# Sorption induced relaxations during water diffusion in S-PEEK

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This paper presents an analysis of the sorption kinetics of water vapor and liquid water in the glassy polymer sulfonated poly(ether ether ketone) (S-PEEK). Sorption isotherms are determined experimentally using a gravimetric sorption balance, and the relative contributions of Fickian diffusion and relaxational phenomena are quantified as a function of the water concentration in the polymer using the model of Hopfenberg and Berens.

Analysis of the sorption isotherms and determination of the sorption kinetics prove the occurrence of both Fickian sorption behavior and relaxational phenomena already at very low water concentrations in the polymer. With increasing water concentration, the relative importance of relaxation phenomena increases, whereas the relative contribution of Fickian diffusion decreases.

Based on the water vapor sorption kinetics only, the Fickian diffusion coefficient increases over two orders of magnitude with increasing water vapor concentration. Taking also the diffusion kinetics from liquid water sorption experiments into account reveals a change of even three orders of magnitude of the Fickian diffusion coefficient when the water concentration in the polymer increases.

## Introduction

The removal of water vapor from gas streams is an important industrial operation and many applications can be found in *e.g.* the dehydration of flue gases,[1] the drying of compressed air[2] and the storage of fruits and vegetables under protective atmosphere.[3] Membrane technology using polymeric membranes is a promising and attractive method for dehydration purposes: it has a small footprint, it is energy efficient and it is easy to implement and operate. In general, polymeric membranes used for such processes have a dense separating layer and water transport occurs through dissolution and diffusion.[4] Often, hydrophobic membranes are used for air humidification control,[5,6] but membranes based on hydrophilic polymers gain increasing interest as gas humidification membranes.[1,7–9] Hydrophilic polymers absorb high amounts of water and therefore enhance the transport of water which is governed by diffusivity and solubility.[10,11] However, sorption of water renders the physical properties of the polymer (*e.g.* the glass transition temperature and the degree of swelling, which results in changes in solubility and diffusivity of the penetrant[12]) and makes transport highly concentration dependent. Sorption phenomena and transport properties of water in polymeric materials are complex and their understanding is of major importance.

We recently demonstrated that a membrane based on sulfonated poly(ether ether ketone) (S-PEEK) shows excellent transport properties in terms of both permeability of water vapor and selectivity of water vapor over nitrogen.[1] However,

very little is known about the fundamental properties and kinetics of diffusion and solubility of water (vapor) in this polymer. In the present work, we analyze the kinetic sorption behavior of water vapor in polymeric films of the glassy polymer S-PEEK. It is known that the sorption of penetrant molecules in a glassy polymer can induce strong plasticization effects.[13–16] Next to Fickian diffusion on a short time scale, long time scale relaxations can be observed.[16] Equilibrium is not reached due to the glassy state of the polymer. Penetrant sorption induces a depression of the glass transition temperature of the polymer.[12,17] Such observations are extensively described for the sorption of carbon dioxide in glassy polymers, however very little systematic experiments are performed for water transport in such ionomeric materials.

## Theoretical background

### Water vapor sorption kinetics

Transport of gases and vapors in dense, glassy polymer membranes is determined by the solubility and diffusivity of these components in the polymer. According to this so called solution-diffusion mechanism, the solute first dissolves in the polymer and subsequently diffuses through the polymer along a concentration gradient.[4]

The sorption kinetics of highly sorbing gases and vapors (*e.g.* water vapor) into glassy polymers can be complex. During sorption, not only Fickian sorption behavior can occur, but next to that, additional mass uptake due to complex non Fickian relaxation phenomena may be observed.[16,18–21] Fickian transport behavior is a rapid, elastic and reversible process, whereas non Fickian transport involves relaxational motions on a much longer time scale. Hopfenberg and Berens[22] proposed that the overall non-Fickian sorption

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behavior of a penetrant in a polymer matrix ($M(t)_{\text{total}}$) can be considered as the sum of two different sorption regimes: a Fickian sorption regime ($M(t)_{\text{F}}$) and a relaxational regime ($M(t)_{\text{R}}$):

$$M(t)_{\text{total}} = M(t)_{\text{F}} + M(t)_{\text{R}} \quad (1)$$

Crank[23] showed that the mass uptake in time due to ideal Fickian sorption of a penetrant in a polymer matrix ($M(t)_{\text{F}}$) can be described as a function of the square root of time, assuming a constant diffusion coefficient:

$$\frac{M(t)}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left\{ -\frac{D(2m+1)^2\pi^2 t}{L^2} \right\} \quad (2)$$

where $M(t)$ [g] is the total amount of vapor absorbed by the polymer at time $t$ [s], $M_\infty$ [g] is the equilibrium sorption mass, $D$ is the diffusion coefficient [cm$^2$ s$^{-1}$] and $L$ is the polymer film thickness [cm]. The Fickian diffusion coefficient can thus be easily determined from a fit of this equation through the experimentally determined sorption data.

The relaxational contribution to non-Fickian sorption can be described as a series of relaxational regimes, of which each can be characterized by its specific relaxation time constant $\tau_{\text{R}}$. Because according to the Hopfenberg–Berens model, non Fickian diffusion can be considered as the sum of the occurrence of a Fickian sorption regime and relaxational regimes, eqn (3) can be derived to describe the overall sorption process:

$$\frac{M(t)}{M_\infty} = M_{F,\infty}\left[ 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \right] \exp\left\{ -\frac{D(2m+1)^2\pi^2 t}{L^2} \right\} + \sum_{i=1}^{\infty} M_{R_i}\left[ 1 - \exp\left\{ -\frac{t}{\tau_{R_i}} \right\} \right] \quad (3)$$

where $M_{F,\infty}$ [g] and $M_{R_i}$ [g] represent the infinite sorbed mass of the Fickian part and the relaxation part of sorption, respectively, and $\tau_{R_i}$ [s] is the characteristic time constant for relaxation.

The diffusion-relaxation model can only be used to determine the contribution of Fickian diffusion and that of relaxational diffusion, when the diffusion contribution and the relaxation contribution are very well separated, e.g. it requires the diffusion rate to be much higher than the rate of relaxation phenomena.

Relaxational contributions in glassy polymers can be considered to be independent of the dimensions of the polymer film. Diffusion phenomena on the other hand, depend on the square of the length of the diffusion pathway and thus the film thickness. The film thickness therefore determines to a large extent if a well defined diffusion and relaxation profile can be distinguished or if both phenomena overlap. To have a well-separated diffusion and relaxation regime, one desires the use of thinner films. Thinner films, however, have much lower time scales for diffusion, thus limiting an accurate determination of the diffusion coefficient because the rapid weight uptake can not be measured accurately. Proper choice of the film thickness is thus extremely important when analyzing diffusion and relaxation data.[16]

The Deborah number for diffusion $(\text{DEB})_D$ quantifies the ratio of the relative magnitude of the rates of diffusion and relaxation:[24]

$$(\text{DEB})_D = \frac{\tau_R D}{L_0^2} \quad (4)$$

In this equation, $\tau_{\text{R}}$ is the characteristic relaxation time and $L_0^2/D$ is the characteristic diffusion time ($L_0$ is the sample thickness (cm) and $D$ is the diffusion coefficient (cm$^2$/s)). If the Deborah number is $\gg 1$, the rate of diffusion is much faster than the rate of the relaxations, while for DEB = 1, the rates of diffusion and relaxation are equal, resulting in a superposition of the two processes. When the Deborah number is smaller than unity, the rate of relaxation is faster than that of diffusion.

