Title: Kinetic and Equilibrium Sorption of Organic Liquids and Vapors in Matrimid

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Graphical Abstract

Kinetic and Equilibrium Sorption of Organic Liquids and Vapors in Matrimid

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This work examines the sorption, diffusion, and polymer relaxation behavior for a variety of organic penetrants in Matrimid. The diffusion-relaxation model for plasticizing penetrants in glassy polymers developed by Berens and Hopfenberg appropriately captures the kinetic behavior of the organic vapor/polymer systems.

Abstract

This work examines the kinetic and equilibrium sorption characteristics of a variety of chemical penetrants in the polyimide polymer Matrimid. Liquid equilibrium sorption for dense films with thicknesses of 50 μm for a large variety of organic species including alkanes, alcohols, acetates, furans, and ionic liquids is presented. Vapor equilibrium sorption isotherms and kinetic sorption behavior for water and C1-C6 alcohols as a function of chemical activity from 0 to 0.9 were measured using a quartz crystal microbalance with films ranging in thickness from 0.07 to 2.0 μm . Diffusion coefficients and relaxation parameters were calculated according to the diffusion-relaxation model for penetrants in glassy polymers. Diffusion coefficients at infinite dilution for water and C1-C6 alcohols are given as a function of van der Waals molar volume and a clear dependency is shown ranging from $2\text{E-}11$ to $6.5\text{E-}13$ cm^2/s for water and hexanol, respectively, for 0.26 μm thick films. Diffusion coefficients for all studied vapor penetrants displayed a marked dependence on thickness spanning approximately two orders of magnitude for each respective vapor penetrant over the range 0.1 to 1.0 μm . Penetrant-induced relaxation behavior accounts for the majority of mass sorption at chemical activities of 0.2 and above for the C1-C6 alcohol vapors.

Keywords

- 1.) Matrimid
- 2.) Kinetic sorption
- 3.) Equilibrium sorption
- 4.) Diffusion-relaxation
- 5.) Quartz crystal microbalance (QCM)

1. Introduction

1.1. Background

As novel applications for high performance polymers and membrane separation processes are developed, an understanding of the sorptive capacity and diffusion properties of the chemical species in which they are in contact must be further investigated. Examples of such novel applications include solvent resistant nanofiltration [1-3] and polymeric membrane reactors [4-7]. In these applications the polymeric membranes encounter chemical environments not often seen in more traditional gas separation processes, including exposure to highly plasticizing and swelling agents such as alcohols, furans, aromatics, and related hydrocarbons [1,8,9]. Gas, liquid, and vapor sorption and diffusion in polymers has been an active area of research for several decades with a large variety of penetrant sorption, diffusion, and polymer behaviors observed [10-16]. Experimental techniques for exploring these phenomena include standard gravimetry, magnetic suspension balance [14], quartz spring microbalance (QSM) [17], FTIR-ATR [13], quartz crystal microbalance (QCM) [18,19], NMR [20], time-lag permeation [21], and pressure decay (PD) [22].

This work investigates the equilibrium sorption of several solvents and the kinetic transport of water and short-chain alcohols in Matrimid 5218 using gravimetry and quartz crystal microbalance techniques. Quartz crystal microbalance is an excellent technique for measuring masses down to the order of nanograms and has been explored and applied for a variety of mass-sensitive uses including high pressure gas sorption [18,19,23], vapor sorption [13,24,25], chemical sensor applications [26,27], and ligand binding [28,29]. QCM was chosen for this work for its ability to examine films with thicknesses in the range of 0.05 to 5 μm , which

encompasses the range of thicknesses often observed in the dense layer of asymmetric polymeric membranes [30-33]. QCM also possesses the potential for high-throughput experimentation considering the use of inexpensive quartz crystals and the immediate availability for data collection assuming the chemical and temperature environments are appropriately controlled. Matrimid is a commercially available amorphous polyimide with a glass transition temperature of 320 °C, whose chemical structure is shown in Figure 1 [34]. Sorption of condensable vapors in glassy materials is often accompanied by swelling or volume dilation of the material [10,11]. In this work the diffusion-relaxation model developed by Berens and Hopfenberg is used to describe the kinetic transport of the studied vapors in Matrimid [10]. Diffusion coefficients and relaxation parameters for the penetrants in Matrimid are calculated using the diffusion-relaxation mathematical framework.

Figure 1 - Repeat unit of Matrimid 5218 polyimide.

