

Vapor Sorption–Desorption Phenomena of HD and GB Simulants from Polyurethane Thin Films on Aluminum Oxide via a Quartz Crystal Microbalance

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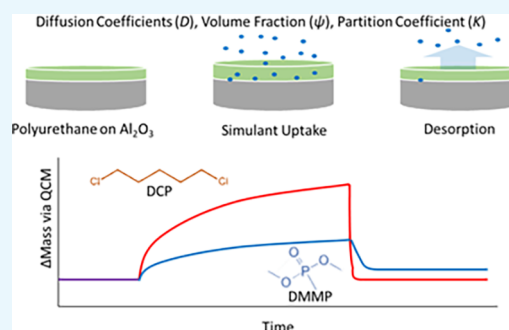


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Supporting Information

ABSTRACT: Protection and decontamination of surfaces after exposure to chemical warfare agents (CWAs) are of considerable interest to the homeland defense and battlespace operation communities. In this work, polyurethane was spin-coated onto aluminum oxide quartz crystal microbalance (QCM) sensors. Polyurethane film thickness was varied by altering the concentration of the polymer/chloroform solution used for spin-coating. Atomic force microscopy confirmed the formation of smooth, homogeneous films on the QCM sensor surface. Aluminum oxide QCM sensors coated with polyurethane were exposed to saturated vapors of dichloropentane (DCP), a mustard gas (HD) simulant, and dimethyl methylphosphonate (DMMP), a sarin gas (GB) simulant, and the mass uptake, diffusion coefficient, volume fraction, and partition coefficient of the simulant in the film were determined from QCM data. Results showed that both DCP and DMMP readily sorbed into the films although the mass uptake of DCP was greater than that of DMMP owing to DCP's higher vapor pressure. Additionally, the CWA simulant uptake increased with polyurethane film thickness. Sorption diffusion coefficients were 1×10^{-13} cm²/s and 1×10^{-12} cm²/s for DCP and DMMP vapor, respectively. Simulant desorption was also measured and showed that some DMMP remained in the film/substrate system, while DCP sorption was fully reversible. Reversible desorption for both CWA simulants was relatively quick and independent over the range of film thicknesses studied, with average desorption diffusion coefficients of 2×10^{-9} cm²/s and 1×10^{-11} cm²/s for DCP and DMMP, respectively. Collectively, this study is expected to inform protection and decontamination strategies of equipment and structures upon exposure to CWAs.



INTRODUCTION

Chemical warfare agents (CWAs) present challenges not only because of their inherent toxicity but also because of their persistent nature. Agents such as sulfur mustard (HD) and sarin (GB) have relatively low vapor pressures and will readily sorb to a variety of metal substrates and porous polymer coatings.¹ The study of CWA mass transport onto aluminum oxide coated with polyurethane is relevant as a wide variety of military vehicles and equipment are composed of aluminum and coated with paint (e.g., polyurethane or alkyd). For additional protection, a chemical agent-resistant coating (CARC) is sometimes applied to vehicle surfaces and consists of a polyurethane coating over a primer.² Regardless, after the initial vapor from a CWA release has dissipated, contaminated materials may continue to off-gas lethal levels of agent for days.^{2,3} Consequently, the study of sorption and desorption phenomena of CWAs to a variety of surfaces and coatings is of interest to the homeland defense and battlespace operation communities. In particular, determination of diffusion coefficients of CWAs within an aluminum oxide/polyurethane substrate and volume fractions and partition coefficients are

useful parameters for the development of models focused on decontamination procedures.^{3,4}

Much of the literature on CWAs has focused on detection and decontamination,^{1,5,6} while relatively few studies have studied the mass uptake and transport of CWAs into polymers and paints.^{3,4,7–9} More often, these studies instead use less toxic CWA simulants to model the sorption and desorption behavior of an agent.^{2,9–14} In these works, desorption diffusion coefficients are usually determined by exposing a surface to a liquid chemical agent or simulant for about an hour, removing the liquid, and then measuring vapor off-gassing from the surface as a function of mass loss over time.^{2,7,8,12–14} Desorption diffusion coefficients for HD and GB vapor from polyurethane and alkyd films were generally on the order of

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10^{-10} to 10^{-11} cm^2/s , respectively.^{7,8} Likewise, the desorption diffusion coefficients for HD simulants ranged from 10^{-7} to 10^{-10} cm^2/s , while GB simulant values ranged from 10^{-9} to 10^{-15} cm^2/s .^{2,9,12–14} The range of values for the desorption diffusion coefficients across the literature is attributed primarily to differences in the types of polymer substrates as the uptake and mass transport of CWAs and CWA simulants in each substrate will vary depending on the intermolecular attractions and permeability of the system.^{2,10,14}

Several novel studies employed alternative methods to measure uptake and sorption phenomena. Willis et al. determined both the evaporation and absorption rate of liquid HD applied to a permeable silicone substrate by monitoring sessile drop profiles, calculating a sorption diffusion coefficient on the order of 10^{-7} cm^2/s . As might be expected, increasing the temperature of the experiment increased diffusivity according to an Arrhenius-type relationship.^{3,4} A Love wave acoustic sensor has also been used to detect both in situ sorption and desorption upon exposure of a polysiloxane polymer to GB and DMMP vapor, enabling determination of the partition coefficient, as well as the sorption and desorption diffusion coefficients. Both diffusion coefficients were around 10^{-15} cm^2/s , though desorption was generally faster than sorption. Diffusion coefficients were also determined for films ranging in thickness from 15 to 40 nm, with thicker films yielding faster diffusion, presumably because of a higher surface roughness and porosity of the thicker films.⁹ Also of note, a quartz crystal microbalance (QCM) was used to determine the uptake and volume fraction of HD simulants on a thin polyurethane film.¹¹ Again, though, these studies illustrate the variability of mass transport parameters based on the coating.

