When Do Sorption-Induced Relaxations in Glassy Polymers Set In?

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ABSTRACT: This study presents the kinetic sorption behavior of six different gases (CO_2, C_3H_8, C_3H_6, Xe, Kr, and Ar) in films of the glassy polyimide Matrimid using a magnetic suspension balance. The dynamic mass uptake was analyzed using a model discriminating and quantifying separate contributions of Fickian diffusion and relaxations. The model provides a quantitative insight into the pressure/concentration-dependent onsets and relative magnitudes of sorption-induced relaxations. We demonstrate that any gas—even noble gases—show non-Fickian diffusion and may induce irreversible sorption relaxations upon reaching a critical amount of volume dilation. Above this critical amount of volume dilation, kinetic sorption behavior becomes non-Fickian. For all gases studied, this critical volume dilation is unique.

1. Introduction

In membrane-based gas separation, the membrane separation performance is often deteriorated due to plasticization of the polymer matrix by highly sorbing penetrant molecules.[1−3] These penetrants cause an increase of the molecular motion of the stiff polymer backbone, resulting in enhanced transport rates of all components diffusing, but in particular an enhanced diffusion of the slower component. This is undesired since it results in a loss of diffusion selectivity. Today, fundamental understanding of sorption-induced plasticization is at its infant state.

Next to permeation studies, sorption kinetics studies are used to experimentally assess more details of plasticization. During sorption kinetics of highly sorbing gases into glassy polymers complex nonideal Fickian transport behavior occurs. Non-Fickian transport behavior can be observed as additional mass uptake in vapor sorption experiments or as excessive volume changes in dilation experiments with glassy polymers.[4−8] Fickian transport corresponds to a rapid, elastic, and reversible volume increase upon penetrant insertion into the polymer network. Relaxational non-Fickian transport occurs when slow relaxational motions of the polymer occur next to the rapid reversible molecular motions. Plasticization and relaxational or non-Fickian sorption kinetics are assumed to be related since also permeation rates slowly increase in time above a certain plasticization threshold pressure.[9] The fundamental understanding of gas sorption-induced relaxational non-Fickian mass uptake is a prerequisite to understand plasticization.

The solubility of a gas in a polymer mainly depends on its relative ease to condense, the free volume distribution of the polymer, and the molecular interactions of the polymer with the polymer matrix (e.g., polar groups). Frequently, it is believed that gases having a high solubility coefficient induce plasticization effects in polymers. Bos et al.[3] refined this view and suggest that not the solubility coefficient but the actual concentration is important to induce plasticization. For a variety of different polymers, a critical gas concentration appeared to exist above which plasticization can be identified in permeation experiments.[3] Others found contradicting results for a different series of polyimides as much higher CO_2 concentrations than the one observed by Bos were required to induce plasticization effects.[10] Rather than a critical threshold concentration, the authors suggest that it seems quite reasonable that the plasticization pressure should correlate with some threshold of the sorbed penetrant partial molar volume. The question remains unsolved whether there exists a physical property with a critical threshold value above which relaxational non-Fickian transport occurs.

Our approach presented here starts with one polymer (polyimide Matrimid) and the sorption of different gases of which we can adjust the concentration in the polymer by varying the pressure. Systematic and precise sorption kinetics experiments allows the distinction of Fickian and relaxational mass uptake. The measurements prove that non-Fickian, relaxational mass uptake occurs above a critical value of absolute volume dilation. This observation unites the contributions of a threshold partial molar volume[10] and critical gas solubility.[3]

2. Characterization of Kinetic Sorption Behavior

2.1. Ideal Fickian Sorption. Crank[4] shows that the sorption of a penetrant in a polymer matrix is proportional to the square root of time, assuming a constant diffusion coefficient. This behavior is called ideal Fickian sorption, and the mass uptake (g) in time ($M(t)$) can be described by

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

where M_∞ is the amount of mass (g) sorbed by Fickian sorption at infinite time, D is the diffusion coefficient (m^2/s), t is the time (s), and L is the sample thickness (m). Fitting of the sorption data to this equation leads to the diffusion coefficients. The diffusion coefficient can vary with gas pressure (different concentrations inside the polymer).

2.2. Diffusion-Relaxation Model. Non-Fickian kinetic sorption behavior can be empirically described using a model proposed by Berens and Hopfenberg.[11] The model considers sorption processes to comprise of two distinct sorption regimes: a Fickian sorption regime (M_F) and a relaxational regime (M_R):

$$M(t)_{\mathrm{total}} = M(t)_F + M(t)_R \tag{2}$$

Because the diffusion-controlled regime is often far more rapid than the long-term relaxational regime, the two sorption processes can be easily distinguished. Consequently, the overall

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sorption process can be considered as a sum of phenomenological independent contributions from Fickian diffusion and polymer relaxation:

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

where $M_{\mathrm{F},\infty}$ and M_{R_i} are the infinite sorbed mass of the Fickian part and the relaxational parts of sorption (g), respectively, of which the sum in principle should equal one upon complete relaxation. τ_{R_i} is the characteristic time for relaxation (s). Often it is sufficient to describe non-Fickian sorption behavior by the sum of Fickian and two relaxational sorption regimes.[6,7] The first, fast relaxation follows diffusion kinetics.[7] The second relaxation is much slower and is considered to cause irreversible alterations of the free volume distribution in the polymer network.

The diffusion-relaxation model can only be used to extract meaningful parameters from sorption kinetics experiments when the two contributions to sorption, Fickian diffusion and polymer relaxation, are well separated in the sorption kinetics. This requires the diffusion rate to be much higher than the relaxation rate. The relative magnitude of the rates of diffusion and relaxation is quantified as the Deborah number and is defined as the ratio of the diffusion rate of a penetrant to the relaxation rate of the polymer matrix with a dimension L. The sorption processes of diffusion and relaxation are well separated when the Deborah number is much larger than unity. The Appendix further illustrates the importance of film thickness on the description of sorption kinetics using the diffusion-relaxation model. In fact, for some gases we need to combine measurements on thick and thin films to distinguish the phenomena. Thick films are used to extract Fickian diffusion coefficients and thin films to quantify relaxational weight uptake.