1.2. Quartz crystal microbalance (QCM) measurement, calculation, and error

The technique of utilizing the piezoelectric property of appropriately cut quartz crystal to measure thin film deposition thickness was originally described and developed by Günter Sauerbrey [35]. The essence of the technique relies on applying an alternating electric field to electrodes on the faces of the cut crystal, which induces a directional mechanical deformation, or shear oscillation, in the crystal matrix [36]. Although the frequency of oscillation in the

crystal depends on crystal cut and thickness, each individual crystal has a unique fundamental frequency. When a thin film is deposited onto the electrodes of the crystal and is mechanically adhered, the frequency decreases in direct proportion to the deposited mass. This mathematical relation is known as the Sauerbrey equation:

$$\Delta f = \frac{2\Delta m f_0^2}{A(\mu_q \rho_q)^{1/2}} \quad (1)$$

where Δf is the frequency change, Δm is the mass change, f_0 is the fundamental frequency of the uncoated crystal, A is the active area of one face of the crystal, μ_q is the shear modulus of quartz (29.47 GPa), and ρ_q is the density of quartz (2.648 g/cm³).

QCM is a highly sensitive technique and is often described as having sub-nanogram mass resolution. There is an upper limit on QCM mass detection and it depends largely on the type of material adhered to the crystal and its viscoelastic properties. Other experiments in the literature investigating polymers using QCM generally work with film thickness less than 5 μm in efforts to avoid significant error induced from viscoelastic effects [18,37]. However, one source suggests that when measuring sorption in polymers, only thicknesses up to 0.2 μm may be considered absent of apparent mass uptake errors due to viscoelastic effects [36]. Although the work of [36] raises caution on the acceptable polymer film thickness, it does not exhaustively rule out the acceptability of using modestly thicker polymeric films. The work of Davis, *et al.* [25], investigated water vapor sorption in polylactide using QCM on a 7 μm film and obtained good agreement with measurements using quartz spring microbalance and ATR-FTIR. Other sources have discussed errors induced from imperfectly smooth quartz crystals, pressure, and temperature effects [19,23]. In this work all QCM measurements were taken at 30 °C and

all polymer coated crystals were exposed to the same thermal history in regards to preparation and drying. Also, all QCM measurements can be considered to be conducted at atmospheric pressure, therefore temperature and pressure induced anomalies should be minimized. Our work focuses on the range of approximately 0.1 to 2 μm , and all relevant figures except Figure 14, present data collected in the 0.2 to 0.3 μm range. Therefore, until a more exhaustive examination of polymer thickness induced errors for QCM vapor sorption analysis is reported, we will assume our results for polymer thicknesses 2.0 μm and lower are considered valid.

2. Experimental

2.1. Materials

AT-cut 5 MHz quartz crystals (1 inch diameter) were purchased from Inficon. Matrimid 5218 was purchased from Huntsman Advanced Materials and used as received. Dichloromethane (certified ACS, purity $\geq 99.9\%$) and all liquid penetrants (certified ACS, purity $\geq 99.9\%$) were purchased from Fisher Scientific or Acros Organics and used as received. A Maxtek Research Quartz Crystal Microbalance was used to perform all vapor sorption QCM experiments. Omega mass flow controllers (FMA5504 0-20SCCM) and ultrahigh purity nitrogen (Matheson Gas) were used for controlling gas phase compositions.

2.2. Equilibrium liquid sorption

Films were prepared from a 2 wt% solution of Matrimid powder dissolved in dichloromethane (DCM). The solution was allowed to dissolve for 48 hours and was 0.45 μm filtered before use. The solution was poured into casting rings with a diameter of 8 cm situated on glass plates where the solvent was allowed to evaporate overnight producing dense films with thicknesses on the order of 30-50 μm . The films were washed with DI water and placed in a vacuum oven at 70 °C for 24 hours. The films were submerged in the liquids of interest for 6 weeks and were then weighed weekly to determine the relative mass uptake. The films submerged in the liquids of interest at the specified temperature were removed, rapidly and carefully blotted dry within 10-15 seconds, and were placed on a balance for mass measurement. This 'blot and dry' technique is seen in several literature examples that examined liquid sorption in polymer films [11,38,39]. It is generally assumed that the mass of penetrant that diffuses and evaporates from the polymer surface is negligible compared to the total equilibrium amount sorbed. After

the sixth week measurement, when the subsequent weekly measurements of relative mass uptake (mass sorbed penetrant / mass polymer) varied by less than $\pm 5\%$ compared to the previous two weeks of measurements, the film was considered to have reached equilibrium with the liquid phase.

