Water Sorption in Ultra-thin Perfluoropolyether Films

Abstract:

The diffusion of water into ultra-thin PFPE (perfluoropolyether) films supported on gold substrates as a function of relative humidity (RH) and of PFPE film thickness from 20 – 100 Å is investigated. The complete adsorptive wave is fit by a two-stage sorption model using a linear superposition of diffusion and polymer relaxation controlled mass uptake. The initial portion of the adsorptive wave, fit by Fickian diffusion, provides a diffusion constant, D, for water sorption as a function of RH and of PFPE film thickness. The D values are 10^{-18} to 10^{-16} m^2/s depending upon RH and PFPE film thickness. The diffusion constant increases non-linearly when RH exceeds ~ 70 - 80%, indicative of a significant change in the PFPE film structure to accommodate the water sorption.

Keywords: Perfluoropolyethers; water sorption; diffusion constant; quartz crystal microbalance.

Introduction:

Perfluoropolyethers (PFPEs) are widely used in many industrial and technological applications because they are room temperature liquids of low surface energy, high chemical resistance, high gas permeability, and low toxicity. PFPEs have served as reliable boundary lubricants on rigid magnetic media for over 25 years, and photocurable PFPEs have become important emergent materials in microfluidic devices [1, 2]. The uniquely high gas permeability in PFPEs is a featured property in many applications. Inside the channels of microfluidic devices, trapped gases can escape, and cells and micro-organisms can be sustained. In cosmetic barrier creams that offer protection and moisture retention, PFPEs allow the skin to breathe [3]. However, not all applications of PFPEs benefit from the high gas permeability. For example, PFPEs are not effective permeation barriers to water vapor which is inextricably linked to corrosion failures in hard disk drives [4]. Finally, if gas or solvent permeation causes polymer swelling, device applications could fail as a result of a change in the physical dimensions of the PFPE films.

Here we investigate the effect of humidity on ultra-thin PFPE films supported on a substrate as a function of PFPE film thickness from 20 – 100 Å. To our knowledge, the diffusion kinetics of water sorption into PFPE films is not well-quantified. Water sorption studies are used to measure the diffusion constant as a function RH and of PFPE film thickness. The initial portion of the adsorptive wave is fit by Fickian diffusion. However, polymer relaxation effects must be included to fit the entire adsorptive wave. The diffusion coefficient for water increases with increasing relative humidity and increasing PFPE film thickness. When the relative humidity exceeds approximately 80 %, water sorption no longer follows Henry's law.

Materials and Methods:

Zdol 4000 and Z03 were purchased from Solvay-Solexis (Italy). The perfluoropolyether (PFPE) lubricant films were applied to the quartz crystals from HFE-7100 (3M) solvent using a standard dip-coating methodology. The concentrations were 0.01 – 0.05 g/liter and a disk withdrawal rate of several mm/sec were used. The thicknesses of the topically applied PFPE films were quantified by specular reflection FTIR (Nicolet Magna Model 560). The FTIR absorption band maximum for each PFPE was in turn correlated to film thickness by XPS (Phi Quantum 2000 ESCA System) using a takeoff angle of 45° and an electron mean free path of 25 Å, Fig. 1 [5].

Sorption measurements were conducted using a quartz crystal microbalance (QCM). The crystal was mounted into a Maxtek probe, and a Hewlett-Packard network analyzer was used to energize the quartz crystal at its resonant

frequency. The quartz crystals were 1 inch diameter AT cut with polished Ti/Au electrodes and resonant frequencies of nominally 5 MHz (Maxtek, Inc). The quartz crystals were washed with a 1% aqueous solution of Valtron SP2200 (Valtech Corporation) under ultrasonication (25 kHz) for approximately 5 min, followed by copious rinsing with deionized water. After drying under N_2, the QCs were rinsed with filtered (0.5 μm particulate) HFE-7100. The QCs were then used directly. The unloaded and loaded frequencies and resistances are summarized in Table 1. The small changes in the resistance after sample loading is indicative that the QC properties did not change.

The switching component of the gas manifold for the water sorption studies is illustrated in Fig. 2. The gas is switched from dry to wet and vice versa with both gas sources flowing continuously at a constant flow. The dry gas is nitrogen and the wet gas is humidified nitrogen obtained by bubbling through water. The RH is quantified via a humidity meter. The frequency change at the desired sampling rate was recorded on a PC permitting a record of the mass uptake as a function of time.