3. Experimental Section

3.1. Materials and Film Preparation. Thick dense polymer films were prepared by solvent evaporation of a 15 wt % Matrimid 5218 (Vantico AG) polyimide in NMP, cast on a glass plate using 0.3 or 1 mm casting knifes. After preparation, the wet films were stored in a closed container flushed with N_2 gas for 3 days to evaporate the solvent. To remove any residual solvent, the films were stored in a vacuum oven at 150 °C for 2 more days. The dry thickness of the film was 30 or 100 μm. All gases used were purchased from Praxair (The Netherlands) and were used without further purification.

3.2. Gravimetric Sorption Balance. Gas sorption in glassy polymers is typically measured using pressure decay or gravimetric methods. The principle of the pressure decay method is based on the measurement of a pressure difference in time due to sorption between two cells with one containing the sample and the other being an empty reference cell. The total pressure decay typically is small compared to the absolute pressure used (<5%). Analysis of the kinetic behavior is often difficult due to limitations in experimental accuracy as well as time-dependent boundary conditions for the pressure in the cell. Gravimetric sorption techniques maintain a constant pressure and are therefore more suitable to accurately record small weight changes occurring as a result of sorption-induced relaxations.

Therefore, the kinetic sorption behavior of the different gases in the polymer films was determined gravimetrically, using a magnetic suspension balance (MSB, Rubotherm), equipped with a vacuum pump ($p_{\mathrm{vac}} < 10^{-3}$ mbar), thermostat bath, and gas supply. The temperature was kept constant at 35 °C (308 K) throughout all experiments. Before each experiment, the samples were degassed for at least 24 h. Mass uptake was measured with incremental pressure steps in a sorption/desorption cycle. The electronic signal shows always large instabilities in the first few minutes of sorption as a result of temperature increases (Joule−Thomson effect) upon pressurization of the sorption balance. For this reason, the first minutes were disregarded in the analysis of the kinetic sorption behavior for thin films. For thick films these temperature instabilities are of less importance since mass uptake takes much longer. The measured weight w_t (g) was corrected for buoyancy according to Archimedes' principle. On the basis of the exact sample volume V_t (m^3) and the initial weight w_0 (g) of the sample and the density ρ_{gas} (g/m^3) of the surrounding gas, the mass gain m_t (g) can be calculated by taking into account the buoyancy effect:

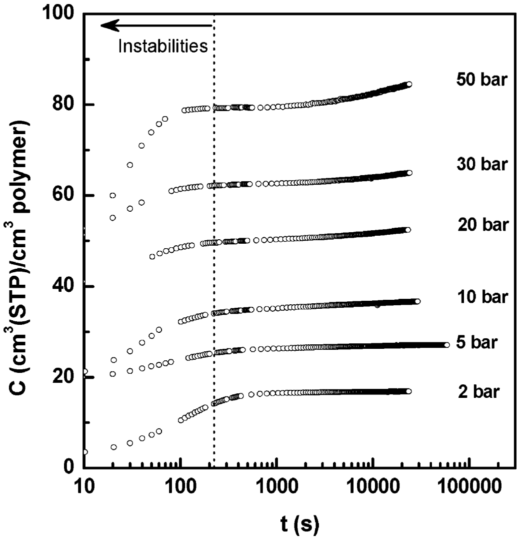

Figure 1. CO_2 concentration in Matrimid polyimide as a function of the logarithm of time for different pressures. Only a selection of experimental pressures is shown.

$$m_t = (w_t + V_t\rho_{\mathrm{gas}}) - w_0 \quad (4)$$

The gas density was estimated using the Peng−Robinson equation of state.[12] The density of the polymer sample was determined at room temperature using a Micromeritics AccuPyc 1330 pycnometer. The gas concentration in the polymer (cm^3 (STP) gas per cm^3 of polymer) was calculated using the molar volume at standard temperature and pressure (STP, 1 bar and 273.15 K), the polymer volume, and the molecular weight of the specific gas. Data fitting with the diffusion-relaxation model was carried out using graphing and data analysis software from Originlabs (Origin Pro 7).

4. Results

4.1. Kinetic Sorption Behavior of Carbon Dioxide. For the quantification of sorption kinetics of CO_2 in Matrimid, subsequent incremental pressure steps of 3, 5, and 10 bar were taken upon pressurization and steps of 10 and 20 bar upon depressurization. Figure 1 shows the CO_2 concentration as a function of time for six different pressures. The data are plotted as a function of the logarithm of time allowing the discrimination of the different sorption regimes.

At 2 bar of CO_2, only one distinctive sorption regime is observed representing ideal Fickian sorption: an initial fast increase (buildup diffusion profile) and subsequent leveling off to equilibrium. Above 2 bar, a second regime emerges, which becomes more pronounced at higher pressures. This additional increase in concentration at higher pressures is due to the onset of irreversible volume relaxations.

Table 1. Fickian and Non-Fickian Contributions and Fickian Diffusion Coefficients for the Sorption of CO_2 in Matrimid Polyimide Obtained from Fitting the Diffusion-Relaxation Model

press. (bar)	m_{F}	m_{R_1}	m_{R_2}	D_{Fick} ($\times 10^{-8}$) (cm^2/s)
2	0.94	0.06		0.67
5	0.87	0.10	0.03	0.93
10	0.77	0.14	0.09	1.25
15	0.63	0.18	0.19	1.75
20	0.59	0.19	0.31	2.35
25	0.43	0.13	0.44	2.60
30	0.44	0.10	0.46	3.48
40	0.31	0.11	0.52	4.60
50	0.22	0.06	0.72	5.80

As previously mentioned, the first minutes of sorption were disregarded due to temperature related drifts in the balance signal. Unfortunately, the first few minutes completely cover the buildup of the diffusion profile, especially at higher pressures. To be able to obtain diffusion coefficients, the CO_2-sorption kinetics of a 100 μm film were measured as well, as this increases the time scale required to build up the concentration profile. Since the separation of the different sorption regimes is better defined with relatively thin films, the kinetic data obtained for the 30 μm film are used to obtain the five other fitting parameters used in the diffusion-relaxation model (see Appendix). Table 1 shows the fitting parameters obtained with the diffusion-relaxation model (fit confidence >98%). The total fraction of the Fickian and relaxational sorption processes is set to one ($m_{\mathrm{F}} + m_{\mathrm{R}_1} + m_{\mathrm{R}_2} = 1$) after 240 min, although the relaxation process is not completed yet.