2.3. *Kinetic vapor sorption*

Vapor sorption experiments were performed with Matrimid spin-coated AT-cut quartz crystals. Matrimid in DCM solutions of 0.5 to 3 wt% were 0.45 μm filtered and about 1.5 mL of the desired solution was placed onto one surface of the crystal situated on the spin-coater. The acceleration of the spin-coating was 750 rpm/sec with a final velocity of 2500 rpm for a total spinning time of 60 seconds. The 0.5 to 3 wt% solutions produced thicknesses ranging from 0.05 to 2.0 μm , respectively, as calculated by the Sauerbrey equation [35]. The coated crystals were placed in a vacuum oven at 60 $^{\circ}\text{C}$ for 24 hours to ensure complete removal of solvent. After drying the coated crystals were placed in the QCM crystal holders under 10 mL/min flowing nitrogen at 30 $^{\circ}\text{C}$ for 6 hours to ensure thermal stabilization of the system. The crystal holders, gas lines, and liquid penetrant reservoir were all positioned inside an isothermal water bath.

Figure 2 - QCM Vapor Sorption Setup – FC denotes ‘flow controller’ and quartz crystal holder contains polymer coated crystal in an o-ring sealed cell with appropriate electrodes for QCM control. The dashed line indicates components were submerged in a temperature controlled (± 0.05 °C) water bath.

The vapor sorption experimental setup is shown in Figure 2. Two streams of nitrogen were proportioned and combined to provide a continuous total flow of 10 mL/min. One of the streams bubbles through a reservoir of the desired liquid penetrant to produce saturated vapor. In this way the chemical activity of the penetrant (P/P^{sat}) to which the polymer is exposed is controlled (± 1.5 % based on the accuracy of the flow controllers). The chemical activity was increased in 0.1 (0.2 for 48 h sorption interval experiments) step changes every 12 hours (or 48 hours for long term comparison experiments) across the activity range 0 to 0.9 for all penetrants studied. Nitrogen is considered an acceptable choice as the vapor phase carrier gas, because under experimental conditions (30 °C, atmospheric pressure) nitrogen sorption is approximately $88 \mu\text{g}/\text{cm}^3$ in comparison to the range of sorbed vapor penetrants being 0 to $2.7\text{E}5 \mu\text{g}/\text{cm}^3$ [33,40]. Frequency measurements were recorded at 1 sample/sec.

2.4. Calculations

Equilibrium liquid sorption values were calculated as the mass of solute or penetrant sorbed per mass of dry polymer, as shown in Equation (2).

$$m_{equil. sorption} = \frac{m_{pol+sol} - m_{dry polymer}}{m_{dry polymer}} \quad (2)$$

Equilibrium vapor sorption was calculated in a similar manner for each 0.1 chemical activity interval. The diffusion and relaxation model developed by Berens and Hopfenberg was used to describe the kinetic behavior of the polymer/penetrant systems and is shown in Equation (3).

$$m_{total} = m_F \left(1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^2} \exp \left[\frac{-D(2n+1)^2 \pi^2 t}{4L^2} \right] \right) + m_R (1 - \exp(-k_R t)) \quad (3)$$

The meanings of the terms in Equation (3) are shown in Table 1. This model separates the total amount of penetrant sorbed into sorption due to relatively rapid Fickian diffusion and sorption due to much slower polymer chain relaxations, $m_{total} = m_{diffusive} + m_{relaxation}$. Figure 3 exemplifies the separation of the diffusion and relaxation sorption processes and indicates what the model parameters represent. The relaxation portion is actually represented by an infinite sum of relaxation processes or stages, but for many polymer/penetrant systems only one relaxation term is needed to capture the behavior [10,13,14,41,42]. The assumption with applying this model is that the time constant for the diffusive sorption is sufficiently greater than that for the relaxation sorption, or more specifically that the Deborah number [43], shown in Equation (4), is much greater than unity.

$$De = \frac{D/L^2}{k} \gg 1 \quad (4)$$

Table 1 - Diffusion-relaxation model terms.

Term	Description
m_{total}	Total mass of penetrant sorbed due to diffusion and relaxation
m_F	Mass of penetrant sorbed due to Fickian diffusion
m_R	Mass of penetrant sorbed due to polymer chain relaxation
D	Diffusion coefficient of penetrant in polymer (cm^2/s)
L	Polymer film thickness (cm)
k_R	Relaxation constant (s^{-1})
t	Time (s)

Data analysis and model parameter calculations were performed using non-linear regression in MATLAB software.

Figure 3 - Ethanol sorption in Matrimid for an activity step change from 0.1 to 0.2 at $t = 0$ over a 12 h time period displayed to exemplify model parameter definitions and the associated approximate time intervals used.