Wessling et al.[25] used the proposed model to analyze the experimentally determined sorption-induced dilation kinetics of $CO_2$ in a polymer film and related the fast dilation kinetics to reversible Fickian relaxation, whereas the slower dilation kinetics could be related to irreversible relaxational phenomena. They proved that it is often sufficient to fit the data with the sum of the Fickian diffusion contribution and two additional relaxation contributions. Visser et al.[16] used this diffusion–relaxation model to quantify the separate contributions of diffusion and relaxation phenomena for different gasses in a glassy polyimide Matrimid film. The work demonstrated that any gas shows a Fickian and a relaxational contribution, and may thus induce relaxational changes into the polymer matrix upon reaching a critical amount of volume dilation.

During gas or vapor sorption, the molecular structure of the polymer film can change due to relaxational changes, and this may have an influence on the material properties as well.[26] An important material property in relation to vapor sorption and relaxational effects is the glass transition temperature ($T_{\text{g}}$), which characterizes the transition of a polymer from its glassy state to its rubbery state. The Fox equation can be used to calculate the theoretical effect of the presence of water vapor inside the polymer on its glass transition temperature:[27]

$$\frac{1}{T_{\text{g}}} = \frac{W_{\text{w}}}{T_{\text{g,w}}} + \frac{W_{\text{p}}}{T_{\text{g,p}}} \quad (5)$$

where $T_{\text{g}}$ [K] is the glass transition temperature of the water/polymer mixture, $T_{\text{g,w}}$ [K] and $T_{\text{g,p}}$ [K] are the glass transition temperatures of the water and the polymer, respectively, and $W_{\text{w}}$ [-] and $W_{\text{p}}$ [-] are the weight fractions of the water and the polymer, respectively. Francis et al.[27] showed that the theoretical values of the glass transition temperature calculated from the Fox equation are maximum 5% higher than the experimental values, making the Fox equation a valuable tool to estimate the glass transition temperature of a water swollen polymer.

## Experimental part

### Membrane preparation

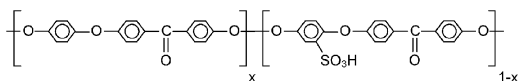S-PEEK (Fig. 1) was prepared by sulfonation of 60 g of PEEK, supplied by Victrex (USA), according to the procedure

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**Fig. 1** Chemical structure of sulfonated poly(ether ether ketone) (S-PEEK).

earlier described by Komkova *et al.*[28] The reaction was performed in 1 1 sulfuric acid (concentration 95–97%) at ambient temperature (25 °C) under continuous stirring. When the desired sulfonation degree was reached, the polymer was precipitated in ice water and washed until pH 6–7. After that, the polymer was dried under nitrogen atmosphere at 60 °C for 3 d. To remove residual water, the sulfonated polymer was further dried in a 30 °C vacuum oven until its mass was constant.

Membranes were cast on a glass plate from a 15 wt% solution of S-PEEK in *N*-methyl-2-pyrrolidon (NMP) supplied by Acros Organics, with a 0.47 mm casting knife. After evaporation of the NMP in nitrogen atmosphere, the film was removed from the glass plate by immersion in demineralized water. The film was washed in ultra pure water for 3 d and the washing water was refreshed twice a day. Subsequently the film was dried under nitrogen atmosphere at 60 °C for 4 d. Further drying was performed in a 30 °C vacuum oven until the mass of the film was constant (∼10 d). The final thickness of the obtained films was measured with a digital screw micrometer. For the sorption measurements, sulfonated PEEK with a sulfonation degree of 59 and 75% was used.

After this treatment, the films are considered to be dry. Nevertheless, this does not imply all water molecules are removed from the 'dry' sample. Complete removal of water would require treatment of the film under harsh conditions at temperatures at which degradation and cross linking occur. For this reason, the measured water vapor sorption data are the values obtained relative to the amount of water molecules still present in the 'dry' polymer. However, the amount of water molecules still present after drying is much smaller than the additional amount of water molecules due to water sorption. This, combined with the fact that the films are all treated in exactly the same way, allows us to draw conclusions from these sorption measurements without taking into account the presence of water molecules in the 'dry' film.

### Sorption experiments

Water vapor sorption experiments were carried out using a gravimetric sorption balance (SGA-CX Symmetrical gravimetric analyzer from VTI (USA) supplied by Ankersmid (The Netherlands)). The membrane sample (weight ∼3 mg, thickness ∼40 μm) was placed in the apparatus and flushed for 24 h with dry nitrogen to remove any residues. The final dry weight of the sample was measured. Subsequently a wet nitrogen stream (saturated with Milli-Q water ((18.2 MΩ cm at 25 °C)) was mixed with a dry nitrogen stream to obtain the desired water vapor activity. The water vapor activity in the gas stream is defined as the ratio of the water vapor pressure at a certain temperature and the maximum water vapor pressure at that temperature. It can be instantaneously changed by varying the mixing ratio of the dry and the wet nitrogen flow. The activity of the gas stream was varied from 0 to 0.9.

The humidified gas stream was fed into the thermostated measuring chamber and the actual activity in the sample chamber was measured and controlled with a dew point mirror. The total gas flow velocity was kept constant to avoid any upward drag force on the sample. The weight of the sample in time was monitored continuously. Sorption and desorption experiments were carried out at 20 °C and the sorption and desorption isotherms were constructed from a stepwise or interval increase or decrease of the water vapor activity.[29] The concentration of water vapor inside the polymer film [cm³ STP cm⁻³ polymer] was calculated from the equilibrium mass uptake of the sample at a certain water vapor activity using eqn (6):

$$c = \frac{(M_\infty - M_{\text{polymer,dry}})V_{\text{H}_2\text{O}}}{V_{\text{polymer,dry}}M_{\text{w,H}_2\text{O}}} \quad (6)$$

where $M_\infty$ [g] is the equilibrium mass of the polymer sample and the absorbed water at a certain water vapor activity, $M_{\text{polymer,dry}}$ [g] is the dry weight of the polymer, $V_{\text{H}_2\text{O}}$ [22 414 cm³] is the volume of 1 mol $H_2O$ at standard temperature [273.15 K] and standard pressure [1.013 bar], $V_{\text{polymer,dry}}$ [cm³] is the volume of the dry polymer and $V_{\text{H}_2\text{O}}$ [18 g mol⁻¹] is the molecular weight of water.

The sorption data were analyzed using the Hopfenberg–Berens model as described earlier, to distinguish between Fickian sorption and non-ideal relaxation phenomena. Calculations and fitting of the experimental data to the theoretical model were performed using graphing and data analysis software from Originlabs (Origin Pro 7.5).

