# Permeation of aromatic solvent mixtures through nitrile protective gloves

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## Abstract

The permeation of binary and ternary mixtures of benzene, toluene, ethyl benzene and *p*-xylene through nitrile gloves were investigated using the ASTM F739 test cell. The more slowly permeating component of a mixture was accelerated to have a shorter breakthrough time than its pure form. The larger differences in solubility parameter between a solvent mixture and glove resulted in a lower permeation rate. Solubility parameter theory provides a potential approach to interpret the changes of permeation properties for BTEX mixtures through nitrile gloves. Using a one-dimensional diffusion model based on Fick's law, the permeation concentrations of ASTM F739 experiments were appropriately simulated by the estimated diffusion coefficient and solubility. This study will be a fundamental work for the risk assessment of the potential dermal exposure of workers wearing protective gloves.
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## 1. Introduction

As chemical protective gloves represent the last line of defense, appropriate choice and use of the protective gloves are primary to prevent hand skin exposure to hazardous chemicals in the workplace. The chemical protective gloves are commercially made of polymeric materials and are not always known to be permeable to many hazardous chemicals such as organic solvents. Under certain conditions of exposure and handling of solvents, however, gloves are not capable of providing adequate protection for the work to be carried out. Organic solvents may permeate through the protective gloves by the diffusion of molecules [1]. For a particular application, selection of the most appropriate glove requires the assessment of the resistance of the material to the chemical.

Most of the laboratory testing has been conducted to investigate the resistance of protective gloves to permeation by a single solvent in its pure form. However, workers may handle the industrial chemicals which are multi-component in composition. The permeation characteristics of the solvent mixture can be substantially different than the permeation of individual solvents, which can make the selection of the appropriate protective glove more challenging. Several researchers have found that one component of a mixture may promote the permeation of other components through the protective glove at a faster rate than their pure form alone [2–5]. This phenomenon is known as the "co-solvent effect". For that reason, there is a need to investigate the correlation of performance data, such as permeation rate and breakthrough time, between individual and mixed solvents.

In this study, the permeation of aromatic hydrocarbons, i.e. benzene, toluene, ethyl benzene and *p*-xylene (BTEX), through nitrile gloves was conducted using the ASTM F739 test cell which has been widely applied to measure the resistance of protective gloves to permeation by liquid chemicals [1,6–9]. The Fick's diffusion coefficients and solubilities of binary and ternary solvent mixtures in nitrile gloves were estimated using several models. Efforts were made to quantitatively interpret the performance data of solvent mixtures to the experimental results of individual pure solvent. The present work will provide a basis

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Table 1
Properties of experimental solvents

| Solvent | Benzene | Toluene | Ethyl benzene | $p$-Xylene |
|---|---|---|---|---|
| Grade | GR | GR | GC | GR |
| Purity (%) | 99 | 99 | 98 | 99.8 |
| SG | 0.88 | 0.87 | 0.87 | 0.86 |
| MW | 78.1 | 92.1 | 106.2 | 106.2 |
| MV | 89.06 | 106.59 | 122.46 | 123.49 |
| $\Delta H_v$ | 8089 | 9080 | 10098 | 10128 |
| $\delta$ | 9.2 | 8.9 | 8.8 | 8.8 |
| $\log K_{ow}$ | 2.12 | 2.73 | 3.15 | 3.15 |
| LDL | 0.06 | 0.75 | 0.31 | 0.04 |

Properties are at 25 °C and abbreviations are as follows: SG, specific gravity (kg/L), MW, molecular weight (g/mole), MV, molar volume (cm$^3$/mole), $\Delta H_v$, molar heat of vaporization (cal/mole) [23], $\delta$, solubility parameter ((cal/cm$^3$)$^{1/2}$), $K_{ow}$, octanol–water partition coefficient [24], LDL, limit detection level (mg/L).

for evaluating gloves effectiveness for protection against solvent mixtures.

## 2. Experimental

### 2.1. Chemicals and glove samples

Binary and ternary solvent mixtures were generated using benzene (Merck, Germany), toluene (Merck, Germany), ethyl benzene (Fluka, Switzerland) and $p$-xylene (Merck, Germany). These solvents were selected because of their wide use in industry and good permeation resistance to nitrile gloves. Some properties of these pure solvents are summarized in Table 1. For the purpose of obtaining permeation data, unlined and unsupported nitrile glove (Nitri-Solve® 737, Best Co., Menlo, GA) was selected as test sample despite its degradation to benzene.

The test samples with a diameter of 60 mm were cut from the palm section of nitrile gloves. A dial thickness gauge (Teclock Co., Japan) was used to determine the thickness of each sample by measuring at five random locations to an accuracy of 0.01 mm. The average thickness of the glove samples was $0.57 \pm 0.02$ mm. Before conducting permeation experiments, glove samples were prepared by rinsing with water and air-dried for 24 h at $25 \pm 1$ °C and a relative humidity of $50 \pm 5\%$.