3. Results and Discussion

3.1. *Equilibrium liquid sorption*

The equilibrium liquid sorption of several chemical species in Matrimid was determined at 30 °C unless otherwise indicated, and the results are displayed in Figure 4. The chemical species are approximately organized into three groups based on chemical identity and amount sorbed, namely, (1) alkanes, (2) alcohols, and (3) other organics, including furans, acetates, aromatics, and a few other highly sorbing species. All of the shown alcohols are of the normal isomeric form unless otherwise indicated. The highest sorbing chemicals in Figure 4 are on the apparent verge of acting as solvents for Matrimid, and one would anticipate that upon slightly elevating the temperature they would become solvents for Matrimid. The chemicals shown in Table 2 completely dissolved Matrimid at the indicated temperature. If one compares the chemical structures of the highest sorbing chemicals in Figure 4 to the listed solvents in Table 2, it is not surprising the relatively high observed amounts of sorption considering their similarity in chemical structure. A somewhat eclectic collection of solvents was tested for sorption in Matrimid, ranging from alkanes to ionic liquids. Rather than exhaustively testing a certain class of chemicals a variety was sought to guide choices for applicable non-solvents for future application development with Matrimid membranes in organic liquid/vapor systems.

Figure 4 - Equilibrium liquid sorption of indicated chemical species in Matrimid at 30 °C. * and ** indicate values taken from literature references at 35 °C and 25 °C, respectively [39,44]. Note that the y-axis ranges over 2 orders of magnitude for the chemical species listed. Species are approximately organized into three groups: alkanes , alcohols , and other organics . Exact values of mass of solute sorbed per mass of polymer can be found in Supporting Information Table A1.

Table 2 - Solvents for Matrimid. These listed chemicals dissolved films of Matrimid at the indicated temperature.

Chemical	Temperature (°C)
Tetrahydrofuran (THF)	25
Ethylbenzoate	25
Gamma-butyrolactone (GBL)	25
Gamma-valerolactone (GVL)	25
1-Ethyl-3-methylimidazolium chloride [EMIM]Cl	25
1-Ethyl-3-methylimidazolium acetate [EMIM]OAc	60

3.2. Equilibrium vapor sorption

The sorption of alcohol vapors (C1-C6) and water in the activity range 0 to 0.9 was measured using QCM and is shown in Figures 5 and 6, for 12 and 48 h intervals, respectively, for each activity step, represented as mass of solute per mass of Matrimid polymer. C3-C6 alcohols were all of the normal isomeric form. The 12 h sorption interval data presented in Figure 5 is

not considered to have reached true equilibrium at each activity level, and by comparing to the equivalent data in Figure 6 for 48 h sorption intervals one sees that the lower activity range (0 to ~0.5) was further from equilibrium than the latter half of the range. The data points for sorption at an activity of one in both Figures 5 and 6 were independent measurements of Matrimid films immersed in the respective liquid penetrant for approximately eight weeks, so more certainty can be placed on the upper bound of all of the presented isotherms. There is a high level of coincidence for the alcohol vapor data, which is not surprising considering the chemical similarity of the C1-C6 alcohols and their similar equilibrium liquid sorption values presented in Figure 4. The longer chain alcohols display a slightly higher sorption amount for each activity level, which is consistent with their relatively higher liquid equilibrium sorption amounts and expected greater condensability in the polymer. An inverse sigmoidal shape is seen for the C1-C6 alcohol isotherms, which is consistent with other literature observations for the sorption of plasticizing penetrants in glassy polymers [41,44-46].

Figure 5 - Vapor sorption for 12 h intervals in Matrimid at 30 °C for 0.1 chemical activity step changes. Values listed at an activity of 1 are taken from equilibrium liquid sorption of dense Matrimid films. All film thicknesses were 0.26 μm ($\pm 0.015 \mu\text{m}$). Error bars omitted for clarity. The standard deviation of six independent measurements of methanol isotherms was at most 5 % of the average value for each 0.1 activity increment.

Figure 6 - Vapor sorption for 48 h intervals in Matrimid at 30 °C for 0.2 chemical activity step changes. Values listed at an activity of 1 are taken from equilibrium liquid sorption of dense Matrimid films. Film thicknesses ranged from 0.50 to 0.70 μm . See Figure 5 caption for error discussion.