For sorption of carbon dioxide in Matrimid polyimide the following trends can be observed from Figure 1 and Table 1: (i) Ideal Fickian sorption is only observed at 2 bar of CO_2. At higher pressures the kinetic sorption behavior is non-Fickian, and relaxational mass uptake sets in. (ii) The fraction of slow relaxational sorption (m_{R_2}) increases with increasing pressure, while the fraction of Fickian sorption (m_{F}) decreases with increasing pressure. The magnitude of the fraction of fast relaxational sorption (m_{R_1}) appears to be independent of pressure. (iii) The Fickian diffusion coefficient is concentration dependent and increases with increasing pressure. (iv) The relaxation times are typically about $\tau_{\mathrm{R}_1} = 1 \times 10^3$ s and $\tau_{\mathrm{R}_2} = 1 \times 10^5$ s and are pressure- or concentration-independent within the accuracy of the experiment.

Figure 2 shows the CO_2 sorption isotherm in a pressurization/depressurization cycle. Since equilibrium is not reached within the time scale of the experiment above a pressure of 2 bar, pseudo-equilibrium values after 180 min of sorption and desorption were taken to calculate the sorbed concentration. The desorption isotherm is higher than the sorption isotherm. Secondary volume dilation introduced during sorption at long time scales cannot consolidate rapidly enough during desorption elevating the desorption isotherm above the sorption isotherm. Even a maximum appears in the desorption isotherm which is related to fact that sorption-induced relaxations continue even though the pressure of the gas phase is lowered.

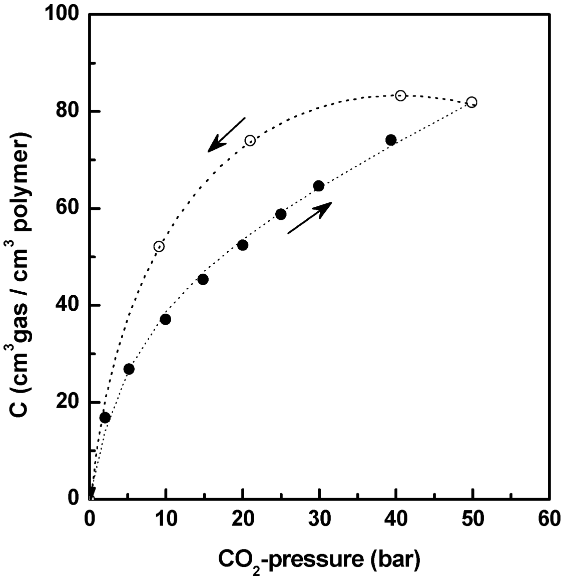

Figure 2. CO_2 sorption isotherm in Matrimid polyimide in a pressurization/depressurization cycle. Values were obtained after 180 min of sorption.

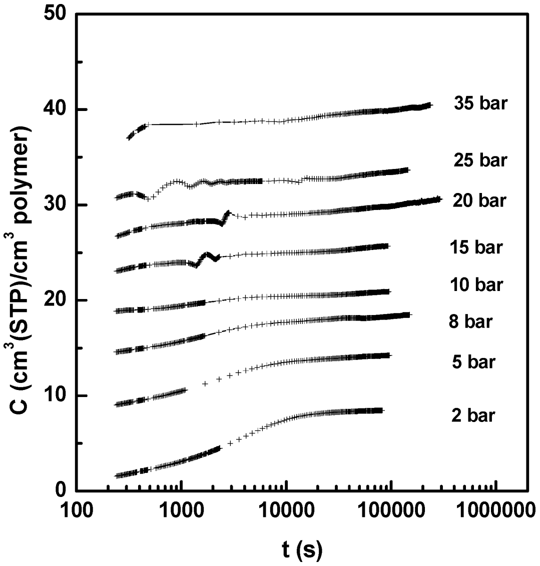

Figure 3. Sorption of xenon in Matrimid polyimide for incremental pressure steps.

Table 2. Fickian and Non-Fickian Contributions and Fickian Diffusion Coefficients for the Sorption of Xenon in Matrimid Polyimide Obtained from Fitting the Diffusion-Relaxation Model

press. (bar)	m_{F}	m_{R_1}	m_{R_2}	D_{Fick} ($\times 10^{-8}$) (cm^2/s)
2	0.94	0.06		0.023
5	0.84	0.05	0.11	0.031
8	0.79	0.02	0.19	0.036
10	0.71	0.04	0.25	0.045
15	0.65	0.04	0.31	0.060
20	0.60	0.05	0.35	0.080
25	0.56	0.05	0.39	0.095
35	0.43	0.08	0.49	0.170

4.2. Kinetic Sorption Behavior of Xenon. Figure 3 shows the xenon sorption kinetics as a function of the logarithm of time for several pressures in Matrimid polyimide. (Small fluctuations are visible in the curves at 15, 20, and 25 bar, which are caused by temperature fluctuations during sorption.) Xenon shows a similar kinetic sorption behavior as carbon dioxide: at 2 bar, almost ideal Fickian sorption is observed, while at higher pressures the kinetic sorption behavior becomes non-Fickian due to the onset of secondary relaxations. This is somewhat surprising as one may intuitively relate the inert character of xenon and its ideal gas behavior to an ideal Fickian sorption kinetics behavior. However, this association of chemical inertness with ideal behavior in sorption is far from correct.

Table 2 shows the fitting results of the kinetic sorption behavior of xenon in Matrimid polyimide obtained with the diffusion-relaxation model. The weight after 2400 min of sorption was taken as the pseudo-“infinite” weight. The observed trends are comparable to the phenomena observed for CO_2,

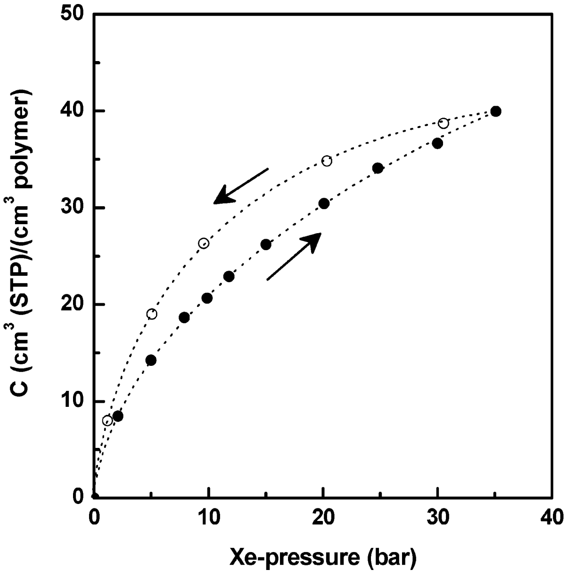

Figure 4. Xe sorption isotherm in Matrimid polyimide in a pressurization/depressurization cycle. Values were obtained after 180 min of sorption.

although the data fitting was less reproducible due to some temperature fluctuations (visible in Figure 3).