Not only the sorption of water vapor was investigated, but also the swelling of the polymer sample in liquid water ($a = 1$) was taken into account. Polymer samples (5 × 5 cm) with a thickness of approximately 200 μm were cut from pre-washed membrane films (films were washed for 3 d in ultra pure water by changing the washing water twice a day), and subsequently dried until equilibrium weight was reached. The size and weight of the sample was chosen this high, to be able to perform accurate swelling measurements. The amount of liquid water absorbed in the polymer sample was determined in time by immersing the membrane sample in Milli-Q water (18.2 MΩ cm at 25 °C) and measuring its weight in time. During each measurement, the sample was removed from the water, carefully dried between tissue paper and the mass of the swollen sample was determined. All experiments were repeated 3 times. The swelling degree (SwD [%]) of the polymer film in liquid water at each time was determined according to eqn (7):

$$\text{SwD} = \left(\frac{M_\infty - M_{\text{polymer,dry}}}{M_{\text{polymer,dry}}}\right) \times 100\% \quad (7)$$

Where $M_\infty$ [g] is the equilibrium mass of the polymer sample and the absorbed water and $M_{\text{polymer,dry}}$ [g] is the dry weight of the polymer.

## Results and discussion

### Sorption isotherms

From the equilibrium mass uptake of water vapor at different water vapor activities, the sorption isotherms of water vapor
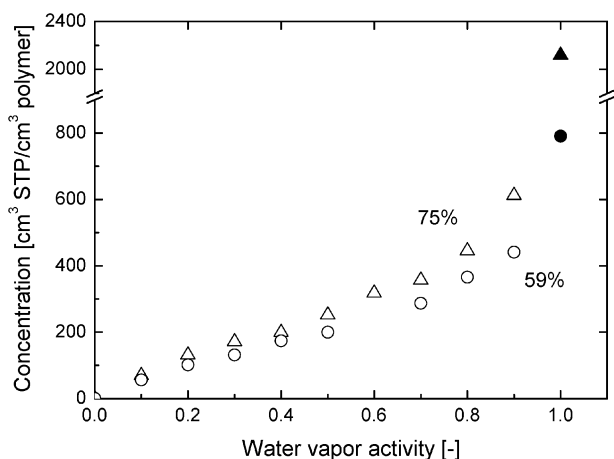
Fig. 2 Water (vapor) sorption isotherms for S-PEEK with a sulfonation degree of 59 and 75% at 20 °C [open symbols represent sorption from water vapor, filled symbols represent swelling in liquid water].

in S-PEEK can be constructed. Analysis of these sorption isotherms using the Hopfenberg–Berens model allows quantifying the separate contributions of Fickian diffusion and relaxation phenomena. In addition, these isotherms can be used to calculate the tendency of water vapor molecules to form clusters in the polymer matrix and to calculate the theoretical glass transition temperature of the water vapor/polymer mixture.

The sorption isotherm at 20 °C for water vapor and liquid water ($a = 1.0$) in S-PEEK films with two different sulfonation degrees (59 and 75%) is shown in Fig. 2. The $X$-axis reports the water vapor activity ($a = 1.0 -$ liquid water), whereas the $Y$-axis represents the corresponding water concentration in cm$^3$ absorbed water (vapor) at standard temperature and pressure per cm$^3$ of dry polymer (cm$^3$ STP (cm$^3$ polymer)$^{-1}$).

The water vapor concentration in the polymer films increases with increasing water vapor activity as shown in Fig. 2. The sorption isotherms show a concave increase for water vapor activities $a < 0.5$ (often described by the simple Dual Mode sorption model[30,31] or the more extended energy site distribution model[32,33]). For activities $a > 0.5$, the sorption isotherm has an inflection point turning to convex
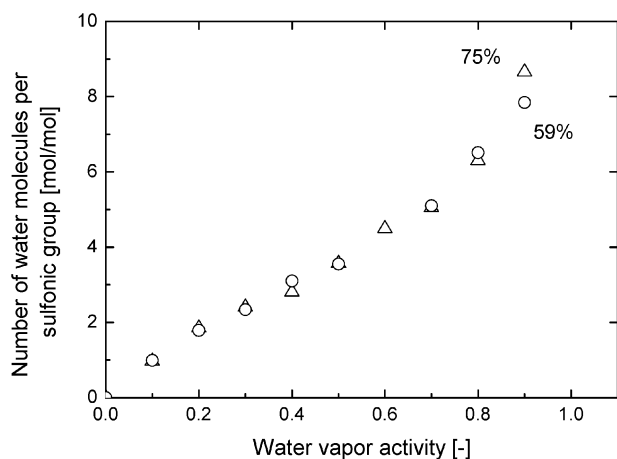
with an exponential increase, which is often described by the Flory-Huggins model. The amount of liquid water absorbed in the polymer follows the exponential increase as predicted by the Flory-Huggins description. Especially at higher water vapor activities the degree of sulfonation has an effect on the solubility of water in the polymer, with the higher sulfonation degree leading to higher water vapor concentrations. The reason for this is the higher concentration of hydrophilic sulfon groups attached to the polymer backbone at higher sulfonation degrees. Nevertheless, the number of water molecules per sulfonic acid group is nearly comparable for both sulfonation degrees and increases with increasing water vapor activity (Fig. 3).

Fig. 4 compares the sorption and desorption isotherms for both sulfonation degrees (59 and 75%). The open symbols represent the sorption run and the filled symbols represent the desorption run, respectively.

Desorption values are higher for both sulfonation degrees. Berens et al.[34] and Wessling et al.[35] interpret this hysteresis as the induction of new free volume sites and subsequent filling of





Fig. 3 Number of water molecules per sulfonic acid group for S-PEEK with a sulfonation degree of 59 and 75% at 20 °C.
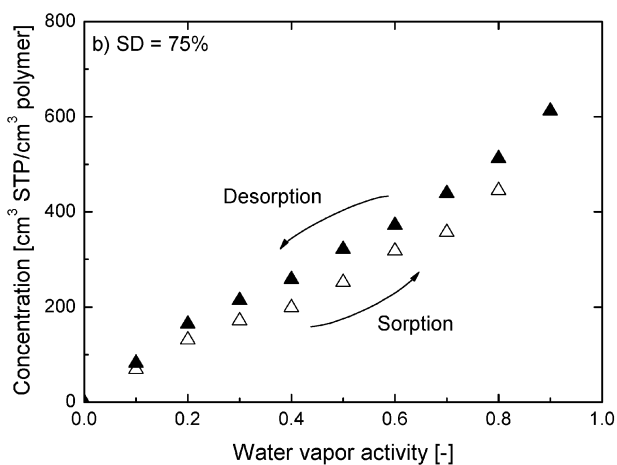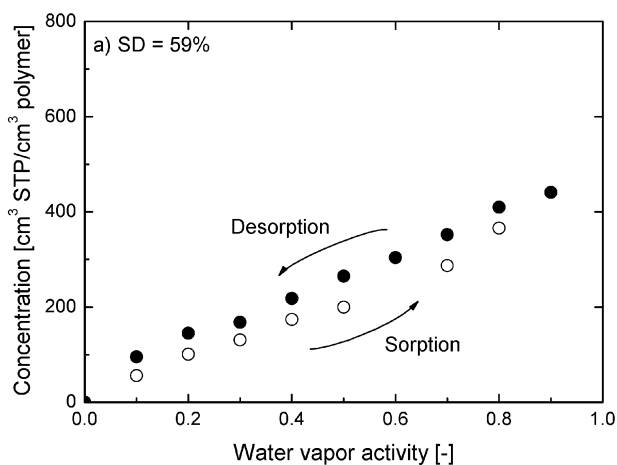


Fig. 4 Sorption–desorption isotherms for S-PEEK with a sulfonation degree of (a) 59% and (b) 75% at 20 °C. Open symbols represent sorption runs and filled symbols represent desorption runs.