Results and Discussion:

The frequency (Hz) and mass (g/cm^2) changes as a function of the PFPE (perfluoropolyether) film thicknesses for Zdol 4000 and Z03 are shown in Fig. 3. The frequency change is linear with PFPE film thickness and both Zdol 4000 and Z03 are observed to fall on the same line. This means that the Sauerbrey relation, Eq. 1, is satisfied such that some PFPE film properties may be calculated [6].

$$\Delta m = -\frac{\sqrt{\rho_Q \mu_Q}}{2 f_o{}^2} \Delta f \qquad (1)$$

Δm is the mass change per unit area, ρ_Q is the quartz density and μ_Q is the shear wave velocity for quartz such that $(\rho_Q \mu_Q)^{1/2} = 8.374 \times 10^5$ $g/cm^2 s$, f_o is the unloaded crystal frequency, and Δf is the observed frequency change upon loading. Thus the slope of the mass change per unit area as a function of film thickness yields a film density of 1.92 g/cm^3 which is remarkably close to the known bulk density of 1.82 g/cm^3 for both Zdol 4000 and Z03, respectively [7].

Since the PFPE systems are well-behaved between 20 and 100 Å, water sorption studies are next conducted. Fig. 4 shows the response of some loaded quartz crystals (QCs) as a function of time and of relative humidity (RH) for Zdol 4000 and Z03. Film thicknesses of 19, 29, 67 and 82 Å are investigated for Zdol 4000 whilst thicknesses of 32, 51 and 94 Å are investigated for Z03. Representative water sorption curves are shown for 19 and 82 Å of Zdol 4000 and 32 Å of Z03. Summary plots for all Zdol and Z03 film thicknesses are shown in Fig. 5.

Referring first to Fig. 4, the frequency changes (Δf) are observed to increase as a function of relative humidity. The magnitude of the frequency changes, $\leq \sim 5$ Hz, is similar for all Zdol and Z03 film thicknesses at similar RH values. The steady state maximum in Δf is reached within a few tens of seconds and, upon reversing the environmental RH from wet to dry, the frequency change returns to its original baseline. The latter observation is indicative that water molecules are not permanently trapped by the PFPE film. Previous water sorption/desorption studies on some PFPEs either at 80% RH using ellipsometry or at 50% RH using the QCM exhibited similar behavior [8, 9]. Rarely a small overshoot is observed which quickly decays away, Fig. 4a (72 % RH). The observation of overshoot in polymeric systems is typically attributed to surface reorganization effects [10]. Given its infrequent occurence in these experiments, no further interpretation is given here.

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Summary plots of the frequency and mass changes as a function of RH are shown in Fig. 5 for all of the PFPE films investigated here. Linear plots with RH are observed for all Δm and Δf up to about 70 – 80% RH, beyond which values Δm and Δf change non-linearly. Since this is observed for all Zdol and Z03 film thicknesses, and the water sorption/desorption plots show no permanent water retention either within the PFPE film or at the PFPE/Au interface (Fig. 4), we suspect polymer relaxation effects must also be operative particularly at the higher RH values. For example, polyacrylamide films (60 – 300 Å) as a function of RH exhibit a similar non-linear increase in film swellability for RH values exceeding about 70 - 80 % RH [11]. These aspects will be discussed further below. Furthermore, the thickness-independence suggests no strong interaction between the substrate and the PFPE molecules. Plots of the normalized mass uptake as a function of RH, Fig. 5, are also informative. Since these curves do not coincide, the diffusion coefficient for water adsorption is PFPE film thickness-dependent.

The details of the water adsorption kinetics in the PFPE films are next discussed. We limit this analysis mainly to the 19 Å Zdol 4000 film which is the most relevant film thickness used in technological applications [2]. The frequency changes (or equivalently the mass uptake curves) can be fit to model the diffusion coefficients. Whilst the data contained in Figs. 4 and 5 are indicative of non-Fickian water diffusion into PFPE films, the initial adsorptive wave is often found to be proportional to the square root of time. Often water sorption in polymer films can be fitted using a two-stage sorption process, the initial stage being Fickian-controlled by chain mobility and free volume, and the second stage being polymer relaxation-controlled attributed to polymer conformational changes and/or swelling. Conformational change and swelling allows additional water molecules to be sorbed into the polymer film. We first attempt to obtain the diffusion coefficient D from the initial adsorptive wave of the QCM data. Fick's second law for diffusion with a constant D in one dimension, Eq. 2, provides Eq. 3 as a possible solution [12].