Consequently, to improve models for CWA uptake and mass transport, it is relevant to study the sorption and desorption of CWA simulants from various substrates and coatings. In this work, the vapor sorption and desorption of CWA simulants from an aluminum oxide substrate coated with a model polyurethane was studied via a QCM. Films of varying polyurethane thickness were generated by spin-coating, and the polymer film thickness was measured by ellipsometry. Polyurethane/aluminum oxide substrates were then exposed to saturated vapors of dimethyl methylphosphonate (DMMP) and 1,5-dichloropentane (DCP). DMMP and DCP are commonly used simulants for GB and HD, respectively, due to their lower toxicity and similar chemical behavior as the actual agents.^{11,15} The mass uptake was monitored with time, and the sorption and desorption coefficients, partition coefficients, and volume fractions of the simulants were determined from QCM data. Collectively, the results of this work are expected to provide CWA simulant mass transport parameters for a polyurethane/aluminum oxide system while also highlighting the utility for acoustic-based mass sensing methods like the QCM for studying CWA sorption and desorption phenomena in situ.

RESULTS AND DISCUSSION

The mass uptake and transport of CWA simulant vapors into polyurethane thin films coating aluminum oxide was studied using a QCM. Polyurethane films of various thicknesses were generated by spin-coating from solutions of 0.4–1.0 wt% polyurethane dissolved in chloroform.¹¹ Film thickness of the spin-coated films was measured via ellipsometry (Table S1). Atomic force microscopy (AFM) confirmed that the spin-

coated polyurethane films were smooth and homogeneous (Figure S1).

Sorption of DMMP and DCP vapors to aluminum oxide and polyurethane-coated aluminum oxide sensor crystals was measured in situ via a QCM. Sensor crystals were mounted into a modified crystal holder that permitted injection of DMMP or DCP liquid through the lid and into a reservoir, creating a saturated vapor environment above the crystal surface (Figure 1). The substrate was exposed to the saturated DMMP or DCP vapor for 1 h.

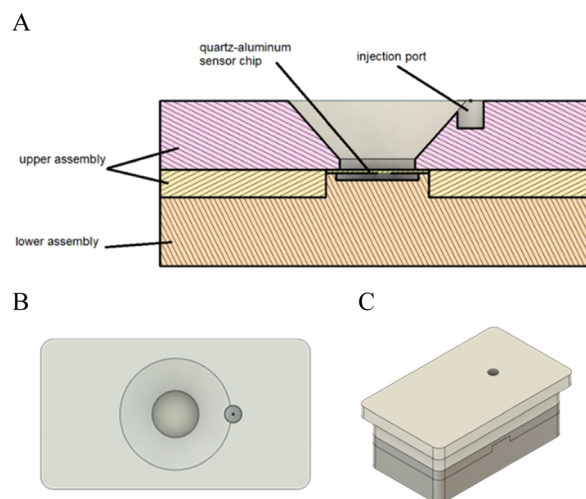


Figure 1. Schematic depicting the (A) plane view, (B) top view, and (C) assembled QCM crystal holder with a lid used in this work. A hole was drilled through the lid and into the upper assembly of the holder to create a sample reservoir for injecting the CWA simulant.

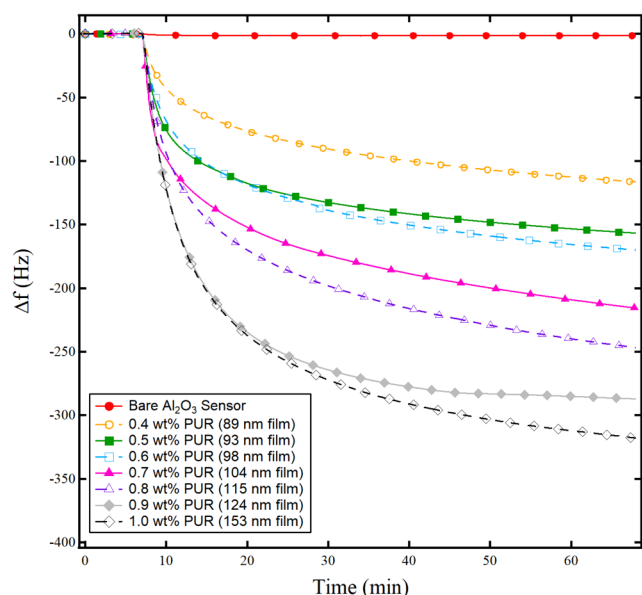
Upon injection of the CWA simulant into the reservoir, the measured resonant frequency of the QCM crystal sensor decreased, indicating vapor sorption to the substrate. While a detailed review of the QCM is outside the scope of this work, monitoring changes in the resonant frequency of the QCM crystal is the basis of measurement. Central to this technique is the piezoelectricity of quartz—application of alternating current to the specifically cut quartz crystal plated with metal electrodes induces a standing shear wave at a particular resonant frequency. Changes in the physical environment coupled to the QCM sensor crystal change the resonant frequency of the crystal.¹⁶ While a QCM has been used to study a variety of phenomena, vapor transport within a rigid film can be quantified in a straightforward manner via the Sauerbrey equation:¹⁷

$$\Delta m = -C_f \left(\frac{\Delta f}{n} \right) \quad (1)$$

where Δf is the change in frequency caused by vapor sorption or desorption to the sensor substrate, n is the frequency overtone ($n = 3$ for this work), and C is the Sauerbrey constant ($0.0177 \mu\text{g}\cdot\text{s}\cdot\text{cm}^{-2}$). Thus, for the case of vapor transport within a rigid film, a decrease in frequency indicates vapor uptake.