The following trends for sorption of xenon in Matrimid polyimide can be distinguished from Figure 3 and Table 2: (i) Ideal Fickian sorption is observed at 2 bar of Xe, while non-Fickian sorption is observed at higher pressures. (ii) The fraction of slow relaxational sorption (m_{R_2}) increases, while the fraction of Fickian sorption (m_F) decreases with increasing pressure. The magnitude of the fraction of slow relaxational sorption (m_{R_2}) is smaller than the value found for CO_2. The fraction of fast relaxational sorption (m_{R_1}) appears to be independent of pressure and is smaller than the value found for CO_2 as well. (iii) The diffusion coefficient is concentration-dependent and increases with increasing pressure. It is 2 orders of magnitude smaller than the diffusion coefficient found for CO_2. (iv) The relaxation times are typically about $\tau_R = 5 \times 10^2$ s and $\tau_{R_2} = 8 \times 10^5$ s and are pressure- or concentration-independent within the accuracy of the experiment.

Figure 4 shows the xenon sorption isotherm in a pressurization/depressurization cycle. The data points shown are pseudo-equilibrium values (above 2 bar) obtained after 180 min of sorption or desorption. The desorption isotherm is higher than the sorption isotherm, as a result of secondary volume dilation during sorption.

4.3. Kinetic Sorption Behavior of Propane and Propylene. *Propane*. Figure 5 shows the sorbed propane concentration in Matrimid polyimide as a function of the logarithm of time for four incremental pressure steps.

Regular Fickian weight uptake cannot be distinguished. The kinetic sorption behavior shows an upward inflection for all pressures, suggesting an immediate non-Fickian sorption behavior at low pressures. Apparently, the rates of diffusion and polymer chain relaxation are almost identical, which is often interpreted as case III or anomalous non-Fickian diffusion.[13] Unfortunately, the diffusion-relaxation model fails when diffusion and relaxation processes occur on the same time scale.[14] Reduction of the time scale for the diffusion process would in principle allow the separation of the two sorption processes. Practically this may be achieved by using thinner polymer films. However, these experiments could not be performed as the fluctuations in the balance signal during the first few minutes make the analysis too inaccurate. It remains an experimental challenge to separate the two contributions to sorption, Fickian diffusion and polymer relaxation, when the time scale of diffusion overlaps with relaxational sorption.

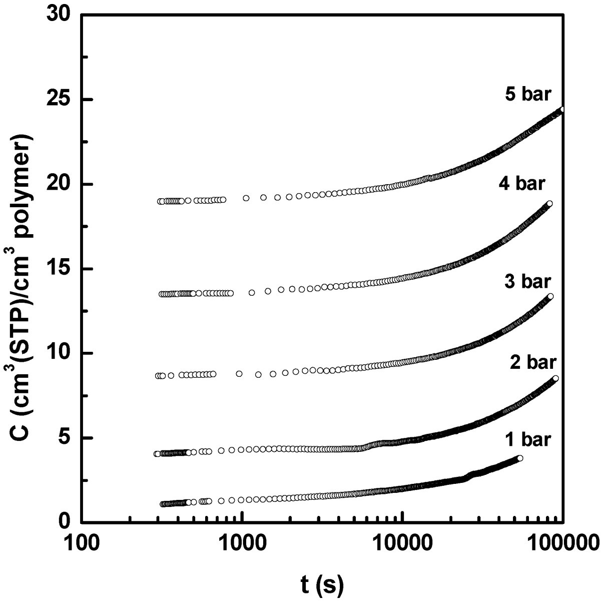

Figure 5. Kinetic sorption behavior of sorption of propane in Matrimid polyimide as a function of the square root of time.

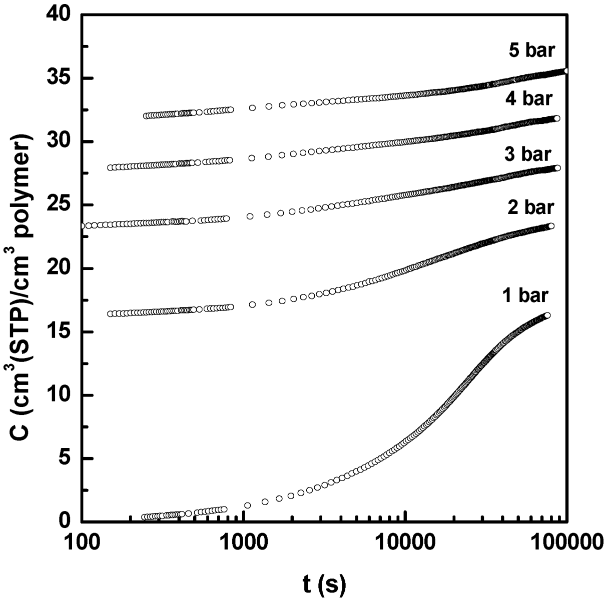

Figure 6. Kinetic sorption behavior for sorption of propylene in Matrimid polyimide as a function of the square root of time.

Propylene. Figure 6 shows the sorbed propylene concentration in Matrimid polyimide as a function of the logarithm of time for five different pressures. As in the case with propane sorption, also propylene shows a clearly non-Fickian kinetic sorption behavior, especially at higher pressures.

In the case of propylene, the sorption processes of elastic, Fickian diffusion and relaxational non-Fickian transport are better separated as compared to using propane, which can be attributed to a higher diffusion coefficient for propylene. Consequently, the diffusion-relaxation model could be applied for propylene, whereas this was not possible for propane. The weight after 1400 min of sorption was taken as the pseudo-“infinite” weight. Table 3 shows the fitting results of propylene sorption in Matrimid polyimide.