### 2.2. Permeation experiment

The test procedure was conducted using the ASTM F739 liquid chemical permeation test method with an open-loop system [10]. The glove sample was mounted in the 51-mm permeation cell (Pesce Lab Sales, Kennett Square, PA) which was immersed in a water bath at a temperature of $25 \pm 1$ °C. Fig. 1 shows the sketch of the experimental system and associated apparatus. The nitrogen gas, with a flow rate of $125 \pm 5$ mL/min (50–150 mL/min suggested in ASTM F739), was initiated into the collection chamber of the permeation cell. The flow rate for nitrogen gas was controlled by a brass needle valve and a flow meter (Cole-Parmer, Vernon Hills, IL). The flow meter was calibrated with nitrogen using the primary standard airflow calibrator (Gilibrator-2, Sensidyne Inc., Clearwater, FL).
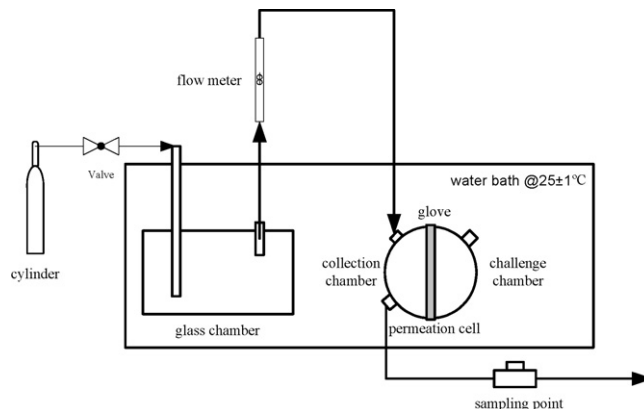


Fig. 1. Experimental setup of ASTM F739 open-loop permeation system.

The test solvents with 75 mL were mixed well and adjusted to $25 \pm 1$ °C using a water bath. The permeant chamber of the test cell was filled with the test solvents covering the entire surface area of the glove sample. All equipments were connected with Teflon tubings and the exhaust of downstream line was collected and discharged into a fume hood.

During the permeation experiments, 100 µL gas samples were taken using a gas-tight syringe from the downstream sampling point every 10–15 min intervals. The gas samples were analyzed using the gas chromatograph (GC) equipped with flame ionization detector (Auto-System XL, Perkin Elmer, Norwalk, CT). The temperature of the capillary GC column (DB-5, J&W, Folsom, CA) was kept at an initial temperature of 60 °C for 1 min, then ramped to 150 °C at a rate of 8 °C/min and held for 1 min. The temperatures of the injection port and detector were maintained at 200 and 250 °C, respectively.

According to ASTM F739 method, the permeation rate, $J$ (ML$^{-2}$t$^{-1}$), of each solvent was calculated as follows:

$$J = \frac{CQ}{A} \tag{1}$$

where $C$ is the permeation concentration of each solvent (ML$^{-3}$); $Q$ the flow rate of collection media ($125 \pm 5$ mL/min); $A$ is the area of glove sample exposed to the permeant (20.4 cm$^2$). In this study, the normalized breakthrough time (BTT) was determined for the elapsed time at which $J$ reached 70 µg/cm$^2$/min.

## 3. Results and discussion

### 3.1. Steady state permeation rate

During the permeation experiments, it was observed that the thickness of glove samples increased by less than 20%. A typical set of experimental results is presented in Fig. 2 showing the permeation concentrations of benzene, toluene and ethyl benzene mixture through the nitrile glove. As seen in Fig. 2, the permeation concentrations stabilized at a steady state value $C_s$. Consequently, the steady state permeation rate, $J_s$ (ML$^{-2}$t$^{-1}$), of each component was obtained by substituting $C_s$ into Eq. (1). As shown in Table 2, the steady state permeation rates for single pure benzene, toluene, ethyl benzene and $p$-xylene were 819,
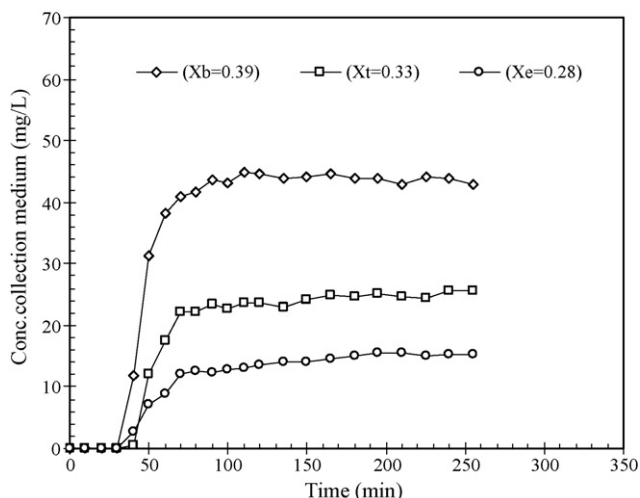
Fig. 2. Permeation concentrations of ternary mixture through nitrile glove.

