

# Diffusion and solubility coefficients determined by permeation and immersion experiments for organic solvents in HDPE geomembrane

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## Abstract

The chemical resistance of eight organic solvents in high density polyethylene (HDPE) geomembrane has been investigated using the ASTM F739 permeation method and the immersion test at different temperatures. The diffusion of the experimental organic solvents in HDPE geomembrane was non-Fickian kinetic, and the solubility coefficients can be consistent with the solubility parameter theory. The diffusion coefficients and solubility coefficients determined by the ASTM F739 method were significantly correlated to the immersion tests ( $p < 0.001$ ). The steady state permeation rates also showed a good agreement between ASTM F739 and immersion experiments ( $r^2 = 0.973$ ,  $p < 0.001$ ). Using a one-dimensional diffusion equation based on Fick's second law, the diffusion and solubility coefficients obtained by immersion test resulted in over estimates of the ASTM F739 permeation results. The modeling results indicated that the diffusion and solubility coefficients should be obtained using ASTM F739 method which closely simulates the practical application of HDPE as barriers in the field.

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## 1. Introduction

Geomembranes in conjunction with compacted or geosynthetic clay liners have been widely used as barriers against the transport and migration of contaminant in waste storage and disposal landfills. Many industrial wastes, such as organic solvents, are currently dumped into landfills, especially for developing countries. Even though, polymeric geomembranes are non-porous materials and are impermeable to liquids, the waste chemicals or landfill leachate may still permeate through geomembranes by diffusion [1–6].

The permeability of geomembrane depends on the solubility and diffusibility of chemical in the geomembrane. Organic liquid permeation through geomembrane is usually measured using the immersion/sorption method. The geomembranes sample is immersed in a sealed container and weighted at specified time intervals. Several researchers have estimated the diffusion and

solubility coefficients of organic solvents in geomembrane using the gravimetric test [2–4,7–11].

On the other hand, ASTM F739 test method has been recommended to assess the permeability of geomembranes for organic solvents [12]. ASTM F739 method is widely applied to measure the resistance of protective gloves to permeation by liquid chemicals [13]. In ASTM F739 method, the specific permeation cell and analytical detection system are used to measure the breakthrough time and permeation rate of chemicals. The geomembrane sample divides permeation cell into two chambers: the challenge chamber which is filled with the permeant, and the collection chamber where the permeant is collected and analyzed.

The immersion method is a simple and expedient gravimetric test [6,11]. In contrast to the ASTM F739 method, both surfaces of geomembrane sample are in contact with the tested chemical for immersion method. However, the experimental conditions of ASTM F739 can be more comparable to the practical application as barriers in field. Further study should be concerned with correlating the data obtained from the ASTM F739 permeation method and immersion test.

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In this study, diffusion and solubility coefficients of eight neat organic solvents in high density polyethylene (HDPE) geomembrane were estimated for ASTM F739 permeation experiments and immersion tests. Typically, the geomembranes in landfills are exposed to aqueous solutions of various contaminants but it is possible that the geomembranes may be exposed to pure solvents especially in developing countries where cans and drums of solvents may be disposed in landfills and in hazardous waste storage areas. As such, experiments of pure solvent done herein are the fundamental work for further study on the investigation of the permeation of aqueous solution through HDPE geomembrane. A temperature dependence of diffusion and solubility coefficients has been used to derive the Arrhenius and van't Hoff activation parameters. Comparisons were made between the steady state permeation rates and simulation of ASTM F739 experiment data using Fick's second law. The present work will provide an approach to quantitatively interpret the immersion test in comparison with data of ASTM F739 experiment results for organic solvents permeation through HDPE.

## 2. Theory

### 2.1. Permeation through polymer films

Permeation of organic solvents through the polymer films is primarily a diffusion mechanism at a molecular level that can be described by Fick's first law:

$$J = -D \frac{dC_Z}{dZ} \quad (1)$$

where  $J$  is the permeation rate per unit area ( $\text{ML}^{-2}\text{T}^{-1}$ );  $D$  the diffusion coefficient of organic solvent in the polymer membrane ( $\text{L}^2\text{T}^{-1}$ );  $C_Z$  the solvent concentration in the membrane ( $\text{ML}^{-3}$ );  $Z$  is the position into the membrane (L).

The diffusion into the polymer film in one-dimension may be expressed by Fick's second law with a constant diffusion coefficient as follows

$$\frac{\partial C_Z}{\partial t} = D \frac{\partial^2 C_Z}{\partial Z^2} \quad (2)$$

Crank employed a diaphragm cell to investigate the permeation of volatile organic compounds (VOC) vapor through polymer film with thickness  $L$  and assumed that the boundary conditions for Eq. (2) were  $C_{Z=L}$  equal to zero at any time, and  $C_{Z=0}$  equal to the solubility,  $S$  ( $\text{ML}^{-3}$ ), of the VOC in the polymer [2,14–16]. According to the solutions of Eq. (2), the diffusion coefficient,  $D_p$  ( $\text{L}^2\text{T}^{-1}$ ), of VOC permeation through the polymer film is given by

$$D_p = \frac{L^2}{6t_1} \quad (3)$$

where  $t_1$  is the lag time (T) which is given by the time-axis intercept from the extrapolation of the steady state permeation portion of the cumulative permeation curve.

