

Interfacial effect of Moisture Absorption in Thin Polyelectrolyte Films

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When two semi-infinite phases are separated by a thin layer the thermodynamic properties of the layer are different from that of the bulk material. This way, the thickness of the layer can influence the concentration of mobile components in it. We checked this hypothesis in the case of D₂O absorption in polyelectrolyte multilayers with different thickness. We observed a decrease in the D₂O content upon increase of the number of PE layers.

The dimension of nano-structured systems may control the concentration of mobile components in these systems. When two semi-infinite phases are separated by a thin layer the thermodynamic properties of the layer are different from that of the bulk material. This difference leads to changes in the thickness of the film, well described by the DLVO theory in the case of easy deformable (fluid) materials. For stiff materials, this effect might create exchange of mobile components between the thin layer and its surrounding. Such dependence should appear, if the dimension of the system under consideration comes into the range of the action of the surface forces (less than 15 nm), where the chemical potential becomes a function of the dimensions and the concentration of a mobile component may change as a result. We checked this hypothesis in the case of the water absorption in polyelectrolyte multilayers (PEM) with different thickness.

Five PEM films were prepared on Si wafers by LbL technique from poly(ethylenimine) (PEI), poly(allylamine hydrochloride) (PAH) and deuterated poly-(sodium 4-styrenesulfonate) (d-PSS). The film structure was PEI(d-PSS/PAH)_n where n = 2, 3, 4, 6 and 10. Neutron reflectometry (NR) experiments were performed in gas tight cell in dry (N₂) and ~ 100 % r.h. D₂O vapour atmosphere at the reflectometer AMOR. The reflectivity curves in dry N₂ and D₂O vapour atmosphere are shown on Figure 1. The amount of D₂O absorbed in the PEM was calculated knowing the scattering length density of the material in dry and wet conditions. We observed a decrease in the D₂O content upon increasing the number of PE layers (Figure 2).

The observed trend supports the theoretical assumption above. The van der Waals (vdW) interaction between the film interfaces (air/film and film/support) depends on the film thickness. The vdW interaction increases with the third power of the decrease in the thickness. If the vdW interaction is attractive this would increase the chemical potential of the components which are presented in the film. The D₂O vapours, being the only mobile component, could be expelled from the film, thus decreasing the chemical potential of the whole system.

One has to keep in mind that the effect might also be explained by a lower density of the PEMs near to the surface of the support or by stronger D₂O adsorption close to the substrate.

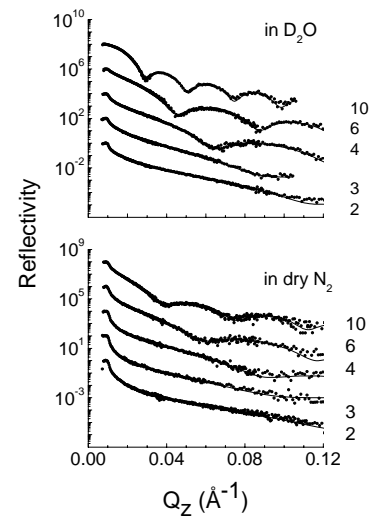


Fig 1: NR curves in dry N₂ and 100% r.h. D₂O atmosphere for sample with 2, 3, 4, 6 and 10 (d-PSS/PAH) bilayers.

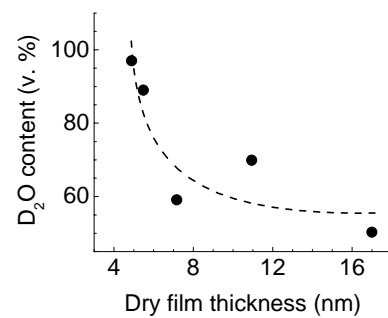


Fig. 2: D₂O content as a function of PEM thickness in dry state (dry N₂).

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