Table 2
Permeation of single pure solvents through nitrile gloves

| Solvent | $J_s$ | $D$ | $S$ | BTT |
|---|---|---|---|---|
| Benzene | 819 | 1.58 | 2.74 | 14 |
| Toluene | 551 | 1.17 | 2.68 | 31 |
| Ethyl benzene | 233 | 0.89 | 1.47 | 52 |
| p-Xylene | 167 | 0.73 | 1.31 | 61 |

$J_s$ (µg/cm$^2$/min), steady state permeation rate; $D$ ($10^{-5}$ cm$^2$/min) diffusion coefficient; $S$ (g/cm$^3$), solubility; BTT (min).

Table 3
Permeation of binary solvent mixtures through nitrile gloves

| $X$ | $J_s$ | $D$ | $S$ | $X$ | $J_s$ | $D$ | $S$ |
|---|---|---|---|---|---|---|---|
| Benzene | | | | Toluene | | | |
| 0.23 | 130 | 1.20 | 0.68 | 0.77 | 539 | 1.33 | 2.56 |
| 0.37 | 378 | 1.27 | 1.72 | 0.64 | 390 | 1.28 | 1.76 |
| 0.54 | 493 | 1.27 | 2.32 | 0.46 | 244 | 1.34 | 1.10 |
| 0.70 | 651 | 1.51 | 2.55 | 0.30 | 167 | 1.54 | 0.64 |
| 0.83 | 727 | 1.67 | 2.57 | 0.17 | 80 | 1.52 | 0.31 |
| Benzene | | | | Ethyl benzene | | | |
| 0.26 | 137 | 0.83 | 0.95 | 0.74 | 189 | 0.85 | 1.29 |
| 0.41 | 261 | 0.92 | 1.58 | 0.59 | 150 | 0.97 | 0.86 |
| 0.58 | 429 | 1.23 | 2.00 | 0.42 | 131 | 1.04 | 0.72 |
| 0.73 | 541 | 1.29 | 2.34 | 0.27 | 89 | 1.27 | 0.40 |
| 0.85 | 621 | 1.31 | 2.66 | 0.15 | 55 | 1.31 | 0.24 |
| Toluene | | | | Ethyl benzene | | | |
| 0.22 | 42 | 0.60 | 0.40 | 0.78 | 191 | 0.91 | 1.17 |
| 0.37 | 187 | 0.78 | 1.30 | 0.63 | 138 | 0.65 | 1.14 |
| 0.54 | 238 | 0.91 | 1.47 | 0.46 | 128 | 0.97 | 0.74 |
| 0.70 | 425 | 1.05 | 2.22 | 0.30 | 112 | 1.10 | 0.56 |
| 0.82 | 489 | 1.23 | 2.30 | 0.18 | 50 | 1.32 | 0.22 |
| Toluene | | | | p-Xylene | | | |
| 0.23 | 59 | 0.71 | 0.49 | 0.77 | 146 | 0.84 | 1.03 |
| 0.37 | 188 | 0.81 | 1.20 | 0.63 | 136 | 0.96 | 0.74 |
| 0.54 | 302 | 0.92 | 1.84 | 0.46 | 94 | 1.00 | 0.52 |
| 0.70 | 511 | 1.02 | 2.56 | 0.30 | 69 | 1.03 | 0.35 |
| 0.82 | 540 | 1.26 | 2.66 | 0.18 | 41 | 1.08 | 0.24 |

$X$, mole fraction; $J_s$ (µg/cm$^2$/min), steady state permeation rate; $D$ ($10^{-5}$ cm$^2$/min), diffusion coefficient; $S$ (g/cm$^3$), solubility.

551, 233 and 167 µg/cm$^2$/min, respectively. For BTEX mixtures, Tables 3 and 4 indicate that the steady state permeation rates of individual component were less than that of the single pure solvent. For example, the steady state permeation rates for benzene of different binary and ternary mixtures were less than 819 µg/cm$^2$/min.

From solubility parameter theory, two pure substances are soluble in one another if the internal energy change per unit volume, $\Delta E$ (ML$^{-1}$t$^{-2}$), is close to zero [1,11–12]. This is known as "like dissolves like". For the interaction of solvent mixture and polymer, the internal energy change is defined as follows:

$$\Delta E = v_m v_p (\delta_m - \delta_p)^2 = v_m v_p |\Delta \delta_m|^2 \qquad (2)$$

where $v$ is the volume fraction; $\delta$ is the solubility parameter (M$^{0.5}$L$^{-0.5}$t$^{-1}$); subscript m and p present the solvent mixture and polymer, respectively. The solubility parameter of solvent mixture, $\delta_m$ (M$^{0.5}$L$^{-0.5}$t$^{-1}$), can be derived as follows [13]:

$$\delta_m = \sum_{i=1}^{n} \left( \frac{X_i MV_i}{X_1 MV_1 + X_2 MV_2 + \cdots + X_n MV_n} \right) \delta_{s,i} \qquad (3)$$

where $X$ is the mole fraction of individual solvent in the mixture; MV the molar volume (L$^3$m$^{-1}$); $\delta_s$ is the solubility parameter of pure solvent (M$^{0.5}$L$^{-0.5}$t$^{-1}$) and can be determined as follows [14]:

$$\delta_s = \left( \frac{\Delta H_v - RT}{MV} \right)^{1/2} \qquad (4)$$

where $\Delta H_v$ is the molar heat of vaporization (ML$^2$t$^{-2}$m$^{-1}$); $R$ the universal gas constant (ML$^2$t$^{-2}$T$^{-1}$m$^{-1}$); $T$ is the absolute temperature (T). The solubility parameters of test solvents are given in Table 1.