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the extra free volume during the sorption cycle. Desorption of the penetrant however, occurs more rapidly than the collapse of the free volume, thus a higher amount of free volume is available in the desorption runs, resulting in higher water vapor concentration during desorption.[26,34,35]

## Kinetic sorption behavior

Fig. 5 shows typical plots of the normalized water vapor uptake $[M_t/M_\infty]$ versus the logarithm of time for a sorption and desorption run of water vapor in S-PEEK with a sulfonation degree of 75% for water vapor activities of (a) 0–0.1 (b) 0.1–0.2 (c) 0.5–0.6, and (d) 0.7–0.8.

Fig. 5 proofs the presence of the different contributions of Fickian sorption and relaxational phenomena at different water vapor activities. Water vapor sorption at low activities (Fig. 5a) shows typical Fickian sorption behavior of water vapor in the polymer. Fickian diffusion is usually accompanied by an increase in relative mass uptake in time, followed by a leveling off of this mass uptake to a constant value at longer time scales (in this case at approximately $\log(t) = 2 \times 10^4$). This is clearly visible in Fig. 5a, both for sorption and desorption. Fig. 5b indicates the onset of the relaxational sorption kinetics. While for sorption Fickian behavior still prevails, desorption shows already non-Fickian contributions to the overall sorption value as a result of relaxational phenomena. The difference between the behavior of the polymer film during sorption and desorption is due to hysteresis, which results in higher water vapor concentrations in the polymer during desorption at the same activity. In the case of relaxational phenomena, the leveling off of the relative mass uptake to a constant value is overlapped and followed by an additional, continuous increase of the relative mass uptake, without leveling off at longer time scales. This additional mass uptake after the initial mass uptake is due to relaxation phenomena. Water vapor sorption/desorption at higher water vapor activities (Fig. 5c and d) thus shows a significant

contribution of both Fickian sorption and relaxational phenomena, both for sorption and desorption.

The Hopfenberg–Berens model described earlier can be used to fit the sorption and desorption data presented in Fig. 5 and allows the extraction of the Fickian diffusion coefficient from the experimental results. Fig. 6 presents this Fickian diffusion coefficient of water vapor in S-PEEK with a sulfonation degree of 59 and 75% for (a) sorption and (b) desorption.

The Fickian diffusion coefficient increases for both sulfonation degrees with increasing water vapor concentration, but levels off to a plateau value at a certain concentration. The plateau is clearly visible for the high degree of sulfonation, and starts to occur for the lower sulfonation degree. The diffusion coefficients from desorption runs almost coincide for different sulfonation degrees, whereas the Fickian diffusion coefficient for sorption runs differs slightly with increasing sulfonation degree. This is in good agreement with the work of Piroux et al. who report diffusion coefficients for water vapor in sulfonated copolyimides.[11] As discussed earlier, the sorption isotherms show two different sorption mechanisms, Dual Mode sorption for lower water vapor activities ($a < 0.5$) and Flory Huggins sorption for higher water vapor activities
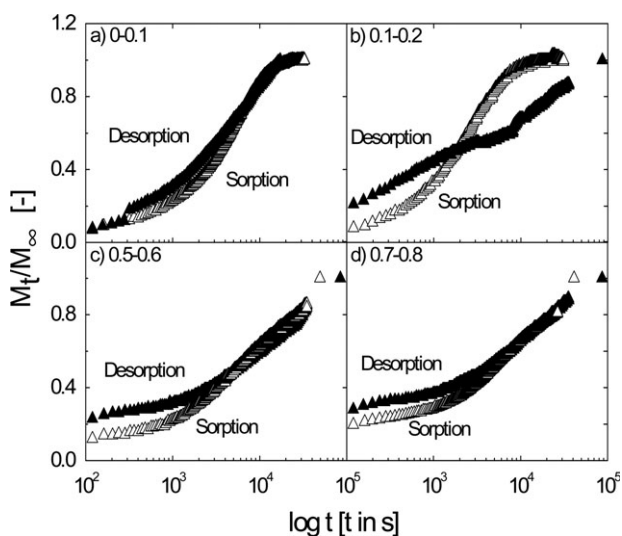


Fig. 5 Typical water vapor sorption/desorption runs in S-PEEK with a sulfonation degree of 75% for water vapor activities of (a) 0–0.1, (b) 0.1–0.2, (c) 0.5–0.6, and (d) 0.7–0.8 The actual mass uptake is normalized for the final equilibrium mass gain of the sample.
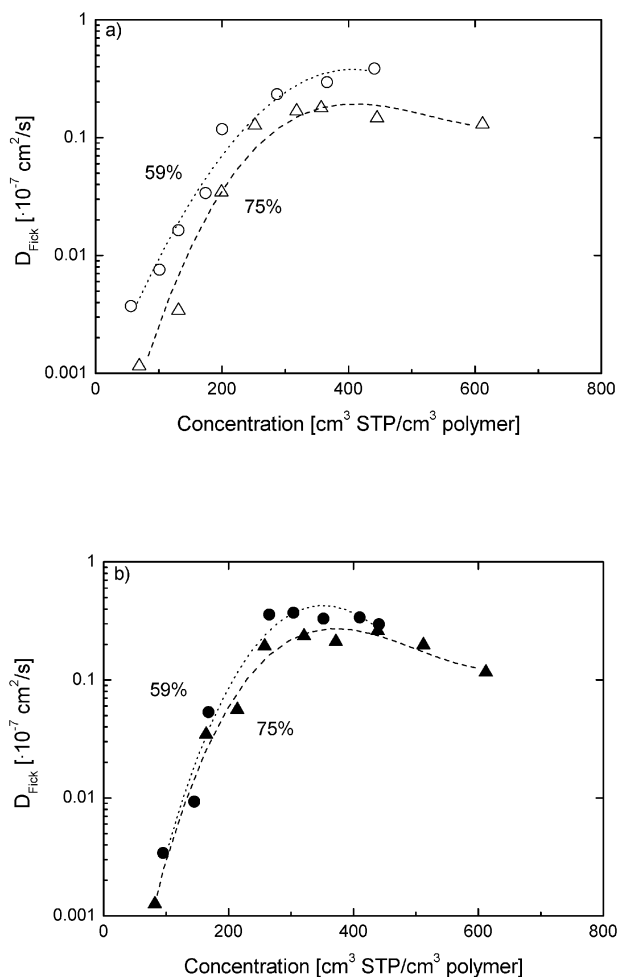


Fig. 6 Calculated Fickian diffusion coefficient of water vapor in S-PEEK with a sulfonation degree of 59 and 75% at 20 °C for (a) sorption and (b) desorption.