$$\frac{\partial N}{\partial t} = D\nabla^2 N \qquad (2)$$

$$\frac{N_t}{N_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}e^{\frac{-(2n+1)^2\pi^2 Dt}{h^2}} \qquad (3)$$

N_t and N_∞ are the number of molecules sorbed into the film at times t and ∞, respectively, D is the diffusion constant, and h is the film thickness. Eq. 3 can be simplified to Eq. 4 for an expression for D in the general case where the permeant molecules sorbed takes the form $N_t \propto t^\alpha$.

$$D = \frac{\pi h^2}{4}\left(\frac{d(N_t/N_\infty)}{dt^\alpha}\right)^{1/\alpha} \qquad (4)$$

The value of α can be determined from a log-log plot of N_t/N_∞ versus time using the best fit to the initial adsorptive wave. When α = ½, a Fickian Type I diffusion characterizes the water permeation at short times. These data are shown in Fig. 6a for α = ½ for the PFPE systems under investigation here. Assuming Fickian Type I diffusion for the initial adsorptive wave, D as a function of relative humidity (RH) for 19 Å Zdol 4000 is summarized in Fig. 6b, Table 2. The D value is observed to increase with increasing RH. The permeant D is known to be a function of both polymer film thickness and RH [13]. The magnitude of the D values also appears to be consistent with literature values when polymer type and film thickness are considered [11, 13]. A plot of D vs RH indicates a nonlinear

increase in D when RH ~ 80%, Fig. 6b. These data indicate that water permeation in PFPE films deviate from Henry's law for higher RH values. The increase with RH is usually associated with an increase in the polymer film swell ability as discussed previously [11].

The analysis for the complete adsorptive wave is next considered using a two-stage sorption model, Eq. 5 [14]. This model utilizes a linear superposition of diffusion (first term) and relaxation (second term) controlled mass uptake.

$$\frac{N_t}{N_\infty} = \phi\left[1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}e^{\frac{-(2n+1)^2\pi^2 Dt}{h^2}}\right] +$$

$$(1-\phi)\left[1 - \frac{\tan\sqrt{\psi}\,e^{\frac{-\psi Dt}{h^2}}}{\sqrt{\psi}} - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{e^{\frac{-(2n+1)^2\pi^2 Dt}{h^2}}}{(2n+1)^2\left(1-\frac{(2n+1)^2\pi^2}{4\psi}\right)}\right] \qquad (5)$$

Φ relates the fraction of mass uptake between diffusion and relaxation control and ψ is the inverse Deborah number. Fig. 7 shows a comparison of fits to the adsorptive wave of 19 Å Zdol 4000 as a function of RH using both Fickian diffusion (φ = 1.00; ψ = 1.00) and the two-stage sorption model (φ = 0.85; ψ = 1.00). In both cases, the experimental D values are used (Table 2) and only φ is changed to fit the adsorptive wave to limit the number of fitting variables in Eq. 5. Using this approach, the two-stage model provides an adequate fit to the experimental data indicating that a 15% correction for film relaxation effects must be included in the analysis of humidity effects on the adsorptive wave of the PFPE films.

Water sorption in Zdol films as a function of Zdol film thickness (19 – 82 Å) at a constant 57 ± 4 % RH is shown in Fig. 8 and summarized in Table 3. Fig. 8a plots the normalized frequency change for the loaded QC against $t^{1/2}/h$ for different Zdol thicknesses. Since the curves do not coincide, a thickness-dependent diffusion is indicated. Fig. 8b shows that D increases with increasing film thickness. The increase in D with increasing film thickness is attributed to the increase in chain motion and randomness that facilitates the permeability of water vapor [15].

Fig. 9 shows a comparison of fits to the adsorptive wave of Zdol 4000 as a function of film thickness at a constant 57 ± 4 % RH using both Fickian diffusion (φ = 1.00; ψ = 1.00) and the two-stage sorption model (φ = 0.85; ψ = 1.00). As before, the experimental D values are used (Table 3) and only φ is changed to fit the adsorptive wave. Again, the two-stage model provides an adequate fit to the experimental data using a 15% correction for film relaxation effects.