Table 4
Permeation of ternary solvent mixtures through nitrile gloves

| Benzene | | | | Toluene | | | | Ethyl benzene | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $X$ | $J_s$ | $D$ | $S$ | $X$ | $J_s$ | $D$ | $S$ | $X$ | $J_s$ | $D$ | $S$ |
| 0.24 | 201 | 1.21 | 0.95 | 0.59 | 395 | 1.02 | 2.21 | 0.17 | 49 | 1.12 | 0.25 |
| 0.29 | 244 | 1.09 | 1.30 | 0.50 | 307 | 1.03 | 1.74 | 0.21 | 69 | 1.13 | 0.36 |
| 0.30 | 219 | 1.10 | 1.16 | 0.25 | 105 | 0.93 | 0.66 | 0.45 | 137 | 0.97 | 0.82 |
| 0.39 | 311 | 1.28 | 1.43 | 0.33 | 174 | 1.14 | 0.90 | 0.28 | 108 | 0.76 | 0.84 |
| 0.66 | 584 | 1.30 | 2.51 | 0.18 | 83 | 1.00 | 0.46 | 0.16 | 58 | 1.20 | 0.27 |

$X$, mole fraction; $J_s$ (µg/cm$^2$/min), steady state permeation rate; $D$ ($10^{-5}$ cm$^2$/min), diffusion coefficient; $S$ (g/cm$^3$), solubility.
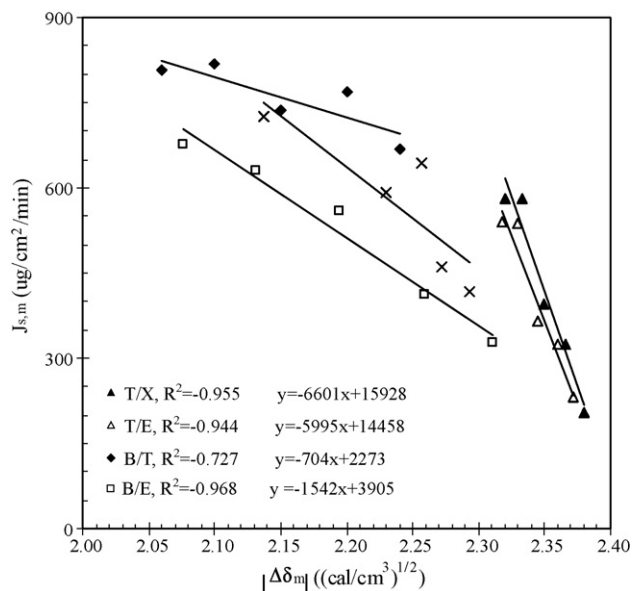
Fig. 3. Correlations of total steady state permeation rates to solubility parameters.



Fig. 4. Comparison of experimental total steady state permeation rates with Eq. (5).

As shown in Eq. (2), if the solvent mixture and polymer have similar solubility parameter (i.e. less $|\Delta\delta_m|$), the solvent mixture will be more soluble in the polymer. For the pure solvent, several researchers have indicated that the steady state permeation rate was inversely proportional to the parameter difference of solvent and polymer glove [7,15–16]. The solubility parameter for nitrile is 11.2 $(cal/cm^3)^{1/2}$ [12]. Fig. 3 shows that the total steady state permeation rates of binary and ternary solvent mixtures, $J_{s,m}$ ($ML^{-2}t^{-1}$), were correlated well to $|\Delta\delta_m|$ with $R^2 > -0.727$ ($p < 0.05$). As a result, the less the difference in the solubility parameter, the more solvent mixture will permeate through the nitrile glove.

Even though the concept of solubility parameter theory is based on pure substances, it would be appropriate to describe the permeation of solvent mixtures through the nitrile gloves under test. It is noted that the interaction between different components in the mixture may have an effect on the permeation process [1]. This can be the possible reason that the correlation equations, shown in Fig. 3, were obviously different for the five binary or tertiary solvent mixtures.

Perkins et al. [15] have indicated that the solvent molecular volume had a significant effect on the permeation rate of nitrile glove. As shown in Tables 3 and 4, the steady state permeation rate of individual solvent was proportional to its mole fraction in the mixture. On the basis of $\delta_m$ determined in Eq. (3), the total steady state permeation rate was hypothesized as follows:

$$J_{s,m} = \sum_{i=1}^{n} \left( \frac{X_i MV_i}{X_1 MV_1 + X_2 MV_2 + \cdots + X_n MV_n} \right) J_{s,i} \quad (5)$$