($a > 0.5$). According to Yampolskii *et al.*,[36] an increase in diffusion coefficient with increasing water vapor concentration can be expected for both Dual Mode and Flory Huggins sorption behavior. This increase in diffusion coefficient can indeed be observed at lower water vapor concentrations ($c$ approximately $< \sim 200$ cm$^3$ STP (cm$^3$ polymer)$^{-1}$). Flory Huggins sorption behavior is usually also accompanied by an increase in diffusion coefficient with an increase in penetrant concentration, but clustering phenomena can lead to reduced diffusion coefficients at higher water vapor activities.[36] The appendix shows that clustering phenomena do not occur in this system.

The thickness of the polymer films used for water vapor sorption analysis is a critical parameter and proper choice of the films thickness is crucial to allow accurate determination of both contributions. To be able to discriminate well between Fickian diffusion and relaxational phenomena, one would desire thinner films. A measure for the ability to discriminate between these two phenomena is the Deborah number $(DEB)_D$. In all our experiments and with the film thickness chosen, this Deborah number was greater than unity (we will come back later to the absolute values of the Deborah number). This shows that Fickian diffusion and relaxation are well separated and in principle allows the extraction of the Fickian diffusion coefficient from the data. Nevertheless we observe an unexpected leveling off in the Fickian diffusion coefficient at high concentrations (Fig. 6). We think this stems from an inaccuracy in the measurements at high water concentrations. In thinner films the time scale for diffusion is relatively low, limiting the accurate determination of the value of the Fickian diffusion coefficient, because the extremely rapid weight uptake cannot be measured accurately. We think this explains the leveling off in Fickian diffusion coefficient at high water concentrations. This idea is supported by our results from liquid water swelling measurements with thicker films, as will be shown later.

Fig. 7 shows the relative contribution of Fickian equilibrium sorption ($m_F$) and relaxation equilibrium sorption ($m_{R1} + m_{R2}$) as calculated with the Hopfenberg–Berens model as a function of the water vapor concentration inside the polymer for the sorption run in S-PEEK with a sulfonation degree of 59 and 75%. The total fraction of Fickian diffusion and relaxational sorption at equilibrium is set to 1. The Hopfenberg–Berens model only allows the quantification of Fickian diffusion and relaxation phenomena when the diffusion contribution and the relaxation contribution are very well separated, *e.g.* it requires the diffusion rate to be much higher than the rate of relaxation phenomena.[16] The same accounts for the difference between fast relaxational sorption ($m_{R1}$) and slow relaxational sorption ($m_{R2}$): differences can only be observed when both relaxations are very well separated. In the present work fast and slower relaxations overlap and a clear distinction between both is not visible. Fig. 7 therefore shows the relative contribution of Fickian diffusion and the combined fractional contribution of both fast and slow relaxations.

For water vapor sorption in S-PEEK with a sulfonation degree of 59 and 75%, the occurrence of solely Fickian sorption can only be observed at low water vapor concentrations ($c < \sim 100$ cm$^3$ STP (cm$^3$ polymer)$^{-1}$). The relative
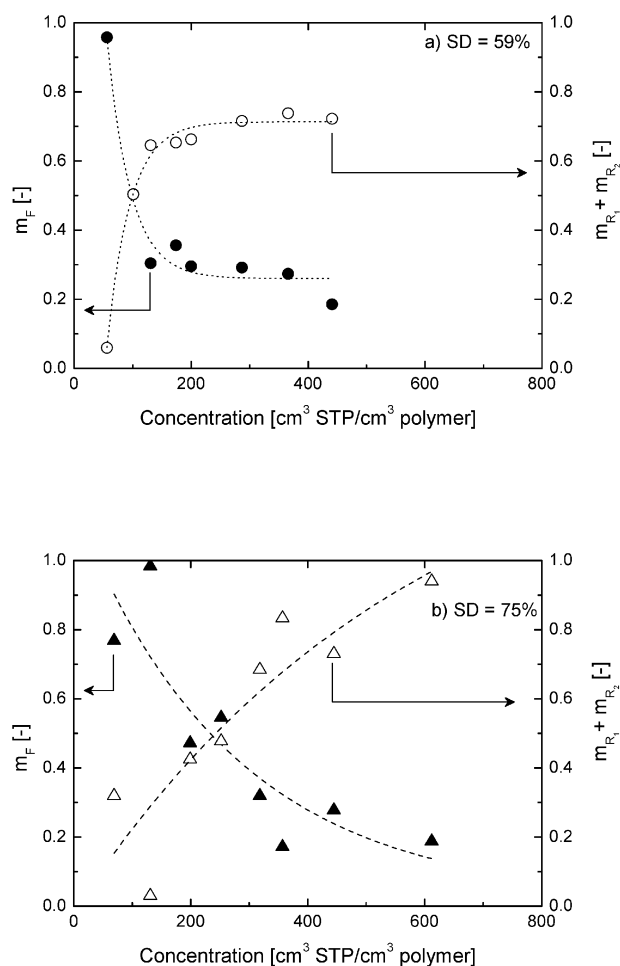


**Fig. 7** Relative contribution of Fickian equilibrium sorption ($m_{F,\infty}$) and relaxation phenomena ($m_{R1} + m_{R2}$) calculated from sorption isotherms for S-PEEK with a sulfonation degree of (a) 59% and (b) 75%. All measurements performed at 20 °C.

contribution of Fickian equilibrium sorption is close to one below this concentration. Above $\sim 100$ cm$^3$ STP (cm$^3$ polymer)$^{-1}$, the kinetic sorption behavior becomes non-Fickian due to the onset of relaxations, as indicated by an increase in the fractional contribution of relaxations ($m_{R1} + m_{R2}$) and a decrease in the contribution of Fickian diffusion ($m_F$) with increasing water vapor activity. The Hopfenberg–Berens model allows to quantify the relative contribution of Fickian equilibrium sorption and relaxational equilibrium sorption, and the results show that already very early in the sorption process ($\sim$ above 100 cm$^3$ STP (cm$^3$ polymer)$^{-1}$ for both sulfonation degrees) relaxational changes appear.

Frequently, data analysis is performed without taking the relaxational contribution into account.[10] This has significant consequences for the interpretation of the dynamic sorption data. The initial concentration dependent increase of the Fickian diffusion coefficient would still be visible; however the slower relaxation weight uptake occurring during sorption runs at higher activities would fall together with faster Fickian weight uptake. This fusion of two distinctly different mechanisms would be falsely interpreted as slowing down of the Fickian diffusion. Such an apparent leveling off is then in turn

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interpreted to be related to a clustering of the water penetrant molecules. The appendix shows that clustering does not occur in this system.

Fig. 8 shows the contribution of Fickian equilibrium sorption ($m_F$) and relaxation equilibrium sorption ($m_{R1} + m_{R2}$) depending on the water vapor concentration inside the polymer as calculated from desorption data in S-PEEK with a sulfonation degree of 59 and 75%.