Changes in QCM sensor resonant frequency upon exposure of polyurethane-coated aluminum oxide substrates to saturated vapors of DCP and DMMP are shown in Figure 2. A CWA simulant exposure time of 60 min was chosen for consistency with other studies.^{7,13} As evident from Figure 2, the resonant

A. DCP



B. DMMP

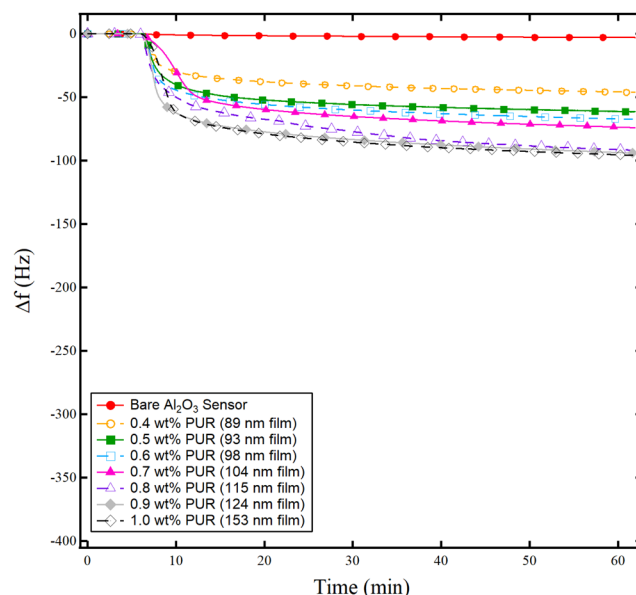


Figure 2. Example data for the change in resonant frequency (Δf) with time for different thicknesses of polyurethane-coated aluminum oxide QCM sensors upon exposure to (A) DCP and (B) DMMP.

frequency significantly decreased upon injection of the CWA simulant into the sample reservoir, indicating vapor uptake. Though not readily apparent, the frequency for the bare aluminum oxide sensor without polyurethane coating did decrease slightly upon exposure to DMMP. While few studies have used DCP as a simulant, DMMP is known to irreversibly adsorb to the surface of aluminum oxide.¹⁸

However, the frequency decrease for polyurethane-coated aluminum oxide substrates was much larger than that for the bare surface, indicating significant uptake of the CWA simulant vapor within the polymer film. This uptake increased with film thickness, highlighting the permeability of the polyurethane to the CWA simulants. As evident from the larger frequency decreases, DCP uptake into the polyurethane was significantly greater than that of DMMP. As DCP has a higher saturated vapor pressure than DMMP (150 Pa vs 79 Pa) at 25 °C, this result was not unexpected.^{19,20}

The change in mass with polyurethane film thickness after exposure to DCP and DMMP saturated vapors is provided in Figure 3. To generate this figure, the total change in frequency at a particular polyurethane thickness after CWA simulant exposure was converted to change in mass using the Sauerbrey equation (eq 1). Dissipation changes were less than 5% of the scaled frequency change, indicating that use of the Sauerbrey equation was valid.²¹ The increase in DCP and DMMP mass uptake with polyurethane film thickness generally appears linear. The saturation concentration of the CWA simulant within the polyurethane film was determined by dividing the absorbed mass ($\mu\text{g}\cdot\text{cm}^{-2}$) by the film thickness, resulting in values of $0.33 \pm 0.06 \text{ g}\cdot\text{cm}^{-3}$ and $0.12 \pm 0.02 \text{ g}\cdot\text{cm}^{-3}$ for DCP and DMMP, respectively. To our knowledge, saturation concentrations for DCP and DMMP into polyurethane thin films have not been previously reported, but the result is comparable to that of HD ($0.17 \text{ g}\cdot\text{cm}^{-3}$) and VX ($0.05 \text{ g}\cdot\text{cm}^{-3}$) into paint.⁷ Of note, saturation concentrations of CWAs and CWA simulants will vary between materials for a variety of reasons, to include chemical interactions, and factors affecting thin film permeability.^{2,10,14} The concentration value for DCP

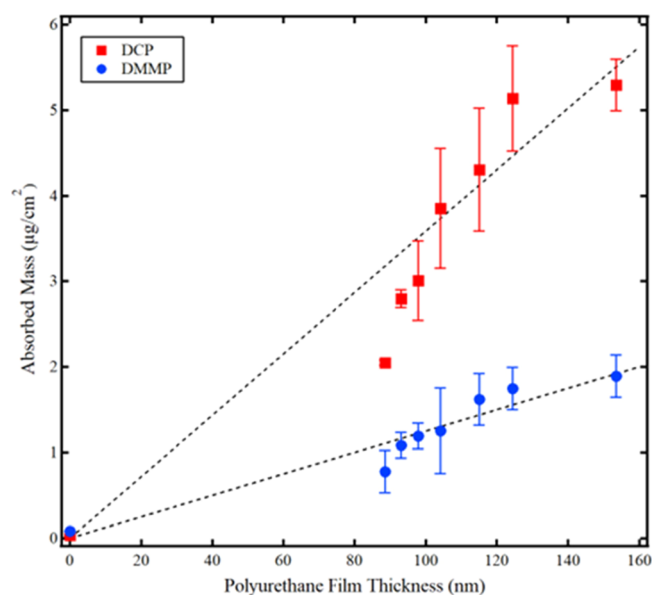


Figure 3. Average mass (Δm) of DCP and DMMP absorbed as a function of polyurethane thickness, with standard deviation error bars. Linear fits are provided as a guide to the eye.

measured in this work was more than double that of DMMP and is attributed to differences in saturated vapor pressure.

Desorption of DCP and DMMP from both the thinnest and thickest polyurethane films was also measured via a QCM after 60 min of vapor exposure. Then, the QCM holder lid was removed, and the frequency change was monitored for 24 h. As shown in Figure 4A, desorption of DCP from the polyurethane film was relatively fast, as indicated by the prompt increase in frequency back to the initial baseline. DCP did not remain within the polyurethane film or adsorb to the aluminum oxide substrate and the time to return to the initial baseline was independent of polyurethane film thickness. Desorption of DMMP was also relatively fast, though slower than that of

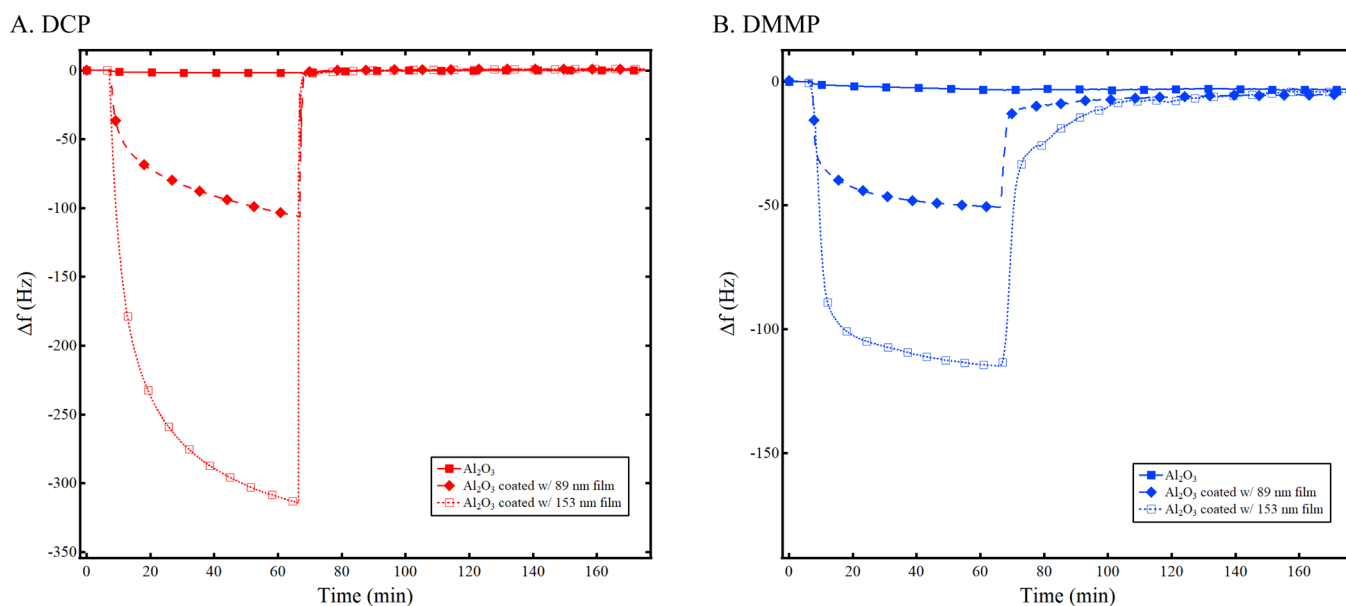


Figure 4. Example QCM data for the change in resonant frequency with time for bare aluminum oxide, an 89 nm polyurethane film, and a 153 nm polyurethane film after exposure to (A) DCP and (B) DMMP for 60 min, followed by subsequent desorption of the CWA simulant.

DCP. However, while the desorption curves for the thinner and thicker polyurethane films are not identical in appearance, they do both converge on the same resonant frequency value as that of the bare aluminum oxide substrate, within experimental error. Thus, DMMP also fully desorbed from the polyurethane, independent of film thickness. Of note, the baseline for DMMP does not return to the initial baseline (e.g., zero) as some DMMP remains adsorbed to the aluminum oxide surface for all three traces.¹⁸ This suggests that DMMP was able to permeate both the thinner and thicker films to reach the aluminum oxide surface.

Sorption and desorption diffusion coefficients for DCP and DMMP from the polyurethane films were also determined via QCM data. Applying Fick's second law, diffusion coefficients (D) were calculated from^{22,23}

$$\frac{M_t}{M_{\text{sat}}} = 4 \sqrt{\frac{D}{\pi}} \frac{t^{0.5}}{L} \quad (2)$$

where M_t is the sorbed vapor mass at a particular time t determined via the Sauerbrey equation, M_{sat} is the saturated sorbed mass at infinite time (approximated to the value at 60 min in this work) for a particular film thickness, and L is the thickness of the polyurethane film. While ellipsometry was used to measure the polyurethane film thickness in this work, film thickness could also have been determined via a QCM by measuring the change in frequency before and after addition of the polyurethane film, converting that frequency to mass via eq 1, and then dividing that value by the density of polyurethane.¹¹

The diffusion coefficient D was calculated from the slope of a plot of M_t/M_{sat} versus the square root of time t for the initial linear sorption or desorption regime. An example plot used to determine D is shown in Figure 5. Values were averaged across all trials to yield average sorption and desorption diffusion coefficients for DCP and DMMP from the polyurethane film (Table 1). As with the example shown in Figure 5, the initial slopes across all trials were linear, suggesting that Fickian diffusion is a reasonable, early-time diffusion model for this

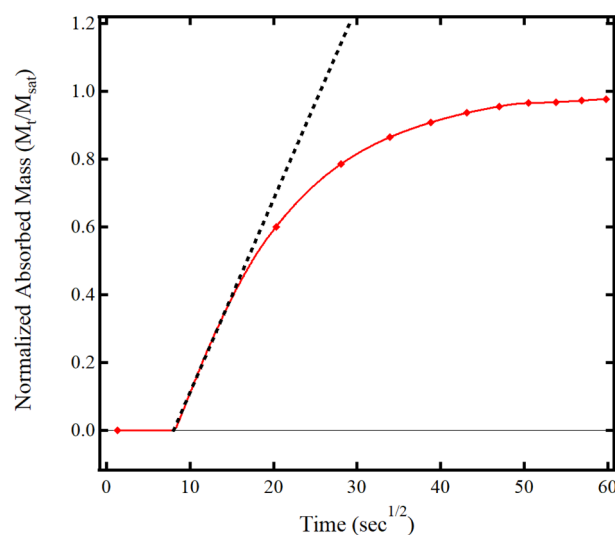


Figure 5. Plot of normalized absorbed mass versus the square root of time. The diffusion coefficient is determined from the slope of the initial sorption rate.

system. No trends in diffusion coefficient were observed for different polyurethane film thicknesses. Vogt et al. studied water vapor diffusion into poly(styrene sulfonate) thin films using both a similar QCM method and Fick's law to determine that diffusion coefficients were essentially independent of film thickness as long as the polymer chains were unconfined (e.g., film was thick enough to permit chain mobility).²⁴ In that study, polymer films with thicknesses between 50 and 200 nm yielded diffusion coefficients within the same order of magnitude, while thinner films yielded diffusion coefficients up to 3 orders of magnitude lower. As the diffusion coefficients determined in this work were independent of film thickness over the range of about 90–150 nm, this suggests that the polyurethane films were unconfined.

Desorption diffusion coefficients from this work fell within the range of HD and GB simulant values reported for other polymer systems and was also similar to literature values of HD

Table 1. Diffusion Coefficients, Partition Coefficients, and Volume Fractions for DCP and DMMP and Polyurethane Thin Films

CWA simulant	diffusion coefficient (cm ² /s)		partition coefficient (K)	volume fraction (ψ_1)
	sorption	desorption		
dichloropentane (DCP)	$1 \times 10^{-13} \pm 48\%$	$2 \times 10^{-9} \pm 52\%$	$4.0 \times 10^5 \pm 16\%$	0.26 ± 0.05
dimethyl methylphosphonate (DMMP)	$1 \times 10^{-12} \pm 43\%$	$1 \times 10^{-11} \pm 37\%$	$2.3 \times 10^5 \pm 32\%$	0.10 ± 0.01

and GB agents from alkyds and polyurethanes.^{7–9,12–14} While some variation between values is expected due to differences in polymer substrates and their permeability,^{2,10,14} the results from the QCM method used in this work generally aligned well with previous studies. Of note, the desorption coefficients were several orders of magnitude larger than the sorption coefficients. Depending on the system, both larger and small desorption coefficients relative to sorption have been reported in the literature.^{23,25,26} For example, studies of water vapor sorption into thin polymer films yielded lower desorption coefficients than sorption coefficients and even two desorption regimes.²⁶ These results were associated with clustering of water and different types of bound water within the film, respectively.²⁶ Conversely, a sorption study of chloroform vapors of different concentrations into polystyrene thin films showed that low chloroform vapor concentrations did not significantly swell the polystyrene film, resulting in slower diffusion and smaller diffusion coefficients.²³ Though the polyurethane films in this work were relatively rigid during the experiment (e.g., dissipation changes were less than 5% of the scaled frequency change), some swelling of the film likely occurred with vapor uptake, leading to increased polymer chain mobility after sorption and resulting in faster vapor desorption.^{23,25}

Partition coefficients and volume fractions of CWA simulants within the polyurethane films were also determined and are shown in Table 1. Partition coefficients provide the ratio of solute between two phases—in this case, the concentration of analyte vapor sorbed by the polymer versus the saturated vapor concentration. Higher partition coefficients indicate greater affinity of a solute for a particular sorbent. Partition coefficients (K) were calculated by²⁷

$$K = \frac{c_{\text{poly}}^A}{c_{\text{sat}}^A} = \frac{RT}{P_A MW_A} \cdot \frac{M_{\text{sat}}}{L} \quad (3)$$

where c_{poly}^A and c_{sat}^A are the concentrations of the analyte in the polymer film and the saturated vapor phase, respectively. The concentration of analyte in the vapor phase was determined using the ideal gas law, where R is the universal gas constant, T is the temperature, P_A is the analyte saturated vapor pressure, and MW_A is the analyte molecular weight. The concentration of vapor in the polymer was determined from the sorbed vapor mass from QCM data, M_{sat} , and the polyurethane film thickness, L , prior to vapor exposure. Average partition coefficients of DCP and DMMP are provided in Table 1. No discernible trend of partition coefficient with film thickness was observed. To our knowledge, the partition coefficient of DMMP and DCP into polyurethane thin films has not been previously reported. However, partition coefficients for DMMP sorption into several different polymers containing fluorine functional groups yielded log K values of 6.3 and 7.1, respectively.^{9,28} The log K value DMMP into polyurethane in this work was 5.5, representing 1 to 2 orders of magnitude lower dissolution of DMMP vapor into polyurethane. As the

polymers containing fluorine were designed for affinity with DMMP through hydrogen bonding between the polymer and the vapor for sensing applications, a lower K value for DMMP with polyurethane is reasonable. Regardless, though, the polyurethane showed relatively high affinity toward both DMMP and DCP.

Related to partition coefficients, volume fraction is a measure of sorbent in a swollen polymer film and is related to the Flory-Huggins interaction parameter used as a measure of quality for polymer solvents.¹¹ Assuming additive volumes, the equilibrium volume fraction was calculated via¹¹

$$\psi_1 = \frac{M_{\text{sat}}/\rho_v}{M_{\text{sat}}/\rho_v + L} \quad (4)$$

where ψ_1 is the volume fraction of vapor within the film, M_{sat} is the saturated sorbed vapor mass, ρ_v is the liquid density of the simulant, and L is the polyurethane film thickness. Average volume fractions of DCP and DMMP are provided in Table 1. No discernible trend of volume fraction with film thickness was observed. Both DCP and DMMP readily penetrated and absorbed into the polyurethane film. To our knowledge, the volume fraction of DMMP in polyurethane has not been previously reported, though the volume fraction of DCP from this work was similar to that of a previous study.¹¹ The volume fraction of DCP was more than double that of DMMP. As the saturated vapor pressure of DCP is about double that of DMMP, this result is somewhat expected. Coupled with the partition coefficient data, this result suggests that the polyurethane is a good solvent for both DCP and DMMP.¹¹

Collectively, the results from this work provide CWA simulant mass transport parameters for a polyurethane/aluminum oxide system. Both DCP and DMMP showed a high affinity for polyurethane.¹¹ The simulants DCP and DMMP readily absorbed into the polyurethane film and penetrated to the aluminum oxide substrate, adsorbing to the surface for the case of DMMP. When removed from a saturated vapor environment, simulant desorption from the film was relatively fast. The mass uptake of the simulant increased linearly with film thickness. Changes in film thickness for smooth, homogenous polyurethane films did not significantly affect the diffusion coefficients, partition coefficients, or volume fractions and, where available, the results of this study were comparable to literature values.^{7–9,11}

While the film thicknesses studied in this work are much lower than the expected thickness of a polyurethane (e.g., paint, CARC) that would coat the aluminum of military vehicles and equipment (e.g., nanometer vs millimeter), the thickness independence of diffusion coefficients, partition coefficients, and volume fractions over the range studied in this work is significant. Study of thicker coatings up to at least several hundred microns should be possible via the techniques presented in this work. Based on the results of this study, it is likely that the mass uptake of CWA simulants would increase with film thickness and simulants would fully penetrate the

coating to the substrate beneath. The diffusion coefficients, partition coefficients, and volume fractions might also increase due to increases in the permeability of the coating caused by increases in roughness.⁹

Not only are the determined parameters useful for the development of models focused on agent decontamination procedures, but this work also highlights the utility of the QCM as a single method for studying vapor uptake and transfer phenomena. As outlined in this work, the QCM alone can be used to determine film thickness, vapor uptake, and changes in vapor concentration within a thin film with time, permitting calculation of diffusion coefficients, partition coefficients, and volume fractions from a single data set. Thus, the QCM is well-suited for future studies of CWA and CWA simulant transport phenomena and for studying coatings for optimized agent resistance or sensing.

CONCLUSIONS

In summary, this work highlights the first report of transport parameters for CWA simulant vapors and a polyurethane thin film coated on aluminum oxide. Both DCP, an HD simulant, and DMMP, a GB simulant, showed high partition coefficients and thus high affinity for the polyurethane film. Uptake of absorbed simulant was independent of film thickness, though the higher saturated vapor pressure of DCP led to a mass uptake that was greater than that of DMMP. Both the absorption and desorption of CWA simulants were relatively fast and independent of film thickness, though DMMP desorbed more slowly than DCP. These results, coupled with the utility of the QCM methods presented here, are expected to inform future studies of CWA simulant uptake and transport and provide data useful for developing improved models for agent decontamination.

MATERIALS AND METHODS

Materials. DMMP (97%, D169102), DCP (99%, D69602), and chloroform (reagent grade, CX1055) were purchased from Sigma-Aldrich. Hydrogen peroxide (H₂O₂, 30 wt%) and ammonium hydroxide (NH₄OH, certified ACS Plus) were purchased from Fisher Scientific. Ultrapure water (Milli-Q Gradient A-10, Milli-Q, 18.2 ΩM·cm, <5 ppb organic impurities) was used for all experiments. A polyurethane with 43% hard-segment was synthesized according to a previously published procedure.^{11,29}

Polyurethane Films. Polyurethane thin films were formed by spin-coating from chloroform solution onto QCM sensor crystals coated with aluminum oxide (QSense QSX-309). Prior to spin-coating, sensor crystals were cleaned by exposure to UV/ozone for 20 min, followed by immersion in a 1:1:5 by a volume solution of H₂O₂:NH₄OH:H₂O at 80 °C for 1 h. Polyurethane solutions of 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 wt % polyurethane in chloroform were used to form films of varied thickness by adding solution dropwise to the sensor crystal and spin-coating at 3000 rpm for 1 min. Coated crystals were then annealed overnight at 100 °C.

Atomic Force Microscopy. Aluminum oxide and polyurethane surfaces were imaged in noncontact mode with a Park Systems AFM (NX10, Park Systems). Images were collected under ambient conditions (20 °C, 50% humidity) using a silicon tip (PPP-NCHR, Park Systems). Reported surface roughness values were determined from the root-mean-square values of 5 μm by 5 μm scan areas.

Ellipsometry. Ellipsometry measurements were conducted using a fixed-angle, multiwavelength ellipsometer (FS-1, Film Sense). Film thickness was calculated using the FS-1 software. A Cauchy model was applied to the polyurethane layer, which was assumed to have a refractive index value of 1.5 at 633 nm.³⁰

QCM-D Experiments. While DMMP and DCP are relatively safe compared to actual CWAs, appropriate personal protective equipment and ventilation are still required. Goggles, lab coats, and gloves were worn during experimentation, and small volumes of DCP and DMMP were used for each run (50 μL) to further limit exposure. Additionally, QCM experiments were conducted in a fume hood under ambient conditions (20 °C, 0.78 atm, 50% humidity) with the sash closed except during the injection of the simulant. Polyurethane-coated aluminum oxide QCM sensor crystals were placed into an open module (QSense QOM 401). The module was modified in that a hole was drilled through the polytetrafluoroethylene (PTFE) lid and slightly into the PTFE base below, creating a small notch that led into the open space above the sensor. The lid was placed over the open module, and the module was then mounted into the QCM (QSense E-4). The sensor crystal was allowed to reach equilibrium at a temperature setpoint of 25 °C. To generate a saturated vapor environment, 50 μL of the liquid CWA simulant was injected into the sample reservoir, allowing the vapor to reach equilibrium with the sample chamber. Based on the saturated partial pressures of DCP and DMMP at 25 °C (150 and 79 Pa, respectively), the volume of the sample chamber (3.7 cm³), and assuming ideal gas behavior, DCP and DMMP required 0.029 and 0.013 μL for vapor saturation, respectively.^{19,20} When injecting the CWA simulant, care was taken to avoid overfilling the notch and causing the CWA simulant liquid to directly contact the sensor surface. Experimental runs were discarded that showed liquid contact upon injection (e.g., by nearly instantaneous frequency decreases of more than 300 Hz and significant increases in dissipation of at least 20 × 10⁻⁶). Keeping the QCM sensor surface at 25 °C (e.g., 5 °C above ambient) prevented condensation of the simulant vapor on the sensor surface. For sorption experiments, the polyurethane-coated aluminum oxide sensor crystal was exposed to saturated CWA simulant vapors for 60 min and the change in sensor resonant frequency with time was recorded. For desorption experiments, after recording the change in frequency for 60 min of exposure to saturated vapor, the PTFE lid was removed and the change in frequency was monitored for 24 h. In generating Figures 2 and 4, QCM traces were shifted to show identical start times for the injection of the CWA simulant to facilitate comparisons between data sets.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c02257>.

Polyurethane film thickness and AFM images of polyurethane films (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Jang, Y. J.; Kim, K.; Tsay, O. G.; Atwood, D. A.; Churchill, D. G. Update 1 of: Destruction and Detection of Chemical Warfare Agents. *Chem. Rev.* **2015**, *115*, PR1–PR76.
- (2) Cooley, K. A.; Pearl, T. P.; Varady, M. J.; Mantooh, B. A.; Willis, M. P. Direct Measurement of Chemical Distributions in Heterogeneous Coatings. *ACS Appl. Mater. Interfaces* **2014**, *6*, 16289–16296.
- (3) Willis, M. P.; Mantooh, B. A.; Lalain, T. A. Novel Methodology for the Estimation of Chemical Warfare Agent Mass Transport Dynamics, Part II: Absorption. *J. Phys. Chem. C* **2012**, *116*, 546–554.
- (4) Willis, M. P.; Mantooh, B. A.; Lalain, T. A. Novel Methodology for the Estimation of Chemical Warfare Agent Mass Transport Dynamics, Part I: Evaporation. *J. Phys. Chem. C* **2012**, *116*, 538–545.
- (5) Ebrahim, A. M.; Plonka, A. M.; Tian, Y.; Senanayake, S. D.; Gordon, W. O.; Balboa, A.; Wang, H.; Collins-Wildman, D. L.; Hill, C. L.; Musaev, D. G.; Morris, J. R.; Troya, D.; Frenkel, A. I. Multimodal Characterization of Materials and Decontamination Processes for Chemical Warfare Protection. *ACS Appl. Mater. Interfaces* **2020**, *12*, 14721–14738.
- (6) Yang, Y. C.; Baker, J. A.; Ward, J. R. Decontamination of Chemical Warfare Agents. *Chem. Rev.* **1992**, *92*, 1729–1743.

(7) Willis, M. P.; Gordon, W.; Lalain, T.; Mantooh, B. Characterization of Chemical Agent Transport in Paints. *J. Hazard. Mater.* **2013**, *260*, 907–913.

(8) Hao, R.-Z.; Cheng, Z.-X.; Zhu, H.-Y.; Zuo, G.-M.; Zhang, C.-M. Transportation of Sulfur Mustard (HD) in Alkyd Coating. *J. Phys. Chem. A* **2007**, *111*, 4786–4791.

(9) Zimmermann, C.; Mazein, P.; Rebière, D.; Déjous, C.; Pistré, J.; Planade, R. Detection of GB and DMMP Vapors by Love Wave Acoustic Sensors Using Strong Acidic Fluoride Polymers. *IEEE Sens. J.* **2004**, *4*, 479–488.

(10) Primera-Pedrozo, O. M.; Fraga, C. G.; Breton-Vega, A.; Zumbach, M. M.; Wilkins, B. P.; Mirjankar, N. S.; Kennedy, Z. C. Sorption and Desorption Study of a Nerve-Agent Simulant from Office Materials for Forensic Applications. *Forensic Chem.* **2020**, *20*, No. 100260.

(11) Grissom, T. G.; Serrine, J. M.; Long, T. E.; Esker, A. R.; Morris, J. R. Interaction Parameters for the Uptake of Sulfur Mustard Mimics into Polyurethane Films. *Prog. Org. Coat.* **2017**, *107*, 14–17.

(12) Levine, F.; Escarsega, J.; La Scala, J. Effect of Isocyanate to Hydroxyl Index on the Properties of Clear Polyurethane Films. *Prog. Org. Coat.* **2012**, *74*, 572–581.

(13) Varady, M. J.; Pearl, T. P.; Bringuier, S. A.; Myers, J. P.; Mantooh, B. A. Agent-to-Simulant Relationships for Vapor Emission from Absorbing Materials. *Ind. Eng. Chem. Res.* **2017**, *56*, 10911–10919.

(14) Dubey, V.; Parmar, T.; Saxena, A.; Agarwal, D. D. Thiocompounds as Simulants of Sulphur Mustard for Testing of Protective Barriers. *J. Appl. Polym. Sci.* **2009**, *111*, 928–933.

(15) Agrawal, M.; Sava Gallis, D. F.; Greathouse, J. A.; Sholl, D. S. How Useful Are Common Simulants of Chemical Warfare Agents at Predicting Adsorption Behavior? *J. Phys. Chem. C* **2018**, *122*, 26061–26069.

(16) Easley, A. D.; Ma, T.; Eneh, C. I.; Yun, J.; Thakur, R. M.; Lutkenhaus, J. L. A Practical Guide to Quartz Crystal Microbalance with Dissipation Monitoring of Thin Polymer Films. *J. Polym. Sci.* **2022**, *60*, 1090–1107.

(17) Sauerbrey, G. Verwendung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung. *Z. Physik* **1959**, *155*, 206–222.

(18) Templeton, M. K.; Weinberg, W. H. Decomposition of Phosphonate Esters Adsorbed on Aluminum Oxide. *J. Am. Chem. Soc.* **1985**, *107*, 774–779.

(19) Goll, E. S.; Jurs, P. C. Prediction of Vapor Pressures of Hydrocarbons and Halohydrocarbons from Molecular Structure with a Computational Neural Network Model. *J. Chem. Inf. Comput. Sci.* **1999**, *39*, 1081–1089.

(20) Butrow, A. B.; Buchanan, J. H.; Tevault, D. E. Vapor pressure of organophosphorus nerve agent simulant compounds. *J. Chem. Eng. Data* **2009**, *54*, 1876–1883.

(21) Höök, F.; Rodahl, M.; Brzezinski, P.; Kasemo, B. Energy Dissipation Kinetics for Protein and Antibody–Antigen Adsorption under Shear Oscillation on a Quartz Crystal Microbalance. *Langmuir* **1998**, *14*, 729–734.

(22) Koutsopoulos, S.; Unsworth, L. D.; Nagai, Y.; Zhang, S. Controlled Release of Functional Proteins Through Designer Self-Assembling Peptide Nanofiber Hydrogel Scaffold. *Proc. Natl. Acad. Sci. U. S. A.* **2009**, *106*, 4623–4628.

(23) Erdogan, M.; Özbek, Z.; Çapan, R.; Yagci, Y. Characterization of Polymeric LB Thin Films for Sensor Applications. *J. Appl. Polym. Sci.* **2012**, *123*, 2414–2422.

(24) Vogt, B. D.; Soles, C. L.; Lee, H.-J.; Lin, E. K.; Wu, W. Moisture Absorption and Absorption Kinetics in Polyelectrolyte Films: Influence of Film Thickness. *Langmuir* **2004**, *20*, 1453–1458.

(25) Duarte, A. R. C.; Martins, C.; Coimbra, P.; Gil, M. H. M.; de Sousa, H. C.; Duarte, C. M. M. Sorption and Diffusion of Dense Carbon Dioxide in a Biocompatible Polymer. *J. Supercrit. Fluids* **2006**, *38*, 392–398.

(26) Chu, L.-Q.; Mao, H.-Q.; Knoll, W. In Situ Characterization of Moisture Sorption/Desorption in Thin Polymer Films Using Optical Waveguide Spectroscopy. *Polymer* **2006**, *47*, 7406–7413.

(27) Schwöpe, A. D.; Klein, J.; Sidman, K. R.; Reid, R. C. Sorption-Desorption Phenomena of Chemicals from Polymer (Paint) Films. *J. Hazard. Mater.* **1986**, *13*, 353–367.

(28) Grate, J. W.; Snow, A.; Ballantine, D. S.; Wohltjen, H.; Abraham, M. H.; McGill, R. A.; Sasson, P. Determination of Partition Coefficients from Surface Acoustic Wave Vapor Sensor Responses and Correlation with Gas-Liquid Chromatographic Partition Coefficients. *Anal. Chem.* **1988**, *60*, 869–875.

(29) Williams, S. R.; Wang, W.; Winey, K. I.; Long, T. E. Synthesis and Morphology of Segmented Poly(tetramethylene oxide)-Based Polyurethanes Containing Phosphonium Salts. *Macromolecules* **2008**, *41*, 9072–9079.

(30) Müller, U.; Philipp, M.; Bactavatchalou, R.; Sanctuary, R.; Baller, J.; Zielinski, B.; Possart, W.; Alnot, P.; Krüger, J. K. Chemically Induced Transition Phenomena in Polyurethanes As Seen From Generalized Mode Grüneisen Parameters. *J. Phys.: Condens. Matter* **2008**, *20*, No. 205101.