Fig. 4 shows that the total steady state permeation rates predicted using Eq. (5) were significantly correlated ($R^2 = 0.914$, $p < 0.001$) to the experimental results. Also seen in Fig. 4, the results were very close to 1:1 line indicating an excellent agreement between the experimentally determined steady state
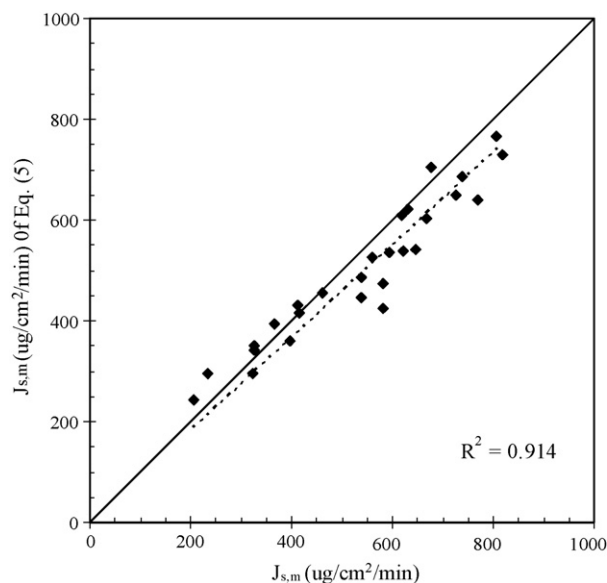
permeation rates and predictions of Eq. (5). The slight deviation from the 1:1 line for $J_{s,m} > 400 \, \mu g/cm^2/min$ may be due to the swelling of the glove sample. For the solvent mixtures of this study, the total steady state permeation rates can be approximately predicted using Eq. (5).

### 3.2. Breakthrough time

The normalized breakthrough times for single pure solvents and mixtures are summarized in Tables 2 and 5, respectively. The more quickly permeating component of a mixture carried along the component which permeated slowly in its pure form. For example, Table 2 shows that the pure benzene, toluene and ethyl benzene broke through the nitrile glove with 14, 31 and 52 min, respectively. For their ternary mixtures of different compositions, the normalized breakthrough times for benzene were retarded to 26–44 min, and the normalized breakthrough times for ethyl benzene were shortened to 36–46 min. Toluene in the ternary mixtures broke through nitrile gloves with 30–32 min. These results were consistent with the hypotheses of "co-solvent effect".

According to solubility parameter theory, polymer materials differing significantly in solubility parameter from that of the chemical are likely to be resistant to the liquid. If the difference of solubility parameter between the pure solvent and polymer (i.e. $|\Delta\delta|$) is less than that of solvent mixture (i.e. $|\Delta\delta_m|$), it is speculated that the normalized breakthrough time for the component of solvent mixture will be longer than its pure form. For the example shown in Table 6, $\delta_m$ for benzene (0.29), toluene (0.5) and ethyl benzene (0.21) mixture was calculated 8.95 $(cal/cm^3)^{1/2}$ using Eq. (3), and $|\Delta\delta_m|$ was 2.25 $(cal/cm^3)^{1/2}$ for the ternary mixture and nitrile glove. $|\Delta\delta|$ for benzene was 2 $(cal/cm^3)^{1/2}$ and less than $|\Delta\delta_m|$, then the normalized breakthrough time of benzene in the ternary mixture was 33 min which was longer than its pure form (i.e. 14 min). Also seen in Table 6,

Table 5
Breakthrough time for binary and ternary solvent mixtures

| X | BTT | X | BTT | X | BTT |
|---|-----|---|-----|---|-----|
| | Benzene | | Toluene | | Ethyl benzene |
| 0.24 | 26 | 0.59 | 30 | 0.17 | 46 |
| 0.29 | 33 | 0.50 | 30 | 0.21 | 36 |
| 0.30 | 44 | 0.25 | 30 | 0.45 | 46 |
| 0.39 | 32 | 0.33 | 31 | 0.28 | 40 |
| 0.66 | 26 | 0.18 | 32 | 0.16 | 36 |
| | Benzene | | Toluene | | |
| 0.23 | 44 | 0.77 | 36 | | |
| 0.37 | 31 | 0.63 | 31 | | |
| 0.54 | 34 | 0.46 | 29 | | |
| 0.70 | 24 | 0.30 | 26 | | |
| 0.83 | 24 | 0.17 | 28 | | |
| | Benzene | | Ethyl benzene | | |
| 0.26 | 54 | 0.74 | 52 | | |
| 0.41 | 37 | 0.59 | 43 | | |
| 0.58 | 35 | 0.42 | 43 | | |
| 0.73 | 23 | 0.27 | 34 | | |
| 0.85 | 23 | 0.15 | 36 | | |
| | Toluene | | Ethyl benzene | | |
| 0.22 | 88 | 0.78 | 44 | | |
| 0.37 | 48 | 0.63 | 50 | | |
| 0.54 | 44 | 0.46 | 44 | | |
| 0.70 | 34 | 0.30 | 37 | | |
| 0.82 | 32 | 0.18 | 40 | | |
| | Toluene | | p-Xylene | | |
| 0.23 | 83 | 0.77 | 59 | | |
| 0.37 | 43 | 0.63 | 40 | | |
| 0.54 | 43 | 0.46 | 44 | | |
| 0.70 | 34 | 0.30 | 39 | | |
| 0.82 | 44 | 0.18 | 49 | | |

X, mole fraction; BTT (min).

