How hard do we dry?

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Equilibrium and kinetic aspects of water exchange between hydrated thin films and humid air are of very general interest. Commonly used experimental setups to study this water exchange include sensitive dynamic gravimetric vapor sorption (DVS) instruments or quartz crystal microbalances (QCM).

We have performed a detailed kinetic water sorption/desorption study of humidity-responsive films (10-100 μ m dry thickness) of oppositely charged polymer-surfactant pairs using a DVS instrument. In our kinetic analysis, we anticipated a limiting situation, where the the transport of water through a stagnant layer in the surrounding humid atmosphere was rate-limiting for the water exchange. For a standard kinetic sorption/desorption experiment, where the mass change of the film is monitored after a small step change of relative humidity (RH), this scenario predicts that, following each step change,

- the mass of water in the film should change exponentially with time, where
- the time constant should be proportional to
 - o the film thickness,
 - \circ $\;$ the thickness of the stagnant layer in the gas phase and
 - \circ the slope of the water sorption isotherm over the step in RH.

These predictions were found to hold almost quantitatively for the investigated films (see Figure 1), as long as the latter contained more than *ca*. 3 water molecules per ion pair.



Figure 1. Fitted time constants (red data, left scale) and measured slopes of sorption isotherms (black data, right scale) vs. RH for polymer-surfactant films of three different thicknesses, following step changes of RH over the indicated 5% RH intervals. The y axes are logarithmic, so parallel lines indicate proportionality between the data.

Studying the substantial recent literature on similar experiments for thin films of other materials (Nafion[®] and other sulfated "ionomers", food biopolymers...) featuring similar water sorption isotherms, we found *no data analysis similar to ours*. Moreover,

- almost noone had measured the rate of water transport through the gas phase in their instruments
- many authors (tacitly) assumed that the water transport *inside* the film, rather than the external transport in the vapor phase, was rate limiting for the total water exchange process.

We therefore conclude that

- our kinetic analysis should be generally relevant for studies of water sorption/desorption of thin films,
- apart from information on the studied films, the analysis gives quantitative kinetic information on the water transport through the vapor phase in the experimental setup used, and
- in common experimental setups, we don't dry nearly as hard as many seem to think.

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