Table 3. Fickian and Non-Fickian Contributions and Fickian Diffusion Coefficients for the Sorption of Propylene in Matrimid Polyimide Obtained from Fitting the Diffusion-Relaxation Model

press. (bar)	m_F	m_{R_1}	m_{R_2}	D_{Fick} ($\times 10^{-8}$) (cm^2/s)
1	0.53	0.25	0.22	0.003
2	0.35	0.26	0.39	0.010
3	0.21	0.21	0.58	0.037
4	0.17	0.23	0.60	0.078
5	0.13	0.27	0.60	0.249

The following trends for sorption of propylene in Matrimid polyimide can be distinguished from Figure 6 and Table 3: (i) At all pressures investigated a highly non-Fickian sorption behavior is observed. (ii) The fraction of Fickian sorption (m_F) decreases rapidly with increasing pressure, while the fraction of slow relaxational sorption (m_{R_2}) increases rapidly with increasing pressure. Apparently, propylene causes very strong sorption-induced relaxations in Matrimid polyimide. Furthermore, the magnitude of the fraction of fast relaxational sorption (m_{R_1}) appears to be independent of pressure and is higher compared to those of CO_2 and Xe. (iii) The magnitude of the secondary volume relaxations (m_{R_2}) is larger than the corresponding values for CO_2 and Xe. (iv) The diffusion coefficient is highly concentration-dependent and increases with increasing pressure. It is 3 orders of magnitude smaller than the values found for CO_2 at a pressure of 1 bar and only 1 order of magnitude at a pressure of 5 bar. (v) The relaxation times are typically about $\tau_{R_1} = 2.5 \times 10^3$ s and $\tau_{R_2} = 4 \times 10^5$ s and are pressure-independent within the accuracy of the experiment.

Sorption Isotherms. Figure 7 shows the sorption isotherms for propane and propylene in Matrimid polyimide up to a pressure of 5 bar. The pseudo-equilibrium concentrations were calculated with data points taken after 1400 min (24 h) of sorption. The sorption isotherm for propylene has a concave shape with respect to the pressure axis as normally is observed for sorption in glassy polymers. Propane shows an almost linear isotherm. The higher sorption values for propylene compared to propane cannot be correlated to physical properties of the two gases: their critical temperatures for instance do not differ much. In amorphous polyethylene, the solubility of propylene and propane are about equal: however, the presence of ether bonds alters a polymer sorption selective for propylene.[15]

4.4. Kinetic Sorption Behavior of Krypton. Figure 8 shows the concentration krypton in Matrimid polyimide as a function of the logarithm of time up to pressures of 60 bar. Not all experimentally investigated pressures are shown to maintain better representation of the data.

At first sight, the kinetic sorption behavior seems to be ideal Fickian at all pressures; an initial steep increase continued by a leveling off to equilibrium. However, at higher pressures (≥20 bar), the concentration further increases slightly after ∼3 h of sorption, suggesting the onset of slow sorption relaxations. Table 4 shows the fitting results at different pressures obtained with the diffusion-relaxation model for the kinetic sorption behavior of krypton in Matrimid polyimide. The weight after 1400 min of sorption was taken as the pseudo-“infinite” weight. The fitting results confirm the presence of sorption-induced relaxations above a krypton pressure of 20 bar.

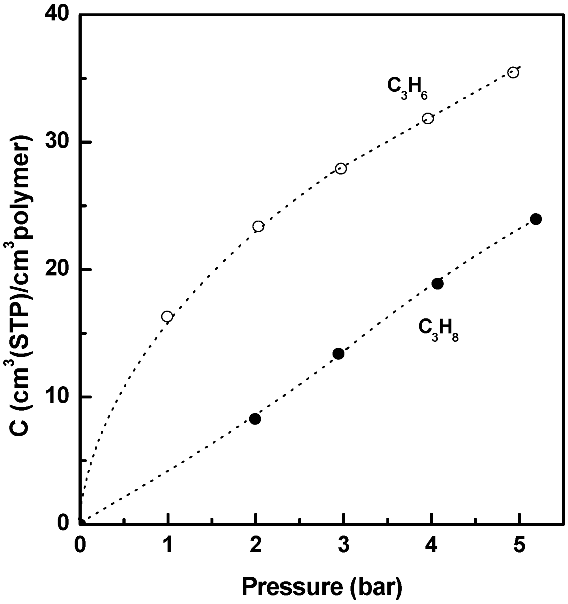

Figure 7. Sorption isotherms for C_3H_6 and C_3H_8 in Matrimid polyimide. Values were obtained after 2400 min of sorption.

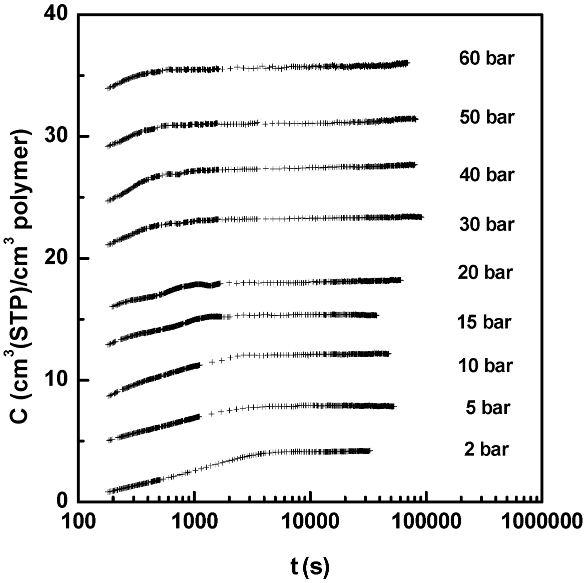

Figure 8. Kinetic sorption behavior of krypton in Matrimid polyimide for incremental pressure steps.