$|\Delta\delta|$ for toluene and ethyl benzene were 2.3 and 2.4 $(\mathrm{cal/cm^3})^{1/2}$, respectively, which were greater than $|\Delta\delta_m|$. On the other hand, toluene and ethyl benzene in the ternary mixture broke through more rapidly than their single pure liquids.

At present there is no study of the solubility parameter theory on predicting the permeation properties of multi-component solutions from the results of tests with single component liquids. Table 7 shows the permeation study originally reported by Mickelson et al. [5]. The breakthrough time of three binary solvent mixtures through nitrile and viton gloves was consistent with the hypothesis of solubility parameter theory. As case II presented in Table 7, methyl ethyl ketone (MEK) rapidly broke through the viton glove with 5 min and no permeation of n-hexane was detected during 4 h in its pure form. The solubility parameter $\delta$

Table 6
Breakthrough time and solubility parameter for ternary solvent mixture

| Solvent | $\delta$ | $\delta_m$ | $|\Delta\delta|$ | $|\Delta\delta_m|$ | BTT (min) | |
|---------|----------|-----------|------------------|--------------------|-----------|---|
| | | | | | Pure | Mixture |
| Benzene (0.29) | 9.2 | | 2 | | 14 | 33 |
| Toluene (0.5) | 8.9 | 8.95 | 2.3 | 2.25 | 31 | 30 |
| Ethyl benzene (0.21) | 8.8 | | 2.4 | | 52 | 36 |

X, mole fraction; $\delta$ $(\mathrm{cal/cm^3})^{1/2}$.

Table 7
Breakthrough time and solubility parameter for literature cases

| Solvent (W/W) | $\delta$ | $\delta_m$ | $|\Delta\delta|$ | $|\Delta\delta_m|$ | BTT (min) | |
|---------------|----------|-----------|------------------|--------------------|-----------|---|
| | | | | | Pure | Mixture |
| Case I, nitrile ($\delta = 11.2$) | | | | | | |
| Methanol (0.25) | 14.5 | 9.98 | 3.3 | 1.22 | 111 | 28 |
| n-Butyl acetate (0.75) | 8.3 | | 2.9 | | 59 | 30 |
| Case II, viton ($\delta = 10.1$) | | | | | | |
| n-Hexane (0.9) | 7.2 | 7.41 | 2.9 | 2.69 | ∞ | 38 |
| Methyl ethyl ketone (0.1) | 9.3 | | 0.8 | | 5 | 40 |
| Case III, nitrile ($\delta = 11.2$) | | | | | | |
| Toluene (0.5) | 8.9 | 8.85 | 2.3 | 2.35 | 33 | 33 |
| p-Xylene (0.5) | 8.8 | | 2.4 | | 53 | 35 |

Data from Mickelson et al. [5], $\delta$ $(\mathrm{cal/cm^3})^{1/2}$.

for viton is 10.1 $(\mathrm{cal/cm^3})^{1/2}$ [12]. $|\Delta\delta_m|$ of MEK and n-hexane mixture was 2.69 $(\mathrm{cal/cm^3})^{1/2}$ and ranged between $|\Delta\delta|$ of pure MEK (0.8) and n-hexane (2.9). Therefore, MEK promoted the permeation of n-hexane in the mixture through viton gloves. The breakthrough time for MEK and n-hexane were 40 and 38 min, respectively. Solubility parameter theory can provide a basis for explanation the results of breakthrough time for solvent mixtures.

### 3.3. Experimental diffusion coefficient and solubility

The permeation rate of organic solvents through a protective glove can be described by Fick's first law [1,8,9,17–22]:

$$J = -D\frac{\mathrm{d}C_Z}{\mathrm{d}Z} \tag{6}$$

where $D$ is the diffusion coefficient of organic solvent in the glove membrane $(\mathrm{L^2 t^{-1}})$; $C_Z$ the solvent concentration in the glove membrane $(\mathrm{ML^{-3}})$; and $Z$ is the distance into the glove membrane (L).

The one-dimensional diffusion into the glove membrane can be expressed by Fick's second law as follows:

$$\frac{\partial C_Z}{\partial t} = D\frac{\partial^2 C_Z}{\partial Z^2} \tag{7}$$

Several models have been proposed to estimate the diffusion coefficient for single-component liquid chemical permeation through polymer gloves [1,8,9,17–19]. Using a diaphragm cell, Crank [17] studied the diffusion of volatile organic compound (VOC) through polymer film with thickness $L$ and assumed that the boundary conditions for Eq. (7) were $C_{z=L}$ equal to zero at any time, and $C_{z=0}$ equal to the solubility, $S$ $(\mathrm{ML^{-3}})$, of VOC in the polymer film. According to the solutions of Eq. (7), Crank proposed that the diffusion coefficient of VOC in the polymer film was:

$$D = \frac{L^2}{6t_1} \tag{8}$$

where $t_1$ is the lag time ($t$) and is given by the extrapolation of the steady state permeation portion of the cumulative permeation curve to the time axis. Eq. (8) has been widely used to esti-

mate the diffusion coefficient of single pure chemical permeation through the polymer glove [8,9,18–19].