Fig. 8 shows the same trends for desorption, as observed for sorption runs. The occurrence of solely Fickian sorption can only be observed at low water vapor concentrations ($c < \sim 100$ cm$^3$ STP (cm$^3$ polymer)$^{-1}$) where the relative contribution of Fickian diffusion is close to unity. With increasing water concentration, the relative contribution of Fickian diffusion decreases, whereas that of relaxational contributions increases. For water vapor concentrations above $\sim 400$ cm$^3$ STP (cm$^3$ polymer)$^{-1}$, the contribution of Fickian sorption equilibrium ($m_F$) increases again, whereas the relative contribution of relaxation sorption equilibrium ($m_{R1} + m_{R2}$) decreases again. This minimum for the Fickian contribution and the maximum for the relaxational contribution are unexpected. This effect might be related to a change in glass
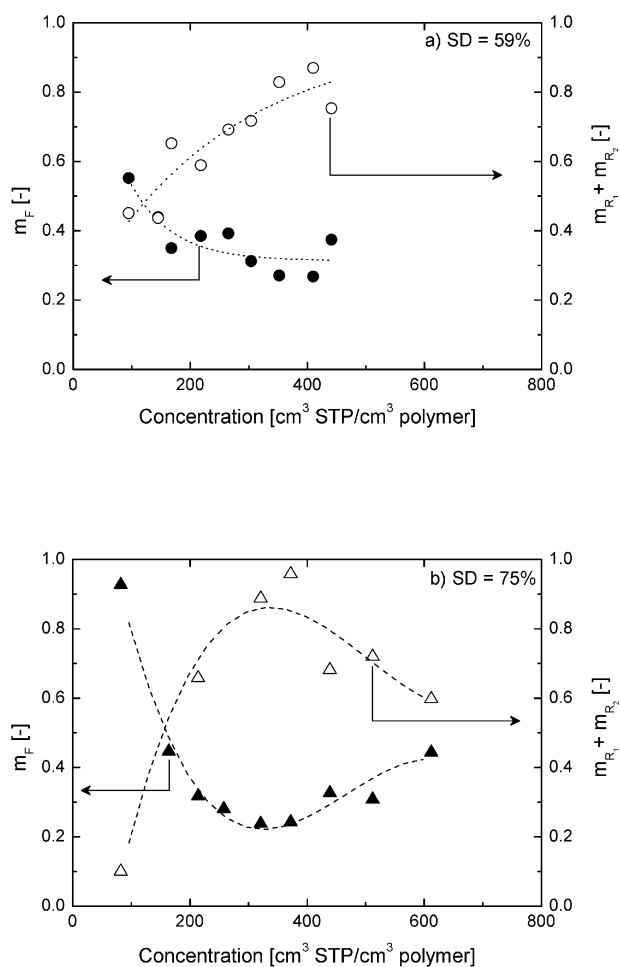


**Fig. 8** Contribution of Fickian equilibrium sorption ($m_F$) and relaxation equilibrium sorption ($m_{R1} + m_{R2}$) at desorption runs for S-PEEK with a sulfonation degree of (a) 59% and (b) 75%. All measurements performed at 20 °C.

transition temperature with increasing water concentration in the polymer and the subsequent transition of the polymer from the glassy state to the rubbery, fully relaxed state at high water vapor concentrations during desorption (during sorption, the polymer mixture does not reach the rubbery, fully relaxed state, as will be shown below). Furthermore, at these high water vapor activities, the build up of the diffusion profile is too fast to allow accurate determination of the Fickian diffusion coefficient.

### Glass transition temperature

The behavior of the polymers during sorption and desorption runs already indicated a change in polymer network structure during water vapor uptake due to slow relaxations. The glass transition temperature is another measure to describe the state of a polymer. The glass transition temperature characterizes the transition of the polymer from the glassy state where both Fickian diffusion and relaxational changes may occur during sorption, to the rubbery state where only Fickian sorption kinetics play a role and the relaxation contribution is considered to be zero because the polymer is in its fully relaxed state. Penetrant sorption reduces the glass transition temperature and the Fox equation is a useful tool to calculate the theoretical glass transition temperature of a polymer at different water concentrations inside that polymer.[27] Fig. 9 shows this theoretical glass transition temperature ($T_g$) as a function of the water concentration inside the polymer.

The calculated values for the glass transition temperature of the polymer at different concentrations of water inside the polymer for different degrees of sulfonation perfectly coincide. A decrease in glass transition temperature with increasing water concentration is clearly visible. The calculated glass transition temperature of the water vapor swollen material almost reaches the experimental temperature of 20 °C, indicating a region close to the transition from a glassy state to a rubbery state. The glass transition temperature calculated
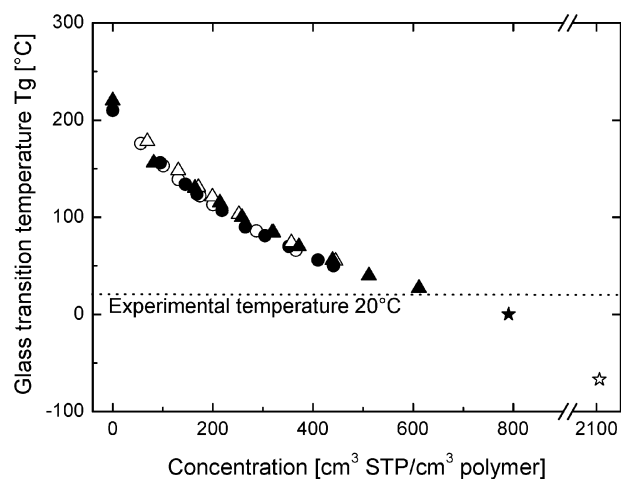


**Fig. 9** Calculated glass transition temperature as a function of the water concentration in S-PEEK with a sulfonation degree of 59% (circles) and 75% (triangles) for sorption (open symbols) and desorption (filled symbols) at 20 °C. The values for sorption in liquid water for S-PEEK with a sulfonation degree of 59% (filled stars) and 75% (open stars) are also presented.

from the swelling experiments in liquid water drops even below the measurement temperature, predicting rubbery behavior in this case.

Fig. 10 shows the relative contribution of relaxational phenomena ($m_{R1} + m_{R2}$) as a function of the measurement temperature (20 °C) minus the calculated glass transition temperature of the polymer at each water vapor concentration during sorption and desorption for both sulfonation degrees.

The contribution of relaxation phenomena ($m_{R1} + m_{R2}$) during sorption and desorption increases when the calculated glass transition temperature of the swollen polymer approaches the experimental measurement temperature (20 °C) for both sulfonation degrees. The contribution of relaxation shows an increasing trend with decreasing difference between the calculated glass transition temperature and the experimental temperature in both polymers. Based on the work of Kamiya et al.,[26] Wessling et al.[25] and Visser and Wessling,[16]



we hypothesize the occurrence of solely Fickian behavior when the glass transition temperature of the polymer/water sample drops below the actual experimental temperature and the system reaches its rubbery and fully relaxed state. To prove this hypothesis, one would need to perform kinetic sorption measurements at higher experimental temperatures or more sorption experiments above $a > 0.9$ with very small step-wise increases in activity. However, such measurements are experimentally intricate and a challenge for future research.

## Swelling in liquid water

Fig. 11 shows the increase in water concentration inside the polymer during swelling experiments in liquid water.

The concentration of water in the polymer initially increases rapidly in time and finally levels off to its equilibrium value. The equilibrium swelling degree (SwD) of S-PEEK with a sulfonation degree of 59% is 44% and a value of 116% is obtained for S-PEEK with a sulfonation degree of 75%. This difference in swelling degree for the two materials is due to the higher concentration of hydrophilic sulfon groups present in the highly sulfonated material.