3.3. Penetrant-induced T_g depression

One implication of sorbing species into the polymer matrix is depression of the glass transition temperature of the polymer-penetrant system ($T_{g,\text{mixture}}$) in relation to the pure polymer T_g . This

phenomenon is well-described in the literature [47-49] and has alternatively been discussed as a penetrant-induced glass transition (P_g) [50]. An estimation of this effect is provided in Figure 7 as calculated by Chow's model [51] and the Fox equation, respectively, using the sorption isotherm data presented in Figure 6 (Figure 5 for water). These calculations are in modest agreement for the alcohols, however must still be viewed as only an estimate, as Chow's model requires the use of the difference in heat capacity of the polymer below and above its glass transition, ΔC_p . The ΔC_p for Matrimid was not directly available in the literature, so an estimate of 0.1 J/gK was used, as determined from a correlation presented by Ref. [52] between ΔC_p and CO_2 diffusivity for a series of polyimides (using $D_{\text{CO}_2/\text{Matrimid}} = 3\text{E-}8 \text{ cm}^2/\text{s}$ [53]). Despite Figure 7 being treated as estimates, the general conclusion to infer is that even under low alcohol penetrant activity conditions (0 to 0.2), the $T_{g,\text{mixture}}$ may be depressed substantially more than 100 °C for all of the alcohol penetrants. This observation has importance as we seek to employ Matrimid and related polymers in membrane applications requiring elevated temperatures and organic liquid/vapor environments.

Figure 7 - T_g depression as calculated by Chow's model (—) and Fox equation (---) using sorption isotherm data. It is stressed that these calculations are estimates.

3.4. Kinetic vapor sorption

3.4.1. Diffusion

Thermodynamically corrected diffusion coefficients for water and C1-C6 alcohols as a function of chemical activity are presented in Figure 8. The transport, or uncorrected, diffusion coefficients can be found in the Supporting Information. The thermodynamic correction factor arises from the nonlinearity in the sorption isotherm, as seen in Figures 5 and 6 where there is significantly higher extents of sorption at very low and high chemical activities. The correction factor is described in detail in [54] and has been applied by others investigating diffusion in non-solvent/polymer systems [55]. The form of the correction factor is given in Equation (5).

$$D = D_{TC} \frac{d \ln p}{d \ln q} \quad (5)$$

where p is the partial pressure of the penetrant, q is the concentration or loading of penetrant in the polymer, and D_{TC} is the thermodynamically corrected diffusivity.

The diffusion coefficients are plotted at the midpoint value of the chemical activity step. For example, the diffusion coefficient for the activity step from 0.1 to 0.2 is plotted at an activity of 0.15. The first general observation is the clear trend that the longer the alkyl chain, the smaller the diffusion coefficient. The diffusional behavior of water is in contrast to the alcohols in that the diffusion coefficient slightly decreases as a function of activity. This is attributed to the clustering behavior that water undergoes at higher activities where water moves in multi-molecular clusters rather than single molecules. More in depth characterization of this behavior is described by others looking strictly at water diffusion in their glassy polymer of interest [13,56,57].

Figure 8 – Thermodynamically corrected vapor diffusion coefficients in Matrimid at 30 °C as a function of chemical activity. All initial film thicknesses were 0.26 μm ($\pm 0.015 \mu\text{m}$). Error bars omitted for clarity. See Supporting Information for error analysis, which places approximately $\pm 25\%$ error on the diffusion coefficient values reported. Lines added for visual aid.

Figure 9 presents diffusion coefficients at infinite dilution for water and the C1-C6 alcohols in Matrimid as a function of van der Waals molar volume. Infinite dilution was estimated by fitting an exponential curve to the data in Figure 8 and extrapolating to an activity of 0. The

trend of decreasing diffusion coefficient with increasing molecular volume is commonly seen in penetrant/glassy polymer systems [30,60].

Figure 9 - Diffusion coefficients at infinite dilution for the indicated chemical species in Matrimid at 30 °C as a function of van der Waals molar volume. All film thicknesses were 0.26 μm ($\pm 0.015 \mu\text{m}$). Error bars represent one standard deviation for 15 independent samples for methanol sorption. See Supporting Information for expanded error discussion.

Figure 10 displays the ethanol sorption profile for 0.1 activity steps every 12 hours. The diffusive portions of each interval are easily identified and are displayed in Figure 11. The general appearance of the sorption profile and respective diffusive portions for each activity interval displayed in Figures 10 and 11 are representative of the other alcohol penetrants studied, C1 and C3-C6. Corresponding sorption profiles can be found in the Supporting Information. Figure 12 gives the sorption profile for propanol using 0.2 activity steps over 48 hour intervals and is included here for comparison to Figure 10 to show the extent of continued relaxation induced sorption over the extended time period.