Using the assumptions of Crank [17], the steady state permeation rate for polymer glove could be determined by Eq. (6) as follows:

$$J_s = D\frac{C_{Z=0} - C_{Z=L}}{L} = D\frac{C_{Z=0}}{L} = D\frac{S}{L} \tag{9}$$

In this study, the diffusion coefficient $D$ was determined using Eq. (8), and the solubility $S$ was obtained by substituting $D$ and $J_s$ into Eq. (9) as follows:

$$S = J_s\frac{L}{D} \tag{10}$$

The diffusion coefficient is generally assumed to be independent of the concentration $C_Z$ [8,9,20]. On the other hand, several studies on polymer gloves have found that the diffusion coefficients varied with the solvent concentrations [14,21–22]. As shown in Tables 3 and 4, the coefficients of variation (CV) for diffusion coefficients were ranged from 14 to 24% for the four organic solvents in different compositions. The diffusion coefficients showed the strong dependence on the composition of binary solvent mixture ($R^2 = 0.662$–$0.99$).

Also indicated in Tables 3 and 4, the solubilities were proportional to the mole fraction ($X$) of solvent mixtures. Furthermore, the prediction of solubility in the mixture, $S_{pred}$ (ML$^{-3}$), can be determined using the value of pure solvent, $S_{pure}$ (ML$^{-3}$), as follows:

$$S_{pred} = X S_{pure} \tag{11}$$

As expected, Fig. 5 shows that the predictions of Eq. (11) were significantly correlated ($R^2 = 0.929, p < 0.001$) to the experimentally determined solubility ($S_{exp}$) of solvent mixtures in test nitrile gloves, especially for $S_{exp}$ less than 0.8 g/cm$^3$. As indicated in Fig. 5, the deviation from the 1:1 line for $S_{exp} > 0.8$ g/cm$^3$

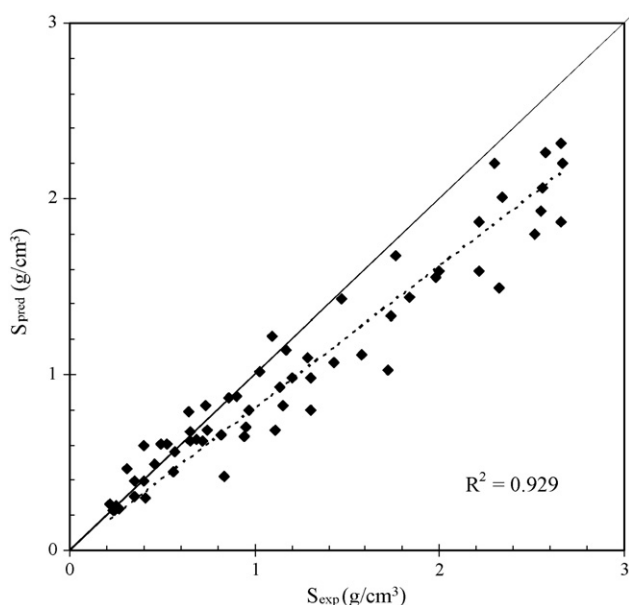may be due to the swelling of the glove membrane. Therefore, sorption between BTEX and nitrile glove can be a linear partitioning process.

### 3.4. Simulation of permeation concentration

Based on the assumptions of Crank's study [17], the concentration profile $C_Z$ in the glove membrane with thickness of $L$ was as follows by solving Eq. (7):

$$C_Z(Z, t) = C_{Z=0}\left(1 - \frac{Z}{L}\right) - 2\sum_{n=1}^{\infty}\frac{C_{Z=0}}{n\pi}$$

$$\times \exp\left(-D\left(\frac{n\pi}{L}\right)^2 t\right)\sin\left(n\pi\frac{Z}{L}\right) \tag{12}$$

By taking the mass balance for the collection medium, the permeation concentration, $C$ (ML$^{-3}$), in the open-loop system was determined as follows:

$$C = D\frac{A}{V}\left[\int^t\left(\frac{C_{Z=0}}{L} + 2\sum_{n=1}^{\infty}\frac{C_{Z=0}}{L}\exp\left(-D\left(\frac{n\pi}{L}\right)^2 t\right)\right)\right.$$

$$\left. \times \exp\left(-\frac{Q}{V}t\right)dt\right]\exp\left(-\frac{Q}{V}t\right) \tag{13}$$

where $V$ is the volume of sampling chamber (100 mL).

The permeation concentration $C$ in Eq. (13) can be solved using Maple software (Waterloo Maple Inc., Waterloo, Ontario, Canada). Fig. 6 shows the simulation results of Eq. (13) for the ternary solvent mixture. The diffusion coefficient $D$ estimated from Eq. (8) was able to appropriately simulate the permeation results with $C_{Z=0} = S$ as the boundary condition on exposed surface. As shown in Fig. 6, the simulated solvent concentrations were slightly higher than the experimental results. This deviation may be a result of neglecting the increase in sample thickness in the simulation model.