Conclusions:
The diffusion of water into ultra-thin PFPE (perfluoropolyether) films supported on gold substrates was characterized as a function of relative humidity (RH) and of PFPE film thickness (20 – 100 Å). The complete adsorptive wave was fit to a two-stage sorption model using a linear superposition of diffusion and polymer relaxation controlled mass uptake. The initial portion of the adsorptive wave could be fit by Fickian diffusion which provided a diffusion constant for water sorption as a function of RH and PFPE film thickness. The diffusion constant increased nonlinearly when the RH exceeded 70 - 80%. This indicated a significant change in the PFPE adsorbed film structure, most likely due to swelling, to accommodate water sorption. A 15% correction for polymer relaxation

effects was used to fit the complete adsorptive wave. Thus, caution is indicated in the interpretation of PFPE data

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generated under ambient RH because unintended changes in the polymer conformation may become the significant determinant in the test results.

Tables:

Table1. Characterization of the unloaded and loaded quartz crystal samples used in the water adsorption studies. Unloaded refers to the bare quartz crystal and loaded refers to the quartz crystal coated with the PFPE film on one side.

PFPE	Thickness (Å)	F (Hz) unloaded	F (Hz) loaded	R (ohm) unloaded	R (ohm) loaded
Zdol 4000	18.8	5010968.8	5010949.5	11.4	11.4
Zdol 4000	28.8	5010946.5	5010920.5	11.4	11.7
Zdol 4000	67.0	5010975.0	5010897.0	11.3	12.0
Zdol 4000	82.0	5011085.6	5010988.6	10.4	12.3
Z03	31.7	5004033.5	5003997.9	9.5	9.8
Z03	51.4	5003964.9	5003896.4	10.6	11.4
Z03	94.0	5010960.7	5010855.7	10.1	13.5

Table 2. Experimental D versus RH for 18.8 Å Zdol 4000.

RH (%)	D (m^2/s) Eq. 4
96	3.7×10^{-18}
72	2.5×10^{-18}
52	1.8×10^{-18}
31	1.2×10^{-18}

Table 3. Experimental D versus thickness for Zdol 4000 at 57 ± 4 % RH.

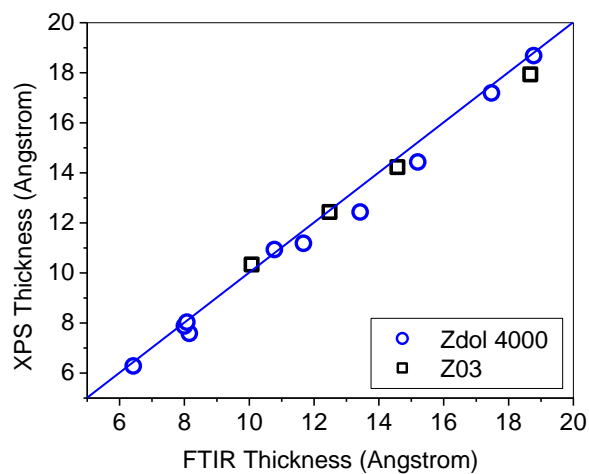| RH (%)	Å	D (m^2/s)
52	18.8	1.8×10^{-18}
60	28.8	4.0×10^{-18}
55	67.0	4.1×10^{-17}
60	82.0	9.8×10^{-17}

Figures:

Figure 1. FTIR thickness calibration by ESCA for Zdol 4000 and Z03 films on gold.
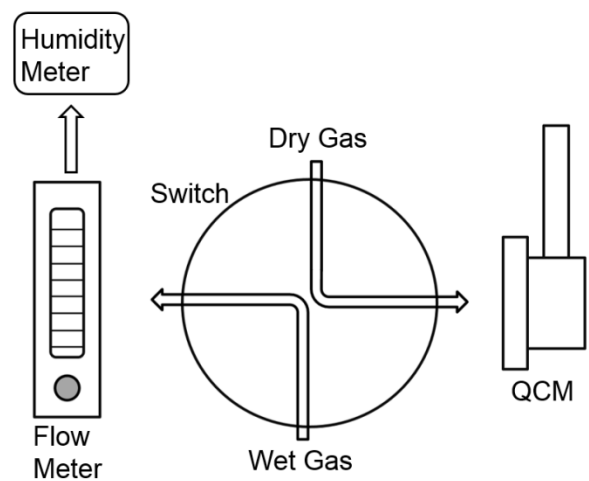