Table 4. Fickian and Non-Fickian Contributions and Fickian Diffusion Coefficients for the Sorption of Krypton in Matrimid Polyimide Obtained from Fitting the Diffusion-Relaxation Model

press. (bar)	m_F	m_{R1}	m_{R2}	D_{Fick} ($\times 10^{-8}$) (cm^2/s)
2	1			0.07
5	1			0.10
10	1			0.12
15	1			0.19
20	0.93	0.01	0.06	0.24
25	0.87	0.03	0.10	0.28
30	0.87	0.04	0.09	0.28
40	0.85	0.03	0.12	0.38
50	0.86	0.02	0.12	0.46
60	0.85	0.04	0.11	0.54

The following trends for the sorption of krypton in Matrimid polyimide can be observed from Figure 8 and Table 4: (i) Ideal Fickian sorption is observed up to a pressure of 15 bar. Above this pressure the kinetic sorption behavior shifts toward non-Fickian due to the onset of secondary volume relaxations. (ii) The fraction of Fickian sorption (m_F) decreases slightly with increasing pressure, while the fraction of slow relaxational sorption (m_{R_2}) increases slightly with increasing pressure. The fraction of fast relaxational sorption (m_{R_1}) seems to be independent of pressure. The magnitude of the relaxations is much smaller compared to CO_2, Xe, and C_3H_6 sorption. (iii) The diffusion coefficient is concentration-dependent and increases with increasing pressure. Furthermore, it is 1 order of magnitude

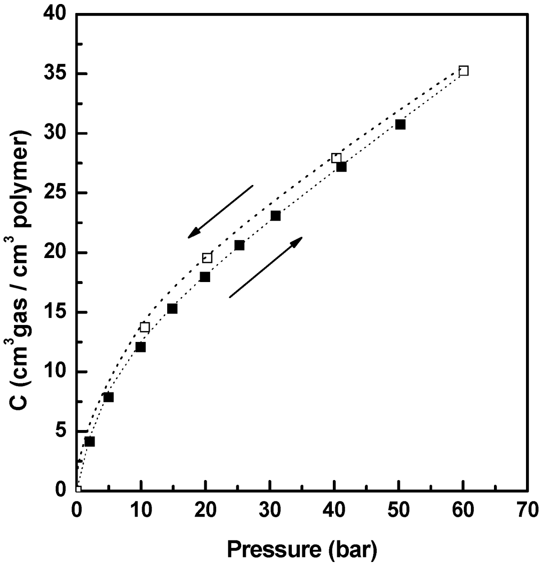

Figure 9. Kr sorption isotherm in Matrimid polyimide in a pressurization/depressurization cycle. Values were obtained after 300 min of sorption.

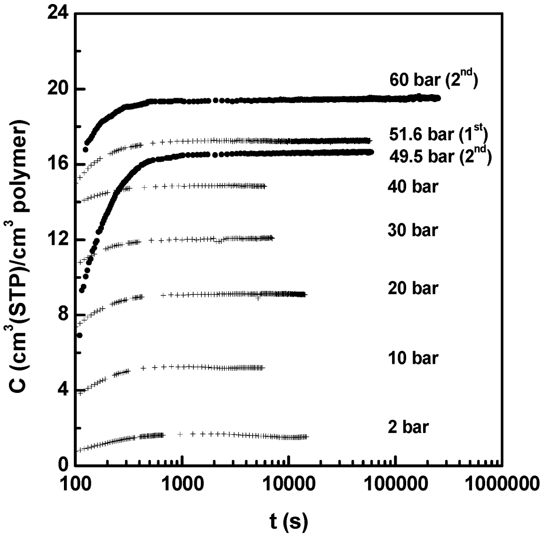

Figure 10. Kinetic sorption behavior of argon in Matrimid polyimide.

smaller compared to that of CO_2. (iv) The relaxation times are typically about $\tau_{R_1} = 5 \times 10^2$ s and $\tau_{R_2} = 4 \times 10^5$ s and are pressure- or concentration-independent within the accuracy of the experiment.

Figure 9 shows the krypton concentration in Matrimid polyimide as a function of pressure in a pressurization/depressurization cycle. The data points shown in Figure 9 were obtained after 300 min of sorption. The desorption isotherm is slightly higher than the sorption isotherm, confirming the non-Fickian sorption kinetics as a result of secondary volume dilation during sorption. The hysteresis is smaller when compared to Xe and CO_2, which is attributed to the lower magnitude of relaxational sorption.

4.5. Kinetic Sorption Behavior of Argon. Figure 10 shows the argon concentration in Matrimid polyimide as a function of the logarithm of time for pressures up to 50 bar for the first film and up to 60 bar for the second film (closed dots, indicated as second). The first sorption step for the second film is carried out with a pressure step from 0 to 49.5 bar. The total argon concentration sorbed at a pressure of 50 bar remains the same irrespective of incremental or integral pressure steps, as will be shown later.

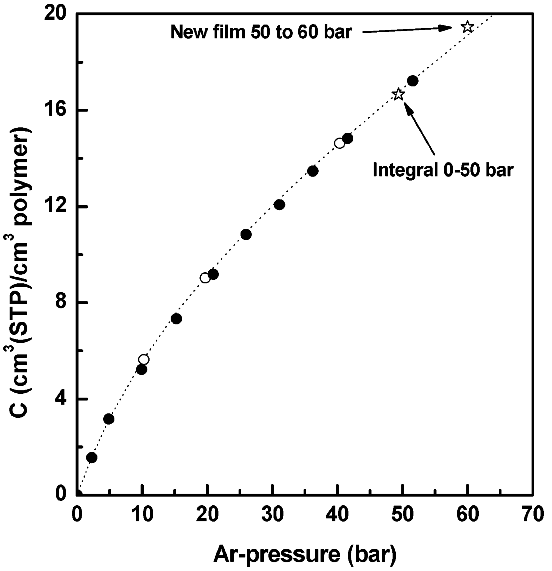

Figure 11. Argon sorption isotherm in Matrimid polyimide in a pressurization (closed dots)/depressurization (open dots) cycle.

Table 5. Argon Diffusion Coefficients in Matrimid Polyimide Determined Using Fickian Sorption Only (Eq 1)

press. (bar)	D_{Fick} ($\times 10^{-8}$) (cm^2/s)	press. (bar)	D_{Fick} ($\times 10^{-8}$) (cm^2/s)
2	0.48	25	0.62
5	0.50	30	0.60
10	0.57	40	0.65
15	0.61	50	0.75
20	0.55	60	0.79

For pressures up to 50 bar the kinetic sorption behavior is clearly ideal Fickian. However, at a pressure of 60 bar, the argon concentration in the polymer film appears to increase slightly at times of ~3 h of sorption. This was confirmed using the diffusion-relaxation model which gave a 6% additional increase in concentration ($m_{R_2} = 0.06$) after buildup of the diffusion profile (pseudo-“infinite” time of 4000 min). The relaxation time was determined to be $\sim 1 \times 10^6$ s. The kinetic sorption behavior of lower pressure (<60 bar) was fitted using regular Fickian sorption (eq 1). The determined diffusion coefficients are shown in Table 5. It can be observed that the argon diffusion coefficient is concentration-dependent and increases with increasing pressure.