As mentioned earlier, the film thickness plays a crucial role in the determination of the Fickian diffusion coefficient and the relaxation phenomena. The Deborah number quantifies the ratio of the rate of Fickian diffusion and that of relaxation. Values larger than unity indicate that diffusion and relaxation are well separated, thus allowing the application of the Hopfenberg–Berens model and the extraction of the Fickian diffusion coefficient from the sorption data, as presented in the present work. Table 1 shows the calculated Deborah numbers for all our experiments. It shows that in all cases, also for swelling in liquid water, the Deborah number was indeed (significantly) larger than unity. Nevertheless, we observed an unexpected leveling off in the Fickian diffusion coefficient at high concentrations, and attributed this to the very fast build-up of the diffusion profile at high concentrations for these thin film thicknesses. The determination of the sorption kinetics in liquid water, however, requires the use of much
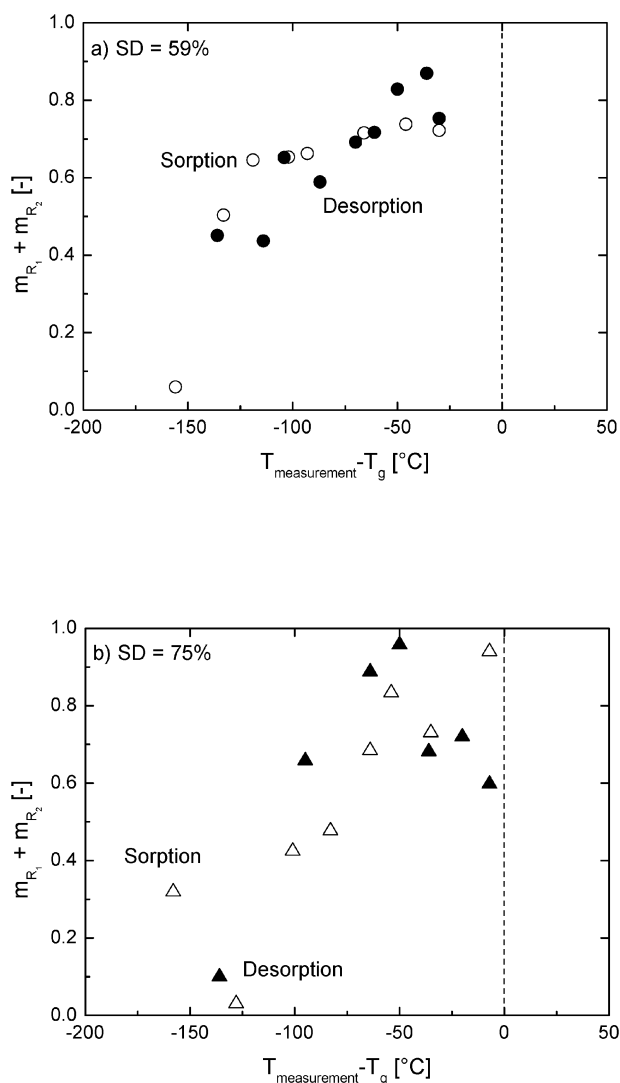


**Fig. 10** Relative contribution of relaxation phenomena ($m_{R1} + m_{R2}$) for S-PEEK with a sulfonation degree of (a) 59% and (b) 75% as a function of the difference between the measurement temperature and the calculated glass transition temperature for sorption (open symbols) and desorption (closed symbols).
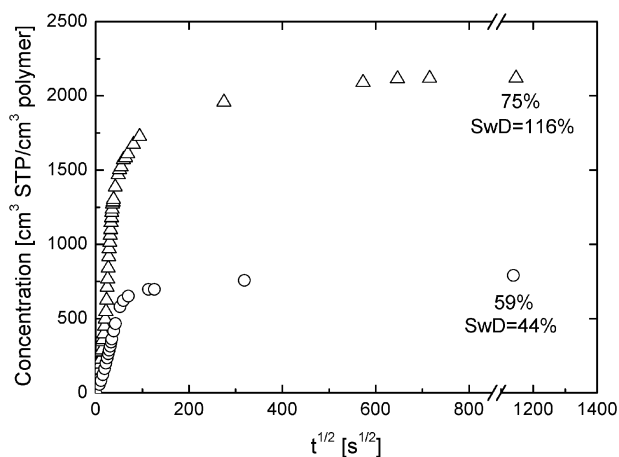
**Fig. 11** Concentration of water inside S-PEEK with a sulfonation degree of 59 and 75% in liquid water as a function of the square root of time ($T = 20$ °C).

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**Table 1** Deborah number to quantify the relative contribution of the rate of Fickian diffusion and relaxational phenomena for water sorption in S-PEEK with a sulfonation degree of 59 and 75% at 20 °C (all values are calculated from water vapor sorption data, except the last row which is marked with * and calculated from the sorption data in liquid water)

| Sulfonation degree 59% | | Sulfonation degree 75% | |
| --- | --- | --- | --- |
| Water vapor concentration cm$^3$ (STP) (cm$^3$ polymer)$^{-1}$ | $(DEB)_D$ — | Water vapor concentration cm$^3$ (STP) (cm$^3$ polymer)$^{-1}$ | $(DEB)_D$ — |
| 101 | 1.64 | 199 | 4.7 |
| 174 | 1.83 | 252 | 21.9 |
| 200 | 10.38 | 318 | 16.0 |
| 287 | 29.65 | 357 | 52.8 |
| 366 | 42.50 | 445 | 15.1 |
| 441 | 15.26 | 612 | 30.9 |
| 791* | 6.22* | 2113* | 8.3* |

thicker films, to allow an accurate determination of the weight uptake and corresponding diffusion coefficient. By doing so, we were able to accurately determine the Fickian diffusion coefficient in liquid water at sufficiently high Deborah numbers. Because of the increased film thickness, the Deborah number of course decreased relative to the measurements with thinner films. The use of thicker films over the whole activity range investigated would not be possible, because in that case the Deborah number would drop below unity at lower activities.

Fig. 12 compares the Fickian diffusion coefficient extracted from water vapor sorption experiments at different water concentrations in the polymer (Fig. 6) and these obtained form liquid water sorption kinetics (Fig. 11), both calculated with the Hopfenberg–Berens model[22] for the two sulfonation degrees investigated.