Eq. (3) has been widely used to estimate the diffusion coefficient of liquid chemical permeation through the polymer film

[2,15]. Based on the assumptions of Crank, the steady state permeation rate,  $J_s$  ( $\text{ML}^{-2}\text{T}^{-1}$ ), for polymer film can be determined by Eq. (1) as follows [15,16]:

$$J_s = -D \frac{C_{Z=L} - C_{Z=0}}{L} = D \frac{S}{L} \quad (4)$$

### 2.2. Estimation of diffusion coefficient from immersion test

During immersion tests, the change of polymer membrane weight,  $C_t$ , is determined as

$$C_t = \frac{W_t - W_0}{W_\infty - W_0} \quad (5)$$

where  $W_t$  is the weight of polymer membrane at time  $t$  (M);  $W_0$  the initial weight of polymer (M);  $W_\infty$  is the maximum weight of polymer for equilibrium sorption (M).

In the case of polymer membrane immersed in the organic solvent,  $C_{Z=0}$  and  $C_{Z=L}$  for Eq. (2) are assumed to be equal to the solubility,  $S_i$  ( $\text{ML}^{-3}$ ), of organic solvent in polymer membrane at any time. By plotting  $C_i$  against the square root of time, the diffusion coefficient,  $D_i$  ( $\text{L}^2\text{T}^{-1}$ ), of organic solvent in polymer membrane with initial thickness of  $L$  can be estimated using the sorption curve as follows [2,7–11,16,17]:

$$D_i = \pi \left( \frac{L\theta}{4} \right)^2 \quad (6)$$

where  $\theta$  is the initial gradient (i.e., before 55% equilibrium) of the  $C_t - \sqrt{t}$  sorption curve.

Several researchers have conducted immersion tests to obtain the solubilities of chemical in polymer membranes [10,11,15]. In their studies, solubility  $S_i$  was estimated using the equilibrium sorption data as follows

$$S_i = \frac{W_\infty - W_0}{V_0} \quad (7)$$

where  $V_0$  is the initial volume of polymer membrane ( $\text{L}^3$ ).

## 3. Materials and methods

### 3.1. Organic solvents and HDPE geomembrane

Organic solvents used for this study were chlorinated hydrocarbons (dichloromethane, 1,2-dichloroethane, chloroform, trichloroethylene) and aromatic hydrocarbons (benzene, toluene, styrene, ethyl benzene). These organic solvents are the components commonly found in landfills and hazardous waste ponds [2,3,10]. The experimental solvents were manufactured by Merck Co. (Darmstadt, Germany) with higher purity (>98%). Some properties of these solvents are summarized in Table 1. Because of the boiling nature of organic solvents, 1,2-dichloroethane, chloroform and trichloroethylene were conducted for experiments at higher temperatures.

HDPE geomembranes were supplied by Huikwang Chemical Co. (Taiwan, ROC) with approximate thickness of 0.5 and 1 mm. The circularly cut HDPE samples (diameter 8 cm) were rinsed with deionized water and air-dried for 24 h at  $25 \pm 1^\circ\text{C}$

Table 1  
Properties of experimental organic solvents

Chemicals	Grade	Purity (%)	Density	MW	$\Delta H_v$	WS	$\delta$	LDL
Dichloromethane	LC	99.9	1.327	84.93	6.93	20,000	9.96	0.48
1,2-Dichloroethane	GR	99.5	1.253	98.97	8.41	8,690	9.95	0.59
Chloroform	GR	99.4	1.484	119.38	7.50	8,000	9.25	0.63
Trichloroethylene	GR	99.5	1.464	131.79	8.27	1,100	9.25	0.33
Benzene	ACS	99	0.877	78.11	8.10	1,780	9.19	0.59
Toluene	ACS	99	0.867	92.14	9.09	515	8.95	0.59
Styrene	GC	99.5	0.906	104.15	10.49	300	9.28	0.64
Ethyl benzene	GC	98	0.867	106.17	10.10	152	8.81	0.65

Properties are at 25 °C; density (g/cm<sup>3</sup>); MW, molecular weight (g/mol) [22];  $\Delta H_v$ , molar heat of vaporization (kcal/mol) [23]; WS, water solubility (mg/L) at 20 °C [24];  $\delta$ , solubility parameter ((cal/cm<sup>3</sup>)<sup>1/2</sup>); LDL, limit detection level (mg/L).

and a relative humidity of 50 ± 20% before use. The average thickness,  $L$ , of each HDPE was measured at several locations on the sample using a dial thickness gauge (Teclock Co., Japan) to an accuracy of 0.01 mm.

### 3.2. ASTM F739 permeation experiment

Permeation experiments were conducted using the ASTM F739 liquid chemical permeation test method with a closed-loop system [13]. The sketch of the experimental system and associated equipment are shown in Fig. 1. The permeation cell (Pesce Laboratories, Kennett Square, PA) was assembled and placed in an incubator at temperature of 25 ± 1, 35 ± 1 and 45 ± 1 °C, respectively. Deionized water was circulated through the collection chamber using a MasterFlex<sup>®</sup> PTFE-Tubing pump system (CZ-77912-00, Cole-Parmer, Vernon Hills, IL.) at 60 mL/min. The permeation cell and associated equipment were connected with Teflon tubing (Nalgene, Rochester, NY).

Every 30 min intervals of the experiment, 4.5 mL aliquots of the collection medium were collected from the downstream sampling point using gas-tight syringes. Simultaneously, 4.5 mL of deionized water was replenished into the well-stirred Teflon bottle of the closed-loop system. This effort was made to maintain the constant volume of the collection medium in the system (approximately 730 mL). The samples of collection medium were extracted using solid phase micro-extraction fiber (polydimethylsiloxane, 57300-U PDMS, Supelco, Bