

Influence of collection solvent on permeation of di-*n*-octyl disulfide through nitrile glove material

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Abstract

The influence of collection solvents hexane and perfluorohexane on the permeation of the non-polar and non-volatile di-*n*-octyl disulfide (DOD) through nitrile glove material was investigated using the American Society for Testing and Materials (ASTM) F739-99a method. The weight and the thickness of the nitrile material increased about 6%, statistically significant at $p \leq 0.05$, after 8 h of DOD permeation for both collection solvents. Infrared reflectance examination revealed no spectral changes to glove surfaces. Gas chromatography/mass spectrometry analysis determined that the apparent DOD steady state permeation rate was $903 \pm 285 \mu\text{g}/(\text{cm}^2 \text{ h})$ for hexane collection, and $6.92 \pm 2.27 \mu\text{g}/(\text{cm}^2 \text{ h})$ for perfluorohexane collection. The ASTM normalized breakthrough time for DOD was 7–30 min for hexane collection, and 30–75 min for perfluorohexane collection. Perfluorohexane is a promising collection solvent for non-polar and non-volatile compounds permeating nitrile material.

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1. Introduction

Protective gloves prevent or reduce direct skin contact to harmful agents. Nitrile material, the copolymer of acrylonitrile and butadiene, is widely available as chemically protective industrial gloves, which exhibit considerable resistance to many chemicals [1–3] and pesticide formulations [4–6]. Disposable gloves have since become available, and many workers prefer these gloves because of comfort, being more tight-fitting, and facilitating manual operations [1,2]. Employers also like their low cost. Much more chemical degradation and permeation data from glove companies are available for chemically protective gloves than for disposable gloves. Our research group has recently focused on permeation studies for disposable gloves [7–9], and the present research continues that focus relative to the effect of the organic collection solvent on the permeation parameters for non-volatile non-polar organics.

The resistance of glove material to chemical permeation is usually tested with the protocol of the American Society for Testing and Materials (ASTM) method F739-99a [3]. Cut circular glove pieces are sandwiched between the challenge and collection glass chambers. The challenge liquid is placed in the challenge chamber. Circulating air or nitrogen is often used to collect volatile permeate for subsequent chemical analysis. Water is placed in the collection chamber, when the challenge chemical is water-soluble and non-volatile, and an organic solvent when the challenge is water-insoluble and non-volatile. However, no specific organic solvent is recommended.

The effects of different organic collection solvents on the permeation parameters of non-polar non-volatile challenge compounds have hardly been studied. A collection solvent should not chemically degrade the glove material. Ideally, it does not permeate the material either. Following these criteria, the choice of collection solvent will differ among different glove materials. The type of challenge chemical is also an important factor because the collection solvent needs to solubilize and remove the permeate from the collection side surface of the glove. Hexane [4–8] and 2-propanol [9] have been used as the collection organic solvent for water-insoluble and non-volatile chemicals, but only Refs. [7–9] refer to disposable glove material data.

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The resistance of a disposable nitrile SafeSkin glove was rated in its provided Chemical Degradation chart in 2001 as “excellent” to both hexane and 2-propanol, even though the glove had not been individually tested and “excellent” was not defined [10]. Permeation and degradation data for a disposable nitrile glove Touch N Tuff stated that breakthrough time was less than 10 min for 2-propanol and more than 480 min for hexane [11]. Hexane was thus expected to be a better collection solvent than the more polar 2-propanol. The apparent swelling of disposable nitrile reported for the latter solvent [9] and hexane [7] was caused by glove conditioning differences relative to the out-of-the-box state. A direct test on analyte permeation for different collection solvents was not performed in those studies. Fluorinated alkanes are even more non-polar than hexane, and they may perform even better as collection solvents as long as the challenge chemical is also soluble, and collection solvent evaporation is still possible to enhance analyte sensitivity.

Besides organic solvent collection, solid phase collection [12], and intermittent washing of the collection side with an organic solvent [13,14], have been tried in permeation testing of water-insoluble and non-volatile compounds. Both methods tend to underestimate the permeation rate. Solid collection requires a flat glove surface and close contact between the glove and the collection medium. It is difficult to determine whether the permeate is sufficiently collected from the glove inner surface. The intermittent method may leave the permeate saturated on the inner surface of glove between washes, so that the measured permeation rate is lower than the true value. Besides, an inappropriate collection solvent may still wet the glove material and degrade it.

Di-*n*-octyl disulfide (CAS registration number 822-27-5; referred to hereafter as DOD) is more non-polar than hexane, because sulfur has the same electronegativity of 2.5 as carbon [15] and DOD has two alkyl (*n*-octyl) chains. At 25 °C, its solubility in water is about 2.2×10^{-7} g/L, and its vapor pressure is 0.0337 Pa [16]. DOD has been identified in a straight-oil metalworking fluid [17]. No toxicological data are available for this compound. In metalworking fluids, sulfur-containing compounds are often used as extreme pressure additives to protect the tool and improve work piece quality [18].

In the present study, DOD served as a model water-insoluble and non-volatile pure compound to permeate disposable nitrile glove material. There are no glove permeation data for it in the scientific literature. Both hexane and perfluorohexane were used as collection solvents, and the collection solvent effects on permeation parameters were determined.

2. Experimental

2.1. Chemicals, solvents, and glove materials

DOD (purity 98.3%) was provided by Chevron Phillips Specialty Chemical (The Woodlands, TX). Its density was measured to be 0.886 ± 0.002 g/mL. 4,4'-Dichlorobiphenyl (CAS registration number 2050-68-2), referred to hereafter as DCBP, was purchased from Chem Service (West Chester, PA). Optima grade hexane (boiling point 67–70 °C) was from Fisher Sci-

entific (Pittsburgh, PA). Perfluorohexane (98.5%; boiling point 59–60 °C) was from Apollo Scientific (Bredbury, Cheshire, UK as distributed in the US by Ryan Scientific, Isle of Palms SC).

Kimberly-Clark SafeSkin nitrile powder-free exam gloves (Kimberly-Clark No. N330) were purchased from Fisher Scientific. The gloves are a copolymer of acrylonitrile and butadiene with many additives [1,2]. This glove has been tested extensively by our research group [7–9].

2.2. Equipment

A calibrated Marathon Electronic Digital Micrometer Model CO 030025 (0–25 mm, 0.001 mm resolution) from Fisher Scientific was used to measure the thickness of gloves before and after permeation testing. A calibrated Mettler analytical balance AE260 DeltaRange (Mettler, Hightstown, NJ) was used to weigh the gloves before and after permeation.

Infrared (IR) spectra were obtained with an Avatar 360 Fourier-Transform (FT) spectrophotometer system (Thermo Nicolet, Madison, WI), a single-beam FT-IR spectrophotometer using the reflectance mode and operated with OMNIC 6.0a software. The crystal was diamond in a single-reflection horizontal attenuated total reflectance mode. The spectral range was $4000\text{--}600\text{ cm}^{-1}$, and the number of scans was 32.

Gas chromatography/mass spectrometry (GC–MS) was performed with an Agilent 6890N Network Gas Chromatograph (Agilent Technologies, Wilmington, DE) connected to an Agilent 5973 Network Mass Selective Detector (MSD) (Agilent Technologies). The MSD was a quadrupole with an electron multiplier detector. The GC column was an HP 5-MS 30 m \times 0.25 mm i.d. (0.25 μm film) fused silica capillary column (Agilent Technologies). The carrier flow of helium (99.9999%, from Air Liquide, Long Beach, CA) was 1.00 ± 0.05 mL/min. The temperature of the injector was 260 °C and that of the transfer line was 280 °C. The 70 eV ion source and the quadrupole were held at 230 and 150 °C, respectively.

2.3. Permeation procedure

The permeation procedure was a modified standard ASTM F739-99a permeation method [3]. In summary, out-of-the box nitrile SafeSkin gloves were conditioned 24 h at $55 \pm 1\%$ relative humidity at room temperature (24–25 °C) in a desiccator containing saturated aqueous sodium dichromate (Fisher Scientific). Circular glove pieces of 42.5 mm diameter were cut from the glove palms. Each piece was held between the two Teflon gaskets and the Pyrex chambers of an I-PTC-600 ASTM-type permeation cell (Pesce Lab, Kennett Square, PA) with the inner surface of the glove facing the collection chamber and the outer surface facing the challenge chamber. The test area of the glove between the two chambers had a diameter of 25.4 mm. Both hexane and perfluorohexane were used as collection solvents. A volume of 10-mL collection solvent was added into the collection chamber; 10 mL of DOD was pipetted into the challenge chamber. Three permeation cells with each collection solvent were immersed in a Fisher Shaking Water Bath model 127 at 34.5 ± 0.5 °C (the temperature is the average for the outside

surface of a tight-fitting Safeskin glove worn in the field). The cells were agitated at an average horizontal shaking speed of 70 ± 5 cycles/min with traveling distance of 10.24 cm/cycle, to ensure no concentration gradients in both sides. Method blanks, with the challenge chamber empty and the collection chamber filled with collection solvent, were also performed.

To determine the mass of permeated DOD at specific times, 100 μL samples were withdrawn from the collection side after 1.0, 2.0, 4.0, 6.0, and 8.0 h, and deposited into 2-mL vials with Teflon-lined screw-caps. To determine the breakthrough time, a second set of permeation experiments was performed, with sampling times at 7, 15, 30, 45, 60, 75, and 90 min. The aliquots were stored at -20°C before they were thawed and analyzed with GC–MS. After permeation testing, the glove pieces were blotted dry with Kimwipes, and re-conditioned in the desiccator for 24 h before thickness, weight, and infrared measurements.

2.4. Glove physical changes

The thickness and weight of nitrile polymer after permeation were measured and compared to those before permeation testing. For thickness, seven readings on different spots were made for each piece of the cut glove before and after permeation. Student *t*-testing determined whether the changes were statistically significant using $p \leq 0.05$ as the criterion. The weight increase of the glove material divided by the material volume (only for the part whose surface had contact with DOD and collection solvent) provided the average concentration of DOD in the material. Surface spectral changes were monitored with FT-IR.

2.5. GC–MS analysis to quantify permeated mass

The MS was operated over the mass to charge ratio (*m/z*) range 50–400 in the total ion current mode (TIC). The GC column was initially at 100°C for 5 min, heated at $20^\circ\text{C}/\text{min}$ to 180°C , maintained at 180°C for another 3 min, heated at $20^\circ\text{C}/\text{min}$ to 300°C , and then kept at 300°C for 2 min. The solvent delay was 3.5 min. The total run time was 20 min. DCBP among other chemicals was tested for feasibility as internal standard (IS). The criteria were that the GC–MS response of the IS was stable, the IS concentration used was in its linear range, and that it did not interfere chromatographically.

DOD standards in hexane, with DOD concentration of 0.00, 0.10, 0.40, 0.80, 4.2, 8.3, 20.8, 41.7, 83.3, 208.3, and 416.7 mg/L and the IS concentration of 20.8 mg/L, were injected. Ratios of DOD area over IS area in the chromatograms were plotted versus corresponding DOD concentration to provide the calibration curve. Box–Cox power transformation was used to linearize the calibration curve where necessary [17]. Linear regression defined slopes, intercepts, their standard deviations, correlation coefficients, and their *p*-values.

To determine whether solvent selection affected GC–MS response to DOD, solutions of 0, 50, 250, and 500 ng DOD in 1 μL of hexane and in perfluorohexane were injected into GC–MS in TIC mode. The chromatographic areas and retention times for DOD with the two solvents were compared.

The amount of permeated DOD and the steady state permeation rate were determined from the first set of experiments (1–8 h). A volume of 20 μL 125 mg/L DCBP stock solution was added directly into the 100 μL hexane collection samples before GC–MS analysis. For perfluorohexane collections, the perfluorohexane was first evaporated; a volume of 100 μL hexane was subsequently added before addition of DCBP stock solution; and then 1 μL was injected into the GC–MS using TIC. Collections were diluted and re-injected when DOD concentration was higher than 21 mg/L.

To determine the breakthrough times, the GC–MS was operated in the selected ion monitoring (SIM) mode at *m/z* 290 (DOD molecular ion, with the second highest abundance) to increase sensitivity with selectivity. Collection samples from the second set of permeation experiments (7–90 min) were used. Both detection breakthrough time (when DOD was first detected in collection) and ASTM normalized breakthrough time (when the permeated DOD was more than $0.25 \mu\text{g}/\text{cm}^2$ [3]) were determined.

2.6. Back permeation of collection solvents

To detect the presence and amount of back-permeated collection solvents, air within the challenge chamber of the ASTM cell for blank permeation was sampled every 5–10 min with a 100 μL gas-tight syringe (Hamilton, Reno, NV). A volume of 50 μL air sample was injected into the GC–MS using the TIC mode. The column was at 100°C during the whole run of 4.5 min without solvent delay.

Standards of hexane and perfluorohexane in air were made by vaporizing a known amount of hexane or perfluorohexane in a Tedlar gas bag filled with a specific volume of air, and mixed by heating with a hair dryer.

3. Results and discussion

3.1. Physical changes of nitrile material after permeation

3.1.1. Thickness

The thickness of the conditioned glove material was 0.120 ± 0.005 mm before permeation. In method blank permeation testing, the glove shrank by 0.002 ± 0.001 mm after 8 h for perfluorohexane collection ($p = 0.04$), a statistically significant $1.3 \pm 0.7\%$ decrease. The method blank shrank by 0.004 ± 0.002 mm ($p = 0.02$) after 8 h for hexane collection, a statistically significant $3.1 \pm 1.3\%$ decrease. Both collection solvents shrank the glove less than 5%.

In 1.5-h DOD permeation testing, the thickness was unaffected for both hexane ($p = 0.47$) and perfluorohexane ($p = 0.27$) collection. In 8-h DOD permeation testing, nitrile swelled by 0.007 ± 0.002 mm ($p < 0.0001$) for both hexane and perfluorohexane collection. In both cases, the thickness increased about 6% ($p \leq 0.05$). Since most disposable gloves are doffed at breaks, the data at the 1.5 h time point are the most relevant for wearing disposable gloves.

3.1.2. Weight

The weight of nitrile materials after 8-h solvent blank permeation increased less than 0.2% for perfluorohexane collection, and decreased less than 1% for hexane collection. These differences were not significantly different at $p \leq 0.05$.

After 1.5-h of DOD permeation, the weight increased $1.5 \pm 0.5\%$ for hexane collection and increased $1.5 \pm 0.7\%$ for perfluorohexane collection ($p \leq 0.05$ for both collections). For 8-h DOD permeation, the polymer weight increased $6.3 \pm 0.7\%$ for hexane collection and $5.9 \pm 2.2\%$ for perfluorohexane collection ($p \leq 0.05$ for both collections). For 8 h permeations, the average concentration of DOD within the contacted material was $0.17 \pm 0.01 \text{ g cm}^{-3}$ for hexane collection, and $0.15 \pm 0.02 \text{ g cm}^{-3}$ for perfluorohexane collection. The amount of DOD solubilized in the polymer was not significantly different for hexane and perfluorohexane collections ($p = 0.28$). Solubility parameters and solubility theory have been used in the literature to estimate challenge solvent solubility in polymers, and to predict the permeation parameters from the solubility of these solvents with limited success, except when severe swelling occurred [1,19,20].

3.1.3. IR

The reflectance infrared spectra of nitrile glove inner surface are shown in Fig. 1. All spectra, before permeation, after blank permeation, and after DOD permeation, had absorption maxima at 2925, 2860, 1450, 1175, 970, and 915 cm^{-1} . They also had a broad absorption between 3250 and 3650 cm^{-1} , the hydrogen bonded hydroxy region [21]. The similarity of the spectra for the inner surface before permeation, after blank permeation with hexane and perfluorohexane collection (Fig. 1A–C) showed that IR detected no surface changes from contact with the collection solvents. These spectra agreed with previous results on the nitrile glove inner surface before permeation [9].

DOD had absorption maxima at the following wavenumbers, the reflectance in percent being in parentheses: 2923 (71), 2853 (82), 2954 (86), 1458 (90), 722 (92), and 1377 (96). The more

intense maxima $\leq 90\%$ reflectance overlapped with the nitrile inner surface reflectances. The last two wavenumbers were of weak intensities, and they were in the highly variable region of the nitrile spectrum. Thus the detection of DOD with IR on and near the glove inner surface (Fig. 1D and E) was inconclusive.

3.2. GC–MS analysis of DOD

3.2.1. Solvent effects on GC–MS analysis

The GC–MS response to DOD was found to be independent of the solvent that solubilized DOD. Solutions of 50, 250, and 500 ng DOD in 1 μL of hexane or perfluorohexane had the same GC–MS response. The retention time of DOD was 15.02–15.04 min. Since solvent selection had no effects on GC–MS response, only hexane solutions of DOD standards were prepared. Hexane was used because it was less expensive than perfluorohexane, and it could solubilize more DOD.

3.2.2. Solubility of DOD in collection solvents

The solubility of DOD in hexane was determined to be more than 96 g/L at 25 °C. The solubilizing capacity of hexane would not limit the permeation of DOD, if the final concentration of DOD in the hexane was less than 96 g/L. Similarly, the solubility of DOD in perfluorohexane was determined to be more than 500 mg/L.

3.2.3. Internal standard calibration curve

DCBP was found to be an appropriate internal standard. The actual concentration of DCBP in standards (21 mg/L) had an interrun reproducibility coefficient of variation of less than 10%. The DCBP concentration of 20.8 mg/L was also in its linear region of GC–MS response.

GC–MS in the TIC mode could not detect DOD in the 0.1 mg/L standard. The lower quantifiable limit was 0.40 mg/L. A plot of GC–MS response ratio versus DOD concentration showed the relationship to be non-linear with the response leveling off above 20.8 mg/L (Fig. 2A). Excluding higher concentrations, the plot of the lower DOD concentrations spanning from 0.40 to 20.8 mg/L deviated from linearity concavely (Fig. 2B). Using Box–Cox transformation for these lower concentrations [17], the optimum power was determined to be 0.75. The new plot of ratio to the 0.75 power versus DOD concentrations was linear, with correlation coefficient r of 0.99936 and $p < 0.0001$ (Fig. 2C).

3.3. Permeation rate of DOD through nitrile

The concentration of permeated DOD in perfluorohexane collections was in the range of the calibration curve (0.4–21 mg/L). Since DOD concentrations in all the perfluorohexane collections were less than the solubility in perfluorohexane of over 500 mg/L, perfluorohexane can effectively remove the permeated DOD from the inner surface. All hexane collections were diluted, some up to 400 times. The concentration of DOD in hexane was well below its solubility of over 96 g/L.

The average permeated DOD mass versus sampling time for three permeation replicates is plotted in Fig. 3 for hex-

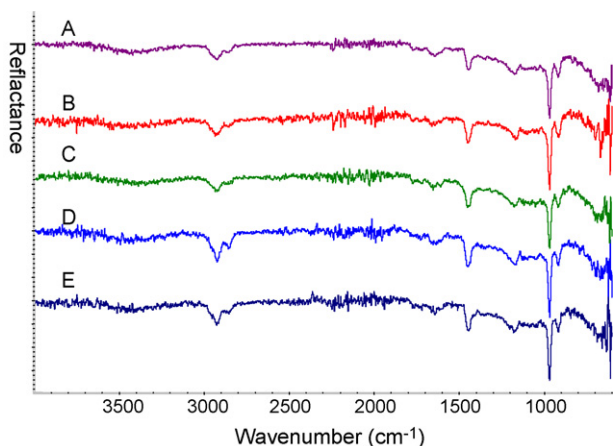


Fig. 1. Reflectance infrared spectra for a disposable nitrile glove inner surface: (A) before permeation; (B) after 8-h hexane blank permeation; (C) after 8-h perfluorohexane blank permeation; (D) after 8-h di-*n*-octyl disulfide (DOD) permeation with hexane collection; (E) after 8-h DOD permeation with perfluorohexane collection.

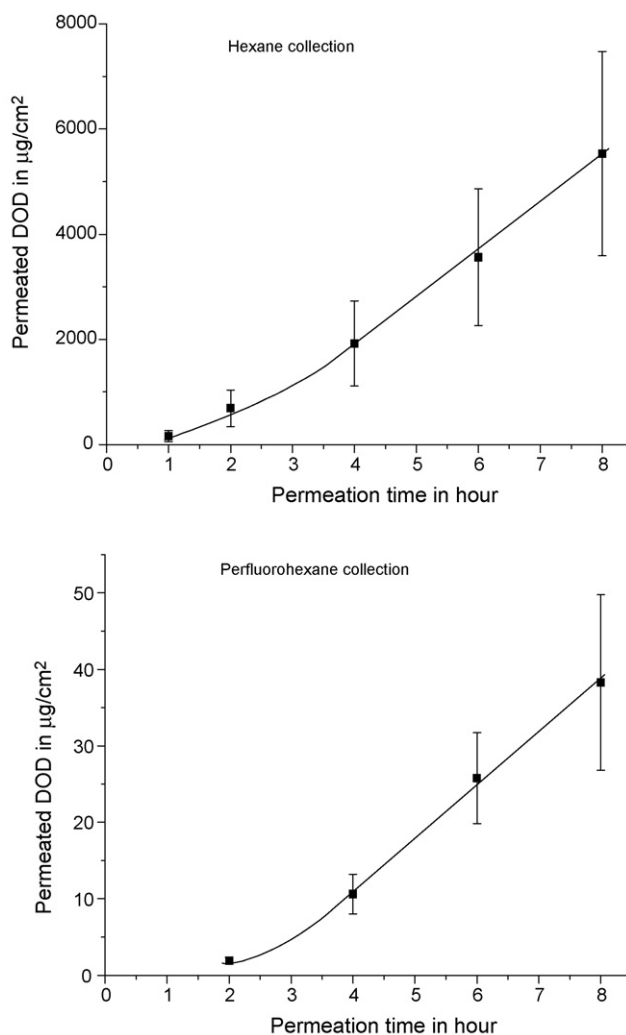
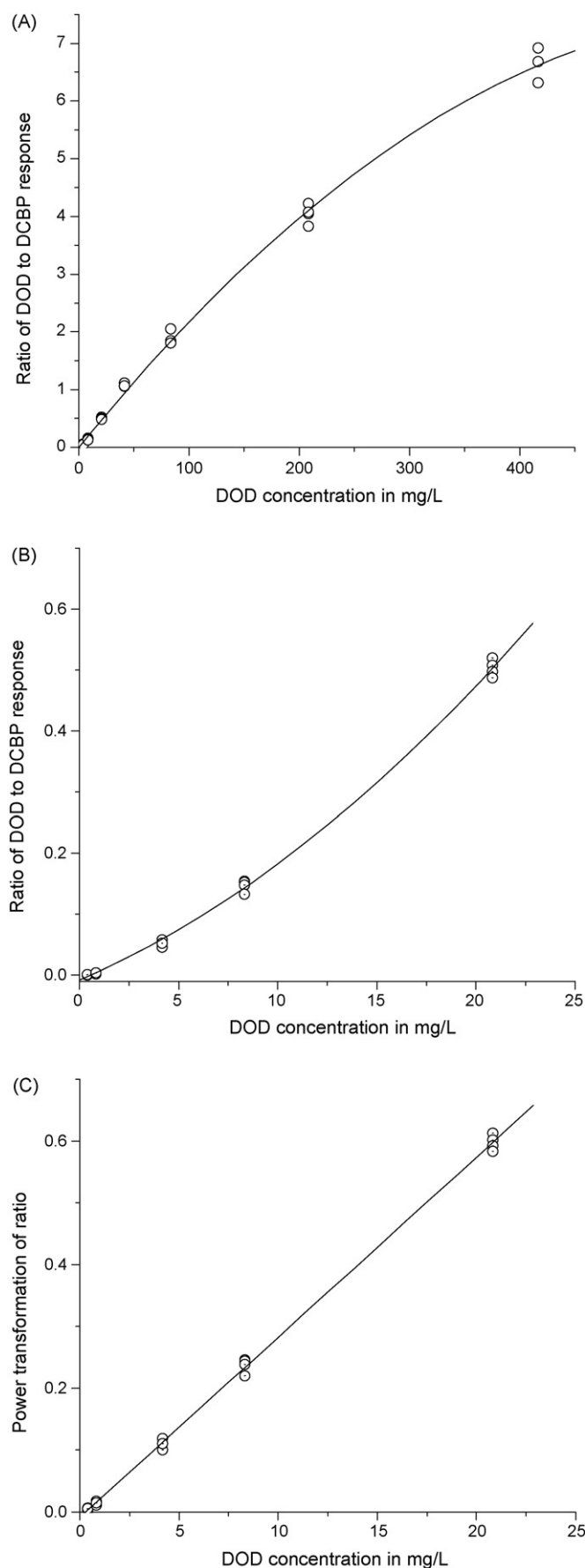


Fig. 3. Permeated DOD in $\mu\text{g}/\text{cm}^2$ (with standard error bars) vs. permeation time in hour for hexane and perfluorohexane collection.

ane collection solvent (top) and for perfluorohexane collection solvent (bottom). After 1 h, permeated DOD was detected by TIC GC–MS for hexane collection, but not for perfluorohexane collection. After 8 h of permeation, $5580 \pm 1940 \mu\text{g}/\text{cm}^2$ DOD permeated for hexane collection, and $38.3 \pm 11.5 \mu\text{g}/\text{cm}^2$ DOD permeated for perfluorohexane collection. The amount of DOD permeated for hexane collection after 8 h was about 140 times that for perfluorohexane collection. It is apparent from Fig. 3 that as the permeation progressed, more variability occurred. The effects of swelling for glove samples can be one of the possible reasons.

The apparent steady state permeation region was between 4 and 8 h with both collection solvents. The steady state permeation rate was $903 \pm 285 \mu\text{g}/(\text{cm}^2 \text{ h})$ for hexane collection, and $6.92 \pm 2.27 \mu\text{g}/(\text{cm}^2 \text{ h})$ for perfluorohexane collection. The

Fig. 2. Internal standard calibration curve for DOD. (A) Ratio of DOD GC–MS response over that of DCBP vs. DOD concentration up to 417 mg/L. (B) Ratio of DOD GC–MS response over that of DCBP vs. DOD concentration up to 21 mg/L. (C) After Box–Cox power transformation, $\text{ratio}^{0.75}$ vs. DOD concentration up to 21 mg/L.

steady state permeation rate for hexane collection was about 130 times that for perfluorohexane collection. DOD permeation with perfluorohexane collection solvent probably had not reached the actual steady state in 8 h. As shown in Fig. 3, the lag time t_l where the steady state period is extrapolated to the time axis is about 2.0 h for hexane and 2.5 h for perfluorohexane. If for both collection solvent the permeation reached the steady state, the DOD diffusion coefficient (D) for perfluorohexane collection solvent was about 80% of that for hexane collection solvent since Fick's law is obeyed and $t_l = l^2/6D$ when glove thickness changes are less than 6% [8]. This 20% difference in D would not cause a 130 times difference in steady state permeation rate. Meanwhile, the permeation before the steady state is clearly different to the steady state for hexane with an apparent t_l of about 0.6 h. The data indicate that there are two distinct phases in the permeation of DOD through nitrile and the underlying phenomena require further investigation. The analogous pre-steady state phase for perfluorohexane collection solvent is much less marked, and actually the apparent steady state between 4 and 8 h for perfluorohexane collection may be the pre-steady state phase. A permeation experiment much longer than 8 h may reveal the steady state, which would have a t_l larger than 2.5 h and a smaller D . However, an experiment with such a long duration would be not applicable to the industrial application of disposable gloves.

The results for hexane collection are probably too conservative for protecting workers from dermal exposure. The permeation data with the more non-polar perfluorohexane are more likely to be closer to reality, since the permeated DOD was not saturated in either collection solvent.

3.4. Breakthrough time

Detection breakthrough time and ASTM normalized breakthrough time are reported in Table 1 based on selected ion monitoring GC–MS data. The detection breakthrough time was 7–30 min for hexane collection, and 15–60 min for perfluorohexane collection. The normalized breakthrough time was 7–30 min for hexane collection, and 30–75 min for perfluorohexane collection. Thus shorter detection and normalized breakthrough times were observed with hexane collection. These data complement the higher steady state rate observed for hexane collection solvent compared with perfluorohexane collection solvent.

It might be noted that at 1.25 h for the hexane collection experiment, the permeation throughput by TIC–GC–MS using Fig. 3 data for the hexane collection solvent experiment was $125 \pm 83 \mu\text{g}/\text{cm}^2$ whereas it was $159 \pm 181 \mu\text{g}/\text{cm}^2$ using the SIM–GC–MS data used to generate Table 1. Similarly for the perfluorohexane collection solvent at 1 h, only one of the three replicates was above the detection limit of TIC–GC–MS for the data in Fig. 3, and was $0.8 \mu\text{g}/\text{cm}^2$. The average permeation throughput at 1 h by SIM–GC–MS using the data to generate Table 1 was $1.13 \pm 1.54 \mu\text{g}/\text{cm}^2$. Since both sets of data are not significantly different at $p \leq 0.05$, this demonstrates how accurate our analytical techniques were and that they agreed in a common data area.

3.5. Collection solvent back permeation

The challenge chamber had a volume of 16 mL. Hexane was detected to back-permeate into the empty challenge chamber 5 min after it contacted the glove. After 10 and 15 min, about 400 and 1000 $\mu\text{g}/\text{cm}^2$ of hexane back permeated. After 30–60 min, about 3300 $\mu\text{g}/\text{cm}^2$ of hexane had back permeated and hexane concentration in the challenge chamber air reached 1.0 mg/mL, the headspace concentration of hexane at 35 °C [22]. After 8 h, however, no liquid hexane was visible in the challenge chamber. Hexane did not degrade or back-permeate the thicker chemically protective nitrile glove Sol-Vex (Ansell, Coshocton, OH) after 8 h [4]. It might be noted that liquid hexane as challenge agent in an open loop ASTM permeation cell system had normalized and actual breakthrough times of less than 3 min for Safeskin disposable nitrile [24].

Perfluorohexane was detected in the empty challenge chamber after 1 h for one replicate, and after 2 h in the other two replicates. At the end of the 8-h experiment, only 0.5 $\mu\text{g}/\text{cm}^2$ of perfluorohexane had back-permeated. The amount of permeated perfluorohexane was negligible compared with that of hexane.

How the back-permeation ability of the collection solvents could influence DOD permeation properties for hexane and perfluorohexane collections solvents is difficult to envisage. More work is required. It is more likely that the much greater solubility of DOD in hexane compared with perfluorohexane is important.

Our research group has found that hexane back permeated through disposable latex and chloroprene gloves during permeation testing with hexane and perfluorohexane collection solvents [23].

Table 1
DOD breakthrough times for hexane and perfluorohexane solvent collection before the steady state permeation period

Collection solvent	Replicate	Detection breakthrough time (min)	Permeated mass ^a ($\mu\text{g}/\text{cm}^2$)	Normalized breakthrough time (min)	Permeated mass ^b ($\mu\text{g}/\text{cm}^2$)
Hexane	1	15–30	1.90	15–30	1.90
	2	7–15	1.48	7–15	1.48
	3	7–15	0.17	15–30	4.54
Perfluorohexane	1	15–30	0.15	30–45	1.03
	2	30–45	0.14	45–60	0.34
	3	45–60	0.15	60–75	0.37

^a At the longest time of the detection breakthrough time range.

^b At the longest time of the normalized breakthrough time range.

4. Conclusions

The present paper is the first to study the back permeation of hexane and perfluorohexane through disposable nitrile using GC–MS, and the first to study collection solvent effects on the steady state permeation rates and the break through times of a challenge chemical. The fluorinated alkane perfluorohexane proved to be a better collection solvent than hexane for determining the permeation kinetics of the non-polar and non-volatile di-*n*-octyl disulfide. Hexane vapor back-permeated into the empty challenge chamber in 5 min, while perfluorohexane vapor did not back-permeate until 1–2 h. The amount of back-permeated hexane was about 3300 $\mu\text{g}/\text{cm}^2$ for 60 min, while the amount of perfluorohexane was about 0.5 $\mu\text{g}/\text{cm}^2$ after 8 h of back permeation. The more polar hexane appeared to enhance the permeation of DOD, and also resulted in a shorter breakthrough time and a larger permeation rate relative to perfluorohexane. After 8 h of permeation, $5580 \pm 1940 \mu\text{g}/\text{cm}^2$ DOD had permeated the nitrile membrane with hexane collection, compared with $38.3 \pm 11.5 \mu\text{g}/\text{cm}^2$ for perfluorohexane collection. Between 4 and 8 h of the permeation, the DOD steady state permeation rate was $903 \pm 285 \mu\text{g}/\text{cm}^2/\text{h}$ for hexane collection, compared with $6.92 \pm 2.27 \mu\text{g}/(\text{cm}^2 \text{ h})$ for perfluorohexane collection. The ASTM normalized breakthrough time was 7–30 min for hexane collection, and 30–75 min for perfluorohexane collection.

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References

- [1] D.H. Anna, Chemical Protective Clothing, 2nd ed., American Industrial Hygiene Association, Fairfax, VA, 2003.
- [2] A. Boman, T. Estlander, J.E. Wahlberg, H.I. Maibach, Protective Gloves for Occupational Use, 2nd ed., CPC Press, Boca Raton, 2005.
- [3] ASTM, Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases Under Conditions of Continuous Contact, ASTM Method F739-99a Annual Book of ASTM Standards, ASTM, West Conshohocken, PA, 2004, pp. 1299–1309.
- [4] Y.W. Lin, S.S. Que Hee, Permeation of malathion through glove materials, Appl. Occup. Environ. Hyg. 13 (1998) 158–165.
- [5] A.A. Khan, X. Chen, S.S. Que Hee, Permeation of chlorpyrifos and endosulfan formulations through gloves, Appl. Occup. Environ. Hyg. 12 (1997) 413–417.
- [6] J. Harville, S.S. Que Hee, Permeation of a 2,4-D isooctyl ester formulation through neoprene, nitrile, and Tyvek protection materials, AIHA J. 50 (1989) 438–446.
- [7] R.N. Phalen, S.S. Que Hee, Permeation of captan through disposable nitrile glove, J. Hazard. Mater. 100 (2003) 95–107.
- [8] W. Xu, S.S. Que Hee, Permeation of a straight oil metalworking fluid through a disposable and a chemically protective nitrile glove, J. Hazard. Mater. 137 (2006) 709–715.
- [9] H. Zainal, S.S. Que Hee, Folpet permeation through nitrile gloves, Appl. Occup. Environ. Hyg. 18 (2003) 658–668.
- [10] SafeSkin Corporation, Chemical Resistance & Barrier Guide, SafeSkin Corporation, San Diego, CA, 2001.
- [11] Ansell Protective Products, Chemical Resistance Guide: Permeation and Degradation Data. 6th ed. Form No. CRG-GC-REV 9-98, Coshocton, OH, 1998.
- [12] D. Ehntholt, I. Bodek, A. Schwöpe, T. Stolki, J. Valentine, U. Frank, M. Royer, A. Nielson, The development of a test method for the evaluation of protective glove materials used in agricultural pesticide operations, Abstr Pap Am Chem S 199 (1990) 179–Agro.
- [13] M.F.S. Pinette, J.O. Stull, C.R. Dodgen, M.G. Morley, A preliminary study of an intermittent collection procedure as an alternative permeation method for non-volatile, water insoluble chemicals, ASTM Special Technical Publication 4 (1992) 339–349.
- [14] V.L. Man, V. Bastecki, G. Vandal, A.P. Bentz, Permeation of protective clothing materials: comparison of liquid contact, liquid splashes and vapors on breakthrough times, AIHA J. 48 (1987) 551–555.
- [15] T.L. Brown, H.E.J. LeMay, B.E. Bursten, J.R. Burdge, Chemistry: The Central Science, ed., Pearson Education, Upper Saddle River, NJ, 2003.
- [16] American Chemical Society, SciFinder Scholar (2006) ed.
- [17] W. Xu, S.S. Que Hee, Gas chromatography–mass spectrometry analysis of di-*n*-octyl disulfide in a straight oil metalworking fluid: application of differential permeation and Box–Cox transformation, J. Chromatogr. A 1101 (2006) 25–31.
- [18] J.P. Byers, Metalworking Fluids ed., Marcel Dekker, New York, 1994.
- [19] J.L. Perkins, A.D. Tippit, Use of 3-dimensional solubility parameter to predict glove permeation, AIHA J. 46 (1985) 455–459.
- [20] E.T. Zellers, D.H. Anna, R. Sulewski, X.R. Wei, Improved methods for the determination of Hansen's solubility parameters and the estimation of solvent uptake for lightly crosslinked polymers, J. Appl. Polym. Sci. 62 (1996) 2081–2096.
- [21] D.A. Skoog, F.J. Holler, T.A. Nieman, Principles of Instrumental Analysis, 5th ed., Harcourt Brace & Company, 1998.
- [22] J.A. Dean, Lange's Handbook of Chemistry, 15th ed., McGraw-Hill Professional, New York, 1999.
- [23] W. Xu, S.S. Que Hee, Permeation of a straight oil metalworking fluid through disposable nitrile, chloroprene, vinyl, and latex gloves, J. Hazard. Mater. 147 (2007) 923–929.
- [24] R.M. Reyes, Chemical resistance charts for commonly used disposable gloves, Kimberly-Clark, February 22, 2002.