

Water Sorption in Glassy Polyvinylpyrrolidone-based Polymers

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1. Uncertainty of the water-sorption kinetics' fittings

The uncertainty of the fittings of Equation 9 with the measured water-sorption kinetics of the main manuscript was evaluated by the average relative deviation *ARD* as displayed in Equation S1.

$$ARD = \frac{1}{n_t} \sum_k^{n_t} \frac{|w_{w,k} - w_{w,k}^{exp}|}{w_{w,k}^{exp}} \quad (S1)$$

Here, *k* is the index for the number of data points *n_t* of the water sorption kinetics, *w_{w,k}^{exp}* is the measured water weight fraction and *w_{w,k}* is the modeled water weight fraction determined from Equation 9 of the main manuscript. The ARDs of all water sorption kinetics are displayed in Table S1.

Moreover, the sorption steps of the main manuscript were terminated after 200/120 min assuming a (pseudo-) equilibrium of the polymer-water mixture at the respective relative humidity RH. The validity of this (pseudo-)equilibrium was evaluated via a comparison of an average sorption rate *SR[∞]* in this (pseudo-)equilibrium and the initial sorption rate *SR⁰*. The sorption rate describes the rate of change of the measured water weight fractions *w_{w,k}^{exp}*. The *SR[∞]* was calculated as displayed in Equation S2.

$$SR^\infty = \frac{1}{n_t^*} \sum_{k=1}^{n_t-1} \frac{w_{w,k+1}^{exp} - w_{w,k}^{exp}}{t_{k+1} - t_k} \quad \forall k \quad t_k > 60 \text{ min} \quad (S2)$$

n_t^{}* is the number of data points where the time *t_k* of the *k*th data point is greater than 60 min. We estimated that the water sorption kinetics reached a (pseudo-)equilibrium at around 60 min. An average of all sorption rates was taken to prevent a bias resulting from the scattering of *w_{w,k}^{exp}*. The initial sorption rate *SR⁰* was calculated as displayed in Equation S3.

$$SR^0 = \frac{w_{w,2}^{exp} - w_{w,1}^{exp}}{t_2 - t_1} \quad (S3)$$

Both *SR[∞]* and *SR⁰* are also displayed in Table S1.

Table S1. Average relative deviation ARD from the water sorption kinetics' fittings at 25 °C of the main manuscript, average sorption rates in (pseudo-) equilibrium *SR[∞]* and initial sorption rates *SR⁰* at the respective relative humidity RH.

RH /10 ⁻²	ARD _{PVP} /10 ⁻²	ARD _{PVPVA} /10 ⁻²	SR _{PVP} [∞] /(μg g ⁻¹ min ⁻¹)	SR _{PVPVA} [∞] /(μg g ⁻¹ min ⁻¹)	SR _{PVP} ⁰ /(μg g ⁻¹ min ⁻¹)	SR _{PVPVA} ⁰ /(μg g ⁻¹ min ⁻¹)
9.24	10.500 ± 2.292	10.381 ± 1.484	0.132 ± 0.179	0.017 ± 0.024	63.39 ± 2.45	30.01 ± 4.88

29.4	2.816 ± 0.475	2.813 ± 0.191	0.212 ± 0.137	0.073 ± 0.066	104.86 ± 35.37	86.67 ± 12.20
44.5	0.845 ± 0.117	1.108 ± 0.107	0.169 ± 0.102	0.166 ± 0.026	72.89 ± 11.33	41.90 ± 5.216
59.9	1.018 ± 0.067	1.033 ± 0.046	0.165 ± 0.281	< 0.001	88.65 ± 31.16	47.29 ± 8.42
73.4	0.705 ± 0.054	1.047 ± 0.031	0.126 ± 0.191	< 0.001	103.02 ± 13.92	79.87 ± 11.49
87.8	0.517 ± 0.057	0.597 ± 0.048	0.028 ± 0.351	0.08 ± 0.456	204.96 ± 49.37	240.28 ± 13.01

The ARDs decrease from 10% to 0.5% with increasing RH, supporting that anomalous sorption behavior occurs mostly in the glassy polymer-water mixtures. The very high ARD of 10% for the lowest RH step limits the significance of the determined water diffusion coefficient in the main manuscript.

All average sorption rates in (pseudo-) equilibrium SR^∞ were lower than $0.212 \mu\text{g g}^{-1} \text{min}^{-1}$. In contrast, the initial sorption rate SR^0 (with $30\text{--}240 \mu\text{g g}^{-1} \text{min}^{-1}$) is several magnitudes more significant than the SR^∞ , showing that the polymer-water mixtures were in a (pseudo-)equilibrium after 60 min.