Below a water vapor concentration of ∼300 cm$^3$ STP (cm$^3$ polymer)$^{-1}$ the Fickian diffusion coefficient increases with increasing water vapor concentration. Above a water vapor concentration of ∼300 cm$^3$ STP (cm$^3$ polymer)$^{-1}$ a plateau can be distinguished in which the Fickian diffusion
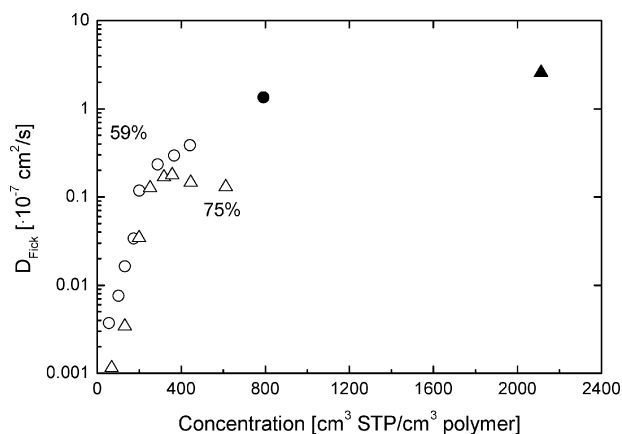


**Fig. 12** Fickian diffusion coefficient as determined from either water vapor or liquid water sorption experiments in S-PEEK with a sulfonation degree of 59 (○) and 75% (△) at 20 °C (open symbols: water vapor sorption; filled symbols: liquid water sorption).

coefficient as determined form water vapor measurements, seems to be more or less independent of the water vapor concentration in the polymer. Due to the use of relatively thick films for the liquid water swelling experiments (filled symbols in Fig. 12), distinct separation of diffusion and relaxation phenomena and an accurate determination of the Fickian diffusion coefficient are possible again from liquid water swelling kinetics.[16] Based on the water vapor sorption kinetics only, the Fickian diffusion coefficient increases over two orders of magnitude with increasing water vapor concentration. Taking also the diffusion kinetics from liquid water sorption experiments into account, reveals a change of even three orders of magnitude of the Fickian diffusion coefficient when the water concentration in the polymer increases.

## Conclusions

This paper presents an analysis of the sorption kinetics of water vapor and liquid water in the glassy polymer sulfonated poly(ether ether ketone) (S-PEEK). Sorption isotherms are determined experimentally using a gravimetric sorption balance and the relative contributions of Fickian diffusion and relaxational phenomena are quantified as a function of the water concentration in the polymer using the model of Hopfenberg and Berens.

The sorption isotherms show Dual Mode sorption behavior for lower water vapor activities ($a < 0.5$) and Flory Huggins type of sorption for higher water vapor activities ($a > 0.5$). Hysteresis between sorption and desorption runs is observed. The hydrophilic nature of the material, especially for higher degrees of sulfonation, results in high water vapor sorption values and high liquid water swelling degrees.

Analysis of the sorption isotherms and determination of the sorption kinetics proof the occurrence of both Fickian sorption behavior and relaxational phenomena already at very low water concentrations in the polymer. With increasing water concentration, the relative importance of relaxation phenomena increases, whereas the relative contribution of Fickian diffusion decreases.

Based on the water vapor sorption kinetics only, the Fickian diffusion coefficient increases over two orders of magnitude with increasing water vapor concentration. Taking also the diffusion kinetics from liquid water sorption experiments into account, reveals a change of even three orders of magnitude of the Fickian diffusion coefficient when the water concentration in the polymer increases.

## Appendix: Clustering analysis of sorption isotherms

In addition to relaxation, other phenomena e.g. clustering of water molecules in the polymer matrix may occur, which can influence the sorption behavior and diffusion kinetics of water vapor in polymers. Solvent molecules like water potentially tend to cluster when absorbed in a polymer. This effect has been attributed to self-hydrogen bonding of water molecules.[37] Water clusters can influence the diffusion of water vapor through the polymer by hindering the diffusion of other water molecules, and thus elongating the diffusion pathway of water vapor molecules.

To provide a measure for clustering, Zimm and Lundberg defined the clustering function:[37]

$$\frac{G_{\text{ww}}}{V_{\text{w}}} = -\Phi_{\text{p}}[\partial(a/\Phi_{\text{w}})/\partial a] - 1 \qquad (8)$$

with $a$ being the vapor activity ($p_{\text{H}_2\text{O}}/p_{\text{H}_2\text{O,saturated}}$ [-]) and $\Phi_{\text{p}}$ and $\Phi_{\text{w}}$ the polymer and water volume fractions [-] determined from the equilibrium mass at sorption runs. $V_{\text{w}}$ is the molar volume of the water vapor penetrant [cm$^3$ mol$^{-1}$] and $G_{\text{ww}}$ is the cluster integral. The quantity $G_{\text{ww}}/V_{\text{w}}$ is a measure for the tendency of solvent molecules to cluster inside the polymer. When $G_{\text{ww}}/V_{\text{w}} = -1$, the solution is ideal: water vapor molecules do not experience any effect of the other water molecules present and have no effect on their distribution. When $G_{\text{ww}}/V_{\text{w}} = 0$, the excluding effect of the central water molecule is just sufficient, whereas when $G_{\text{ww}}/V_{\text{w}} > 0$, the water molecules touch each other and form a cluster. When $G_{\text{ww}}/V_{\text{w}} < -1$, the water molecules prefer to remain isolated.

Water vapor clustering phenomena inside polymer matrices are reported in literature.[10,11,38–41] Detallante et al.[10] report the water vapor sorption in naphthalenic sulfonated polyimide. The diffusion coefficient calculated via Ficks law of diffusion seems to pass a maximum with increasing water vapor concentration. The authors attribute this to water clusters formed in the polymer during water vapor sorption. Nonetheless, the authors did not perform a cluster analysis.

From the sorption isotherms as presented in this work and eqn (8), the cluster integral (or the tendency of water molecules to form clusters in the polymer) can be calculated (Fig. 13).

When the cluster integral $G_{\text{ww}}/V_{\text{w}} > 0$, the water molecules tend to form clusters in the polymer. Fig. 13 clearly shows that water molecules do not tend to cluster in the S-PEEK films investigated. The results show that the water molecules in the sulfonated PEEK films investigated remain isolated at almost all water vapor concentrations, and that cluster formation does not influence the sorption kinetics of water vapor molecules in the S-PEEK films investigated in this work.
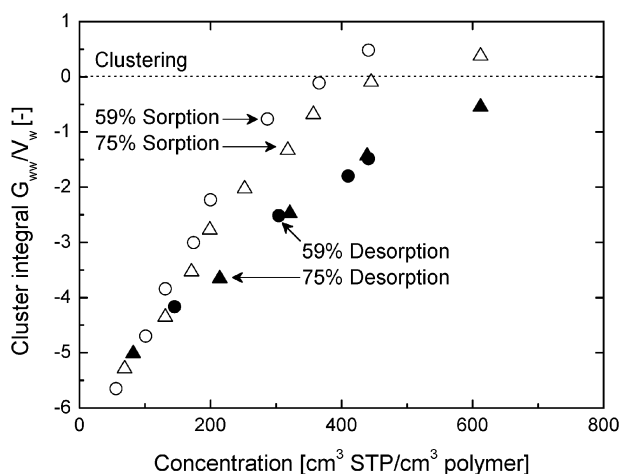
The cluster integral increases with increasing water vapor concentration and the values for sorption and desorption at low water vapor concentrations (c approximately < 200 cm$^3$ STP (cm$^3$ polymer)$^{-1}$) are comparable. At higher water vapor concentrations, the values obtained from desorption runs are lower than the ones from sorption runs. This is most probably due to the higher amount of free volume accessible in desorption runs.[34]

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**Fig. 13** Cluster integral as a function of the water vapor concentration in the polymer during sorption (open symbols) and desorption (filled symbols) at 20 °C for S-PEEK with a sulfonation degree of 59 and 75%.

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