. In other words ϕ_{swell}' depends on the isotope and ϕ_{total} do not.

Taking *void water* into account for analysis of experimental data, gives similar amounts of incorporated water for heavy and light water. Obviously, there is no isotopic effect irrespective of the ionic strength and type of salt used for preparation [14]. Differences in swelling against D_2O and H_2O, reported in other studies [24,25] are minor.

To summarize, the total amount of water should be determined by the third model via Eqs. (3) and (4). Beside the determination of two types of water and of the multilayer density in the swollen and dry state, the presented method allows also an independent calculation of the scattering length density of the pure polyelectrolytes.

An overview about the swelling behavior of specific PEM systems calculated by different models is given in [21].

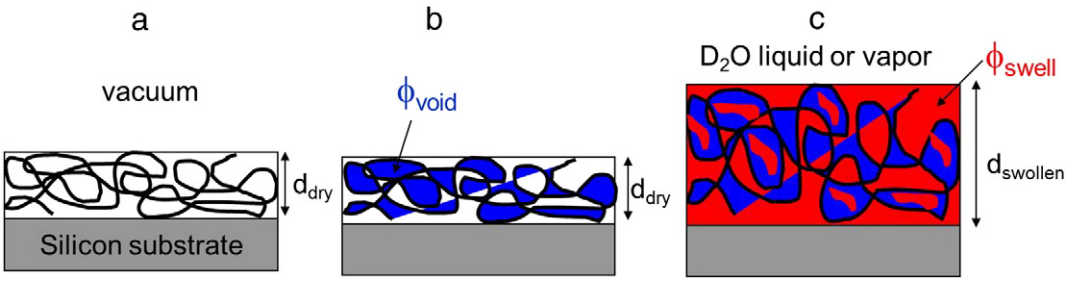

Fig. 1. Scheme explaining model 3: a) dry state with vacuum voids; b) "void water", which contributes to changes in scattering length density but not in thickness; c) "swelling water" which contributes to changes both in thickness and in scattering length density.