For the selection of an appropriate glove, however, it is impractical to perform permeation tests for all the possible com-
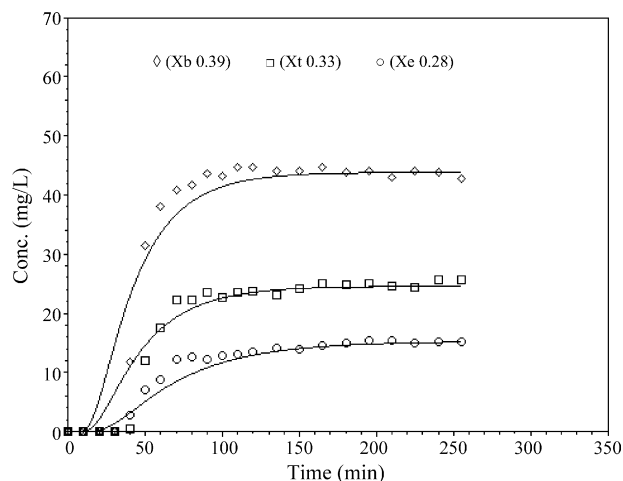


Fig. 5. Comparison of experimentally determined solubilities with predictions of Eq. (11).



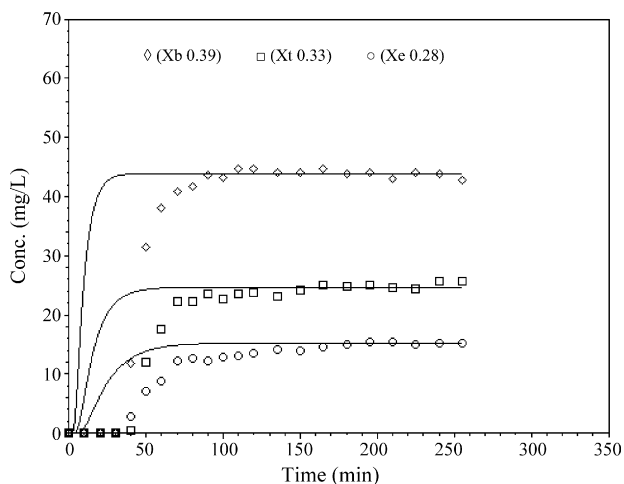Fig. 6. Simulated concentrations of ternary mixture in collection medium using $D$ and $S$.

Fig. 7. Simulations of permeation concentrations for ternary mixture using $D_E$ and $C_E$.

binations of solvent mixtures to obtain the diffusion coefficients of Eq. (8). Chao et al. [9] investigated the permeation of single pure solvent through nitrile gloves using the ASTM F739 cell. $C_{Z=0}$ was assumed to be its concentration of liquid chemical, $C_E$ ($ML^{-3}$). The effective diffusion coefficient, $D_E$ ($L^2 t^{-1}$), was determined using Eq. (9) as:

$$D_E = J_s \frac{L}{C_E} \tag{14}$$

In this study, $C_E$ was equal to the individual solvent concentration of mixture. Fig. 7 shows the simulation results of Eq. (13) using diffusion coefficient $D_E$ and boundary condition $C_{Z=0} = C_E$. As shown in Fig. 7, $D_E$ and $C_E$ were able to approximately simulate the permeation concentrations for the ternary solvent mixture at steady state. On the contrary, the simulated concentrations were obviously greater than the experimental results during the initial period of permeation. Similar results were also found for the other solvent mixtures. An over estimation of permeation was primarily due to neglecting the effect of solvent sorption onto the nitrile glove. As a result, it implied that the outside surface of the glove sample may not be in equilibration with the organic solvent.

For practical purposes, an over estimation in permeation concentration can be a safety approach for workers using the protective glove. Moreover, $J_s$ can be determined from the permeation test of individual pure solvent using Eq. (5), and $C_E$ is directly obtained by the composition of solvent mixture. For that reason, this approach can be considered as a preliminary risk assessment for work task.

## 4. Conclusion

In this study, solubility parameter theory provided a potential approach to interpret the permeation properties of BTEX mixtures through the test nitrile gloves. The slowly permeating component of a mixture broke through nitrile gloves earlier than its pure form, which may pose a significant risk for the worker exposure to hazardous chemicals. The larger differences in sol-

ubility parameter between solvent mixture and glove samples resulted in a lower permeation rate. If the single pure solvents could permeate through the protective glove, it is speculated that the steady state permeation rates of multi-component mixtures will depend on their molecular volume and mole fraction in composition. The four solvents used in this study are structurally similar, and further studies are required to resolve the hypothesis of chemicals interaction. Solvents with a wide range of solubility parameters can be considered as the test permeant for future studies.

Fick's diffusion coefficients and solubilities of BTEX in nitrile gloves were obtained using their lag time and steady state permeation rate. The diffusion coefficients and solubilities varied with the compositions of solvent mixture. The permeation concentrations of ASTM F739 experiments were simulated well using a one-dimensional Fick's diffusion equation and appropriate boundary conditions for the steady state. The modeling work presented herein can provide a risk-based decision to assess the dermal exposures of workers wearing protective gloves.

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