Figure 10 - Ethanol sorption profile for 0.1 chemical activity steps every 12 h at 30 °C. Film thickness = 0.278 μm .

Figure 11 - Initial short-time interval for each 0.1 activity step change for ethanol sorption. $\Delta t = 1$ second. (---) represents fit BH equation. D_F signifies the Fickian or transport diffusion coefficient. D_{TC} signifies the thermodynamically corrected diffusion coefficient. It was determined that the sorption data for activity change 0 to 0.1 exhibited Case II diffusion, so coefficients are not reported for that interval.

Figure 12 - Propanol sorption profile for 0.2 chemical activity steps every 48 h at 30 °C.

One consideration with extracting diffusion coefficients from sorption data is what diffusion regime the sorption data exhibits, *i.e.* Case I, anomalous, or Case II diffusion. A method to classify the diffusion regime present is to fit the initial portion of the sorption curve with the equation $M/M_{\infty} = kt^n$ over the respective time interval for $M/M_{\infty} < 0.5$. A value of $n = 0.5$ suggests purely Fickian diffusion, $0.5 < n < 1.0$ indicates anomalous diffusion, and $n = 1$ indicates Case II diffusion. Case I and anomalous diffusion behavior are considered appropriate for determining regressed diffusion coefficients in Fickian and Berens-Hopfenberg frameworks, respectively. Case II sorption data is generally not considered appropriate for Fickian or Berens-Hopfenberg analysis due to conflation of penetrant diffusion and the moving front velocity of the penetrant within the polymer [55,58,59]. A sorption case analysis for each penetrant is provided in the Supporting Information. For all of the penetrants studied it was found that the first activity step from 0 to 0.1 nominally exhibited Case II diffusion, however, that initial step also included the actuation of the penetrant stream flow valve producing a non-instantaneous

activity change, which influences the first few seconds of sorption. Regardless of the physical reason, the value of n for that step for all penetrants and film thicknesses was approximately 1, therefore the extracted coefficients for an activity step from 0 to 0.1 are not included in any relevant figures. All subsequent 0.1 activity steps from 0.1 to 0.9 for all penetrants and film thicknesses (~ 0.07 to $1.5\ \mu\text{m}$) had n values in the range 0.5 to approximately 0.9.

A notable challenge in determining accurate diffusion coefficients was estimating the film thickness increase as a function of activity. Although no experimental dilatometric values for C1-C6 alcohols in Matrimid could be found in the literature, detailed swelling measurements for CO_2 sorption in Matrimid are given in [53]. At 30 bar of CO_2 pressure, the solubility in Matrimid was reported as approximately $65\ \text{cm}^3(\text{STP})/\text{cm}^3$ and film thickness increase given on the order of 4-5 %. Another source provides regressed values for swelling parameters used when applying the non-equilibrium lattice fluid model to Matrimid-methanol and Matrimid-acetone systems [44]. One may then use those parameters to calculate polymer/penetrant system density as a function of penetrant activity, and assuming isotropic film expansion, make some estimate regarding film thickness. Calculations show that the thicknesses at an activity of 1 and temperature of $30\ ^\circ\text{C}$ increase by 5 and 16 % for methanol and acetone, respectively. In the absence of experimentally determined thicknesses, it seems reasonable based on [53] and [42] to estimate a thickness increase on the order of 5-10 % at an activity of 1 for the alcohol vapor/Matrimid systems. Therefore, diffusion calculations were performed assuming a 5 % increase in film thickness for C1-C3 alcohols, 10 % increase for C4-C6 alcohols, and no increase for water at a chemical activity of 1. The larger increase for C4-C6 was decided based on the higher sorption amounts for the longer alkyl-chain alcohols, as shown in Figures 5 and 6, and

conversely no increase for water due to its significantly lower sorption amount by comparison. Figure 8 assumes a linear increase in thickness over the entire activity range, although sources do indicate that increases in volume are greater at higher activities [42]. It is noted, though, that increasing the film thickness by 10 % in the calculation only increases the diffusion coefficient value by approximately 20%, which is still within the margin of error given for our reported diffusion coefficients. The Supporting Information provides an expanded error analysis and discussion.