Figure 11 shows the argon sorption isotherm in a pressurization/depressurization cycle carried out up to a pressure of 50 bar (visualized as dots). The values obtained for the second film are included as well (visualized as stars). As expected, for the first film no hysteresis is observed up to a pressure of 50 bar. As relaxations are observed at a pressure of 60 bar, it is expected that depressurization would have caused some hysteresis. However, probably the effect is too small to be visible in Figure 11.

5. Discussion

Gas solubility in a polymer is influenced by (1) specific molecular interactions and (2) gas condensability. Polymer modifications (the introduction of for example polar groups) can drastically alter gas solubility.[16] For different gases, solubility increases with an increase in relative condensability. The condensability of a gas increases with increasing values for its the Lennard-Jones force constant (ϵ/k) or critical temperature (T_c), of which values can be obtained from ref 17.

Figure 12 compares the overall sorption isotherm for all experimentally used gases at 35 °C. C_3H_6 has the highest

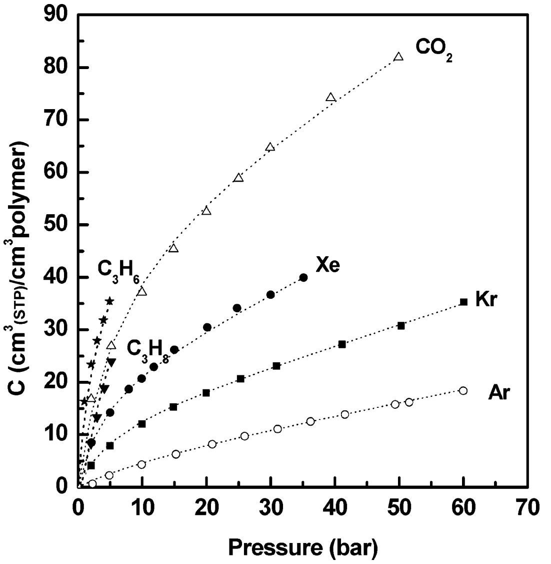

Figure 12. Gas concentration in Matrimid polyimide as a function of pressure for all gases investigated.

solubility in Matrimid polyimide, followed by CO_2, C_3H_8, Xe, Kr, and Ar. This order in magnitude of gas solubility reflects the differences in relative condensability well. As the relative condensability of Xe is higher than those of Ar and Kr, Xe has the higher solubility in Matrimid polyimide. On the other hand, the gases CO_2 and Xe have similar condensability, although the solubility of CO_2 is significantly higher. This can be attributed to specific molecular interactions between CO_2 and Matrimid polyimide.

We now turn to the comparison of the magnitude of mass uptake and the induction of relaxational mass uptake. Relating the sorption isotherms of Figure 12 and the onset values for relaxational weight uptake, we must conclude that higher gas solubilities do not automatically result in lower pressures required to induce relaxational weight uptake. The sorption of propylene and propane causes slow relaxations at much lower pressures and concentrations than CO_2 and Xe. Besides, the solubility of propylene in Matrimid polyimide is higher than that of propane, while they induce relaxations at more or less the same pressure. Also, the onset of relaxations in the case of CO_2 and Xe occurred at more or less the same pressure, but the concentration of sorbed gas at this pressure was significantly different. At a pressure of 50 bar Ar, Matrimid polyimide contains the same concentration of gas as at 1 bar of propylene or 4 bar of propane. The sorption kinetics of argon starts to show only little relaxational mass uptake at these high pressures. In contrast, for propane and propylene at the same concentration, non-Fickian relaxational sorption is clearly present.

In contrast to our earlier finding that the onset of plasticization effects is related to a certain critical gas concentration,[3] the results presented here suggest the concentration only is insufficient to find a unique property at which sorption relaxations set in. Wind related the onset of plasticization effects to a threshold value of the partial molar volume.[10] The partial molar volumes of Ar, Kr, and Xe in PDMS do not differ significantly from that of CO_2, while completely different pressures were required to observe the onset of sorption relaxations. The ability of CO_2 to plasticize Matrimid polyimide can be mainly attributed to the fact that it has much higher gas solubility than the noble gases, as shown in Figure 12. The solubility of C_3H_8 was slightly lower than that of CO_2, while the onset of sorption relaxations was observed at a lower pressure. This may be attributed to the higher value of the partial molar volume of C_3H_8 compared to CO_2. These results suggest that the onset of relaxations is not determined by a critical value of the partial molar volume nor the concentration alone, but by both parameters simultaneously.

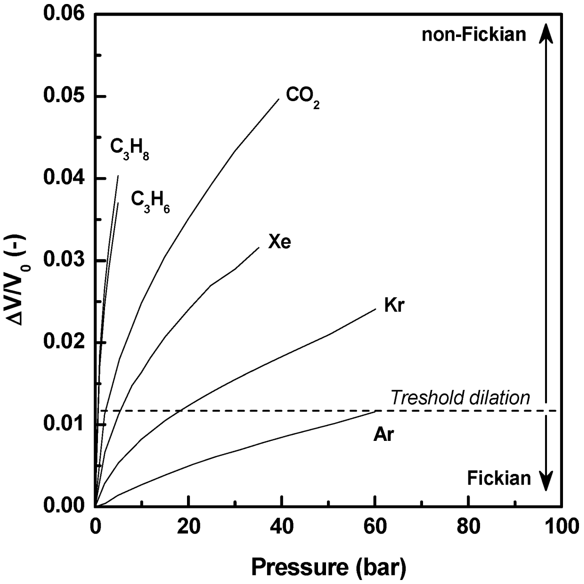

Figure 13. Estimated dilation isotherms in Matrimid polyimide for the gases investigated. The dashed lines indicate a threshold amount of dilation required to induce non-Fickian sorption kinetics.

The volume dilation ($\Delta V/V_0$) of a polymer exposed to a gas is defined as the product of penetrant concentration c (cm^3 (STP)/cm^3 polymer) and partial molar volume V_p of penetrants (cm^3/mol):[18]

$$\frac{\Delta V}{V_0} = cV_p/22400 \tag{5}$$

Dilation isotherms for Matrimid polyimide can be estimated using eq 5, the experimental sorption data, and an assumed partial molar volume in Matrimid. Values for the partial molar volume in glassy polymers can be estimated from corresponding values in organic liquids or rubbery polymers as it is known that the partial molar volume scales exponentially with the glass transition temperature of a polymer.[19] The values in Matrimid polyimide with a T_g of 313 °C are estimated to be ~30% of those in PDMS. Figure 13 shows the predicted volume dilation as a function of gas pressure in Matrimid polyimide for the gases investigated.