Figure 2. Schematic for the gas switching component of the gas manifold used in the sorption studies.
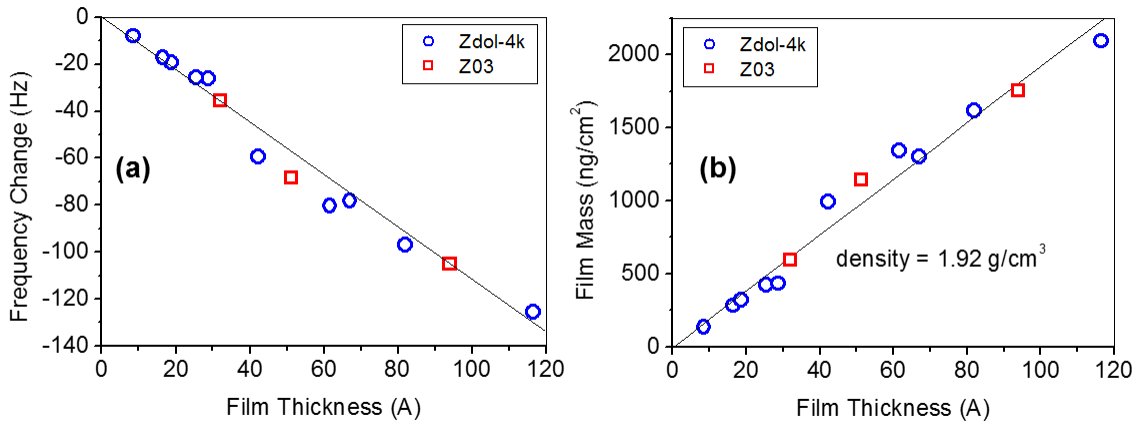
Figure 3. (a) QCM frequency change and (b) corresponding film mass as a function of Zdol 4000 and Z03 film thickness at ambient.
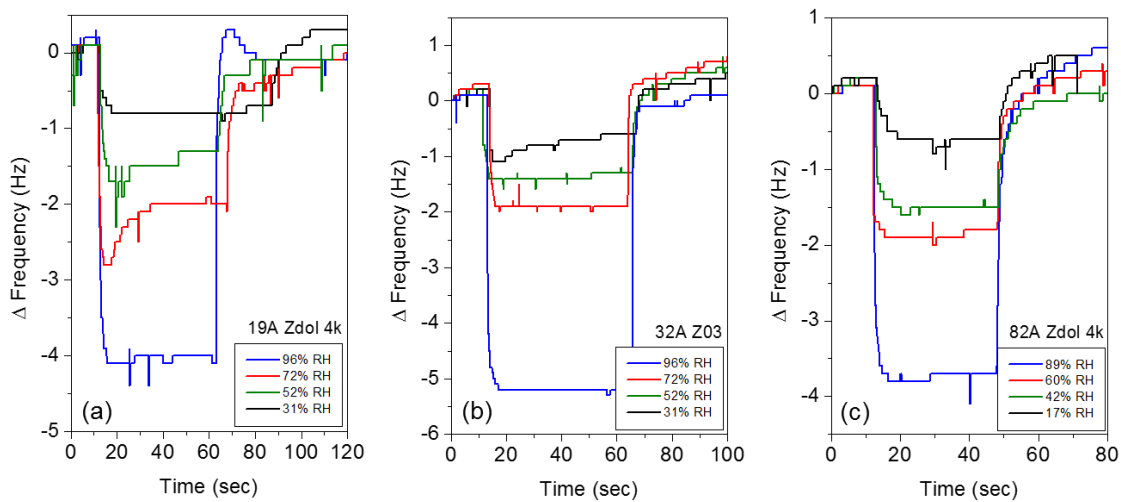