3.4.2. Polymer relaxation

Penetrant-induced polymer relaxation is a well-documented phenomenon observed in glassy polymers for a wide variety of penetrants, including noble gases [14], CO₂ [19], water vapor and liquid [17], and organic vapors and liquids [10,55,60]. It is often classified as non-Fickian diffusion or sorption behavior and is usually observed on several orders of magnitude longer time scales than Fickian diffusion processes for glassy polymer/penetrant systems. When the initial observed Fickian diffusion process occurs on a time scale comparable to the penetrant-induced polymer relaxation and consequent sorption, it is difficult or even impossible to isolate the two processes and only the superposed sorption behavior is empirically visible. To separate the two phenomena, the Deborah number, which is the ratio of the time constants for the Fickian sorption process and the penetrant-induced relaxation sorption process, must be significantly greater than unity ($De \gg 1$). In the case that the system seems to present strictly Fickian behavior, relaxation may also still be occurring, but its contribution to overall sorption is either insignificant or negligible over the time scale of observation.

The parameters associated with the relaxation portion of sorption are $\phi = m_F$, which is the fraction of total mass uptake for an activity interval that is attributed to the initial Fickian sorption process (conversely, $1 - \phi$ represents the fraction of sorption that is attributed to the penetrant induced relaxation process), and k , the relaxation parameter. These values can be found in the Supporting Information.

Deborah numbers were calculated for all chemical species using the associated diffusion coefficient values and k values for each 0.1 activity interval (excluding 0 to 0.1 for reasons described in Section 3.4.1) and the initial film thickness. All calculated Deborah numbers were greater than two orders of magnitude above unity, except those for the C4-C6 alcohols at activity less than 0.3, as shown in Figure 13. This observation supports the ease of separating the initial diffusive sorption from the relaxation sorption stages. As expected, the trend of the Deborah numbers for all of the penetrants is quite similar to the diffusion coefficient trend, as the relaxation parameter for all penetrants only varied by approximately a factor of 4 across the entire activity range. Relaxation parameter values for the studied vapor penetrants for 0.26 μm films are shown in Supporting Information Figure A2.

Figure 13 – Deborah number as a function of chemical activity calculated using regressed diffusion coefficients and relaxation parameters. All film thicknesses were $0.26 \mu\text{m}$ ($\pm 0.015 \mu\text{m}$).

3.5. Thickness dependence on diffusion and relaxation

Figure 14 displays diffusion coefficients at infinite dilution for water and C1-C6 alcohols over a film thickness range of 0.07 to $2 \mu\text{m}$. Values at infinite dilution were determined by extrapolating an exponential curve fit to thermodynamically corrected diffusion coefficients over an activity range of 0.1 to 0.4 to an activity of 0 . There is a clear trend of decreasing diffusion coefficient values as film thickness decreases. This phenomenon has been shown to occur for a variety of penetrant/polymer systems, not only for diffusion [56,61,62] but for other physical phenomena, including changes in glass transition temperature [63], polymer dynamics [64], and permeability [65-67]. Thickness-dependent phenomena in glassy polymer systems are often correlated to the accelerated effects of physical ageing and loss of fractional free volume (FFV) with decreasing thickness [68,69]. There are also discussions related to the increasing dependence on the environment at the interface of the polymer film surface and the media with which it is in contact, for example free-standing films versus supported films [70-72].

It is notable that the water and methanol diffusion coefficients span over two orders of magnitude for only a single order of magnitude in thickness over the range 0.1 to 1.0 μm . This observation becomes extremely important if one considers the submicron effective thicknesses of polymers used in applications such as membrane separations, coatings, and drug delivery. Extrapolating measurements of thick films or bulk systems where the properties are measured on samples with thicknesses greater than 1 μm may lead to incorrect predictions for the transport behavior of the systems. Figure 14 gives additional data for water diffusion coefficients in Matrimid at infinite dilution from [56] for comparison to values obtained for thick films (regressed from film permeation data at 35 $^{\circ}\text{C}$). Another noteworthy observation is that the water diffusion coefficient values in [56] are also given as a function of activity spanning an activity range 0 to 1 and decreased by a factor of approximately three over that range. This is nearly identical to the trend for water diffusion coefficients reported here, as shown in Figure 8. No dependence of the relaxation parameter, k , on film thickness could be discerned over the thickness range studied in this work, approximately 0.1 to 2 μm .

Figure 14 - Diffusion coefficients at infinite dilution for the indicated chemical species at 30 °C as a function of film thickness. The filled symbols (●) represent diffusion coefficients for water in Matrimid at 35 °C taken from [56] for comparison to thick film values. An expanded view of this plot is found in the Supporting Information.