Now, Figure 13 allows the comparison of the pressure at which relaxational mass uptake sets in, and one must conclude these onset pressures correlate with one single value for the amount of volume dilation. This illustrates that for any gas investigated the same critical threshold amount of volume dilation is required to induce sorption relaxations. Below the threshold, only elastic reversible distortion of the glassy polymer occurs, resulting in ideal Fickian sorption, while plastic irreversible distortion occurs above the threshold, resulting in non-Fickian sorption phenomena. CO_2 causes much more volume dilation than Kr, Ar, and Xe, as a result of a much higher solubility in Matrimid polyimide, while C_3H_8 causes more volume dilation than CO_2 due to its higher partial molar volume. It demonstrates that the critical threshold depends on both the gas solubility and the partial molar volume of a gas.

Future work with respect to the induction and onset of sorption-induced relaxations should address questions such as magnitudes of the critical volume dilation for other polymers and their relationship with bulk properties of the material.

Furthermore, the methodology described here should be extended toward water and organic vapor sorption. The sorption-induced glass transition temperature depression as a function of the penetrant gas may be related to the onset and the magnitude of non-Fickian relaxational sorption. Measuring the glass transition temperature depression as a function of sorbed gas concentration is possible[20] but remains an experimental challenge.

6. Conclusions

The kinetic sorption behavior of six different gases (CO_2, Xe, C_3H_6, C_3H_8, Kr, and Ar) in Matrimid polyimide was investigated using a gravimetric sorption balance. The empirical diffusion-relaxation model allows quantifying the fractions of Fickian and relaxational sorption increase. With increasing penetrant concentration, the contribution of relaxational mass uptake increases whereas Fickian sorption decreases. The diffusion coefficient is concentration-dependent for all gases investigated. Combining the partial molar volume and the actual concentration of the penetrant in a glassy polymer into the absolute volume dilation results in the identification of a unique critical threshold value of volume dilation above which sorption relaxations are induced and kinetic sorption behavior becomes non-Fickian.

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Appendix. Influence of Film Thickness on CO_2 Kinetic Sorption Behavior

It is reasonable to assume that the relaxation processes occurring in glassy polymers upon sorption are independent of the polymer dimensions. Diffusion-controlled sorption, on the other hand, varies with the square of the polymer dimensions.[1] Therefore, the sample thickness affects the overlap in time of diffusion and relaxation in sorption kinetics. To discriminate between the kinetics of Fickian and relaxational weight uptake, one desires to use relative thin polymer samples. Thinner films reduce the time scale for diffusion so that the analysis of the diffusion coefficient becomes impossible because the rapid weight uptake cannot be measured accurately. On the other hand, thicker films may result in a superposition of the two sorption processes. To apply the diffusion-relaxation model there should be a distinct separation of the two sorption processes.[14,21,22] The relative magnitude of the rates of diffusion and relaxation is often characterized by the diffusion Deborah number ($\mathrm{DEB_D}$), which is defined as[22]

$$(\mathrm{DEB})_\mathrm{D} = \frac{\tau_\mathrm{R} D}{{L_0}^2} \tag{A1}$$

where τ_R is the characteristic relaxation time and $L_0{}^2/D$ is the characteristic diffusion time, with L_0 the sample thickness and D the diffusion coefficient. For $(\mathrm{DEB})_\mathrm{D} \gg 1$ the rate of diffusion is much faster than the response of polymer relaxation, while for $(\mathrm{DEB})_\mathrm{D} \approx 1$, 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.

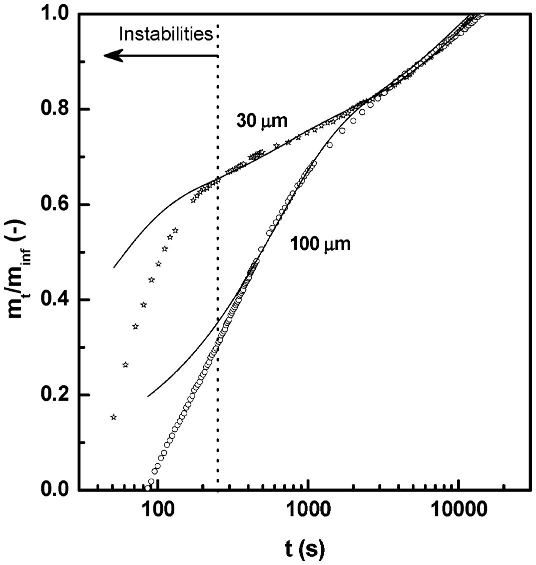

Figure 14. Film thickness dependence on the kinetic sorption behavior at 20 bar of CO_2.

Figure 14 shows the effect of film thickness on the kinetic sorption behavior at 20 bar of CO_2 for 30 and 100 μm Matrimid polyimide films. The symbols represent the experimental values while the solid lines represent the calculated fits from the diffusion-relaxation model. At a film thickness of 100 μm diffusion and relaxation kinetics start to overlap, while the diffusion profile is relatively short at a film thickness of 30 μm. Deborah numbers of ∼25 for the 30 μm film and less than 3 for the 100 μm film were calculated.

Figure 14 shows that the contributions of diffusion and relaxation are well-separated in the case of the 30 μm film. However, the first 240 s of the experimental measurements was not taken into account due to significant disturbance of the electronic signal (temperature fluctuation), which causes deviations between model and experimental data. As a result, 30 μm films cannot be used to determine diffusion coefficients. In the case of the 100 μm the buildup of the diffusion profile is long enough to provide a good determination of the diffusion coefficient. As relaxation parameters are independent of the sample dimensions, this diffusion coefficient calculated from the 100 μm film can be used for the 30 μm as well. This allows the calculation of the other fitting parameters based on the 30 μm film. Figure 14 shows that the calculated fits (solid lines) have good agreement with the experimental data, but it also shows that the choice for the right film thickness for kinetic gas sorption experiments is essential to be able to distinguish between Fickian and non-Fickian kinetic sorption behavior.

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