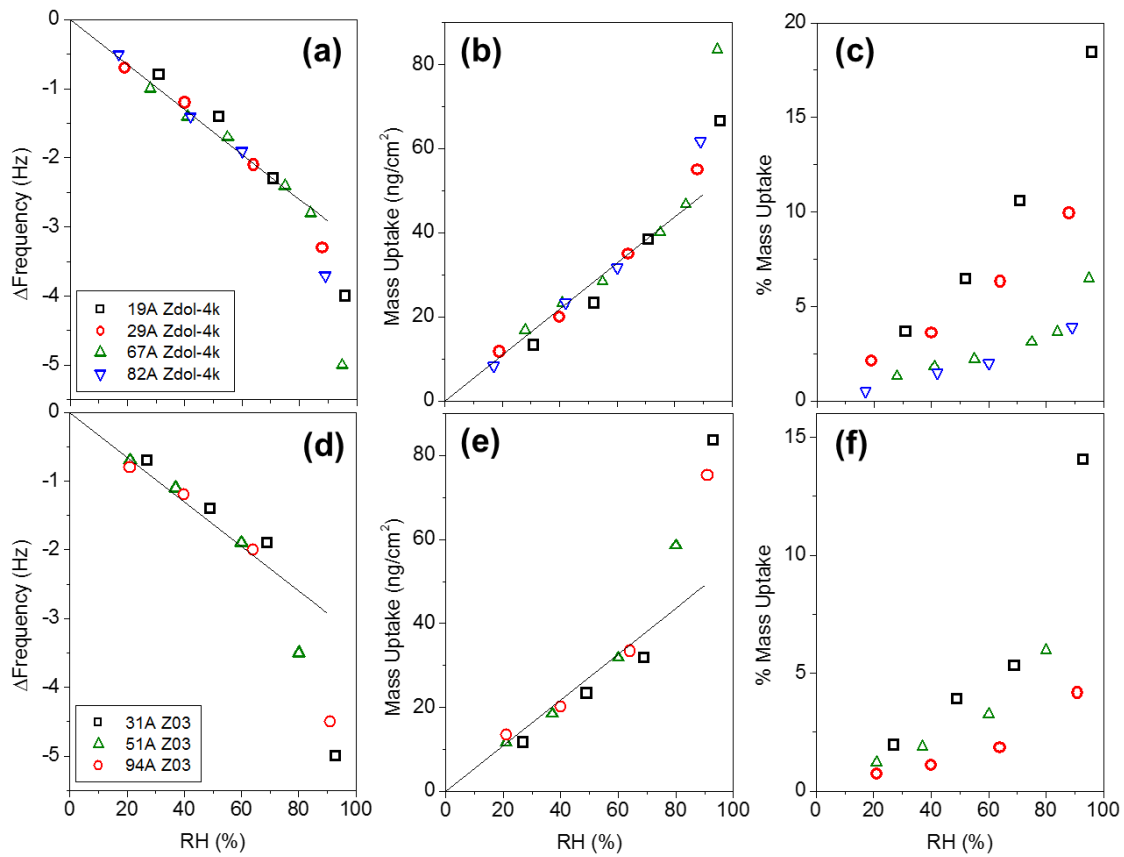**Figure 4. QCM frequency change as a function of time and of RH at 20 ºC for (a) 18.8 Å Zdol 4000; (b) 82 Å Zdol 4000; and (c) 32 Å Z03.**