4. Conclusions

This work has presented the equilibrium sorption of a large variety of liquid penetrants in Matrimid. Also presented was the kinetic and equilibrium sorption of water and C1-C6 alcohol vapors in Matrimid at 30 °C. Isotherms for these species over the chemical activity range 0 to 1 are given. Significant polymer relaxation behavior was observed over the entire activity range for all penetrants. Vapor sorption, diffusion, and polymer relaxation were measured using a quartz crystal microbalance. Diffusion coefficients and relaxation parameters were regressed from the data by applying the diffusion-relaxation model developed by Berens and Hopfenberg, which appropriately captured the behavior of the studied penetrant/polymer systems. Analysis of the Deborah number for all of studied systems indicated clear separation of diffusional and relaxation sorption processes. Film thicknesses studied ranged from 0.07 to 2.0 μm and an approximate two to one order of magnitude dependence of diffusion coefficients on film thickness was determined for all penetrants.

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Captions for Figures and Tables	
Figure 1	Repeat unit of Matrimid 5218 polyimide.
Figure 2	QCM Vapor Sorption Setup – FC denotes ‘flow controller’ and quartz crystal holder contains polymer coated crystal in an o-ring sealed cell with appropriate electrodes for QCM control. Dashed line indicates components were submerged in temperature controlled (± 0.05 °C) water bath.
Figure 3	Ethanol sorption in Matrimid for an activity step change from 0.1 to 0.2 at $t = 0$ over a 12 h time period displayed to exemplify model parameter definitions and the associated approximate time intervals used.
Figure 4	Equilibrium liquid sorption of indicated chemical species in Matrimid at 30 °C. * and ** indicate values taken from literature references at 35 °C and 25 °C, respectively [39,43]. Note that the y-axis ranges over 2 orders of magnitude for the chemical species listed. Species are approximately organized into three groups: alkanes , alcohols , and other organics . Exact values of mass of solute sorbed per mass of polymer can be found in Supporting Information Table A1.
Figure 5	Vapor sorption for 12 h intervals in Matrimid at 30 °C for 0.1 chemical activity step changes. Values listed at an activity of 1 are taken from equilibrium liquid sorption of dense Matrimid films. All film thicknesses were 0.26 μm (± 0.015 μm). Error bars omitted for clarity. The standard deviation of six independent measurements of methanol isotherms was at most 5 % of the average value for each 0.1 activity increment.
Figure 6	Vapor sorption for 48 h intervals in Matrimid at 30 °C for 0.2 chemical activity step changes. Values listed at an activity of 1 are taken from equilibrium liquid sorption of dense Matrimid films. Film thicknesses ranged from 0.50 to 0.70 μm . See Figure 5 caption for error discussion.
Figure 7	T_g depression as calculated by Chow's model (—) and Fox equation (- - -) using sorption isotherm data. It is stressed that these calculations are estimates.
Figure 8	Thermodynamically corrected vapor diffusion coefficients in Matrimid at 30 °C as a function of chemical activity. All initial film thicknesses were 0.26 μm (± 0.015 μm). Error bars omitted for clarity. See Supporting Information for error analysis, which places approximately ± 25 % error on the diffusion coefficient values reported. Lines added for visual aid.
Figure 9	Diffusion coefficients at infinite dilution for the indicated chemical species in Matrimid at 30 °C as a function of van der Waals molar volume. All film thicknesses were 0.26 μm (± 0.015 μm). Error bars represent one standard deviation for 15 independent samples for methanol sorption. See Supporting Information for expanded error discussion.
Figure 10	Ethanol sorption profile for 0.1 chemical activity steps every 12 h at 30 °C. Film thickness = 0.278 μm .
Figure 11	Initial short-time interval for each 0.1 activity step change for ethanol sorption. $\Delta t = 1$ second. (- - -) represents fit BH equation. D_F signifies the Fickian or transport diffusion coefficient. D_{TC} signifies the thermodynamically corrected diffusion coefficient. It was determined that the sorption data for activity change 0 to 0.1 exhibited Case II diffusion, so coefficients are not reported for that interval.
Figure 12	Propanol sorption profile for 0.2 chemical activity steps every 48 h at 30 °C.

Figure 13	Deborah number as a function of chemical activity calculated using regressed diffusion coefficients and relaxation parameters. All film thicknesses were 0.26 μm (± 0.015 μm).
Figure 14	Diffusion coefficients at infinite dilution for the indicated chemical species at 30 °C as a function of film thickness. The filled symbols (●) represent diffusion coefficients for water in Matrimid at 35 °C taken from [56] for comparison to thick film values. An expanded view of this plot is found in the Supporting Information.
Table 1	Diffusion-relaxation model terms.
Table 2	Solvents for Matrimid. These listed chemicals dissolved films of Matrimid at the indicated temperature.