Figure 5. Summary plots frequency change, mass uptake, and % mass uptake as a function of RH and of PFPE film thickness at 20 ^{o}C for (a) – (c) Zdol 4000 and (d) – (f) Z03.
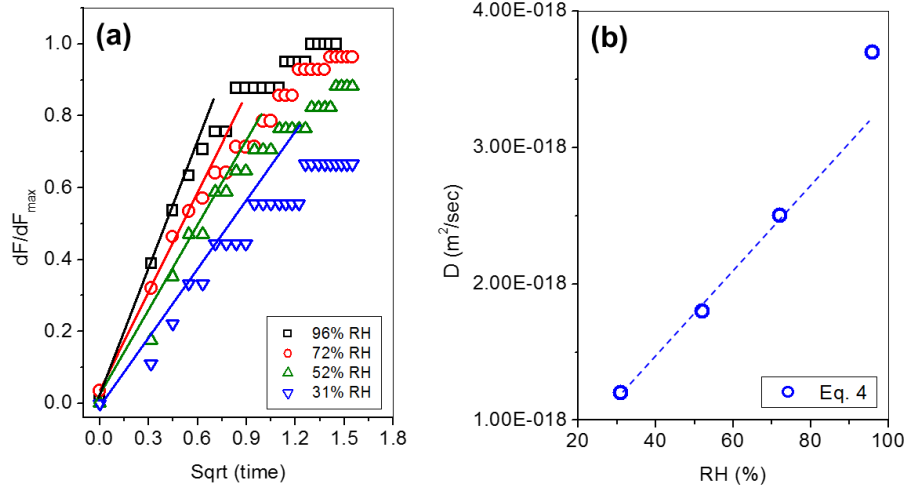
Figure 6. (a) The normalized frequency change as a function of time$^{1/2}$ at 20 ^{o}C for 18.8 Å Zdol 4000. (b) The experimental diffusion constant D as a function of RH at 20 ^{o}C for 18.8 Å Zdol 4000.
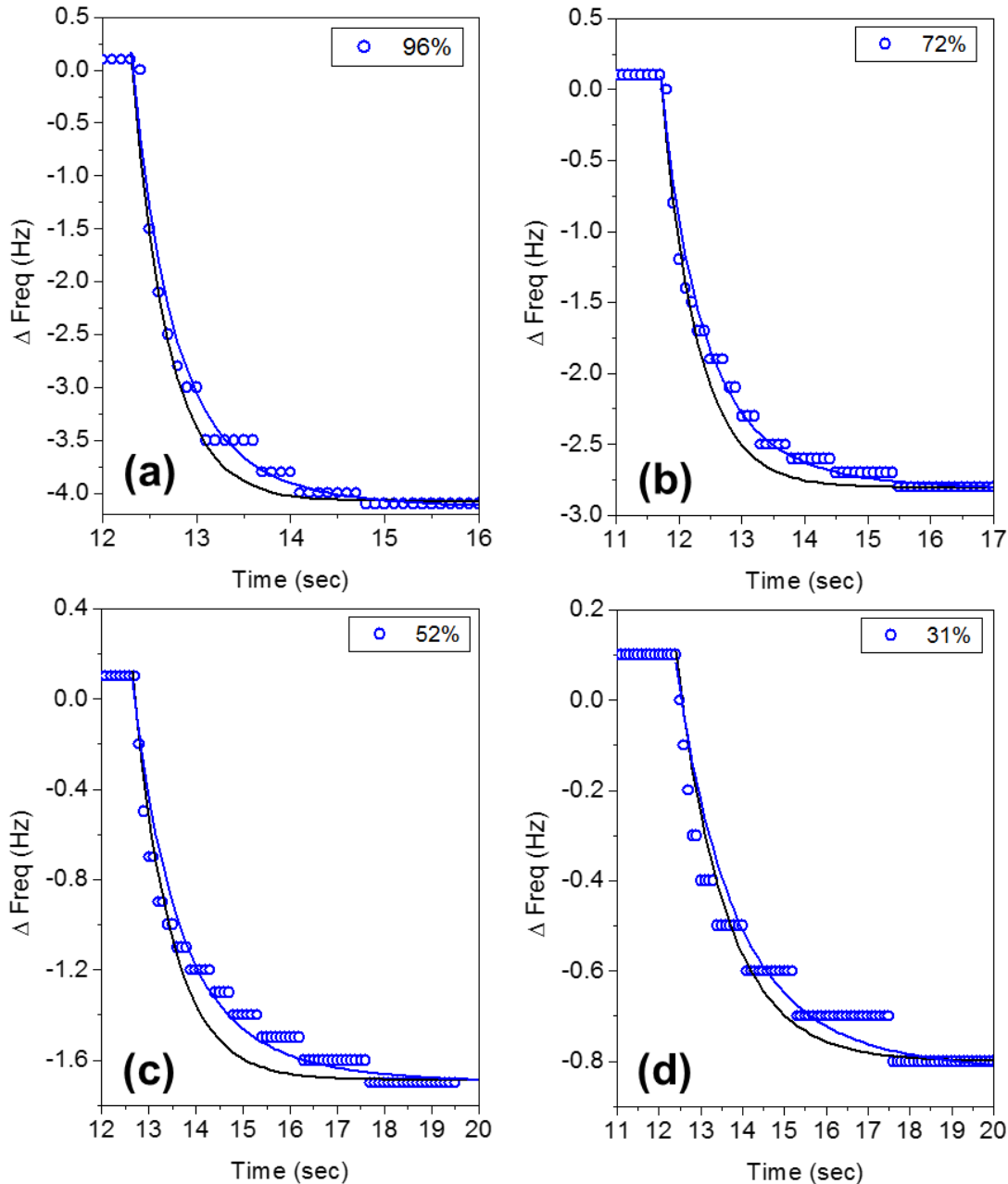
Figure 7. Fit to the adsorptive wave of 18.8 Å Zdol 4000 as a function of RH using the D values from Table 2 and Eq. 5 for: (a) 96 %; (b) 72 %; (c) 52 %; and (d) 31 % RH. Each figure plots the Fickian fit ($\varphi = 1.00$) as shown by the dashed curves and the two stage sorption model ($\varphi = 0.85$; $\psi = 1.00$) as shown by the solid curves. The experimental data points are shown by the black circles.
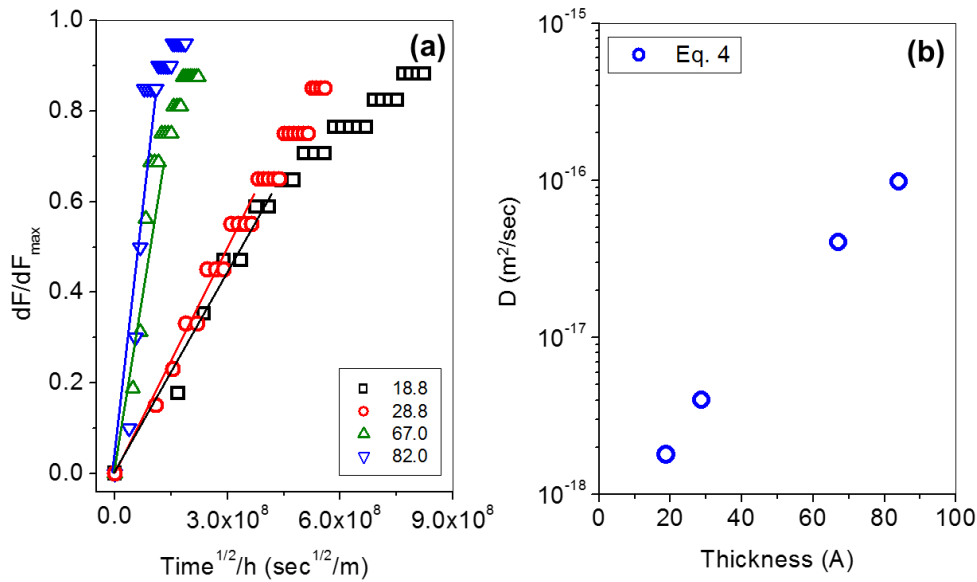
Figure 8. (a) The normalized frequency change as a function of time$^{1/2}$/h at 20 °C and 57 ± 4 % RH for Zdol 4000 as a function of the film thickness h. (b) The corresponding experimental diffusion constant D as a function of Zdol 4000 film thickness.
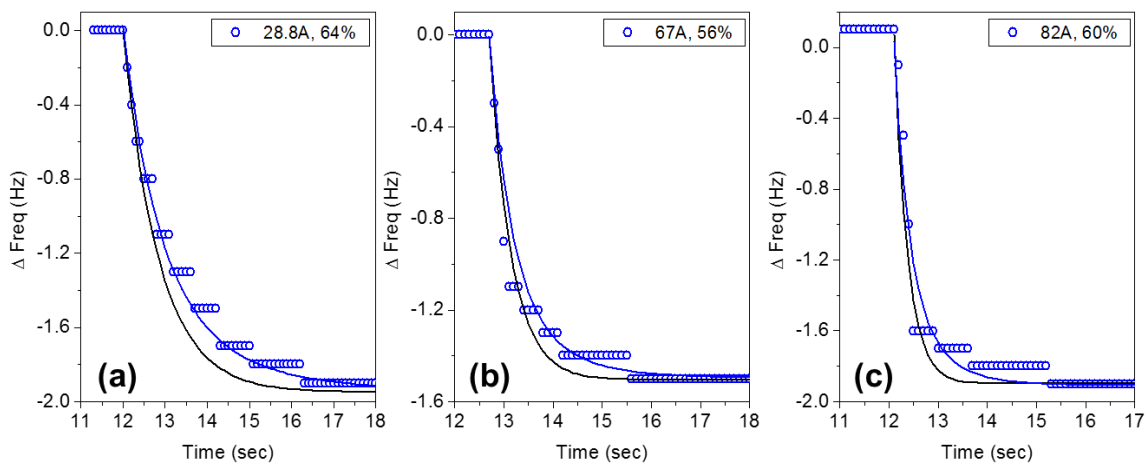

Figure 9. Fit to the adsorptive wave for (a) 28.8; (b) 67; and (c) 82 Å Zdol 4000 at 20 °C and 57 ± 4 % RH using the D values from Table 3 and Eq. 5. Each figure plots the Fickian fit ($\varphi = 1.00$) as shown by the dashed curves and the two stage sorption model ($\varphi = 0.85$; $\psi = 1.00$) as shown by the solid curves. The experimental data points are shown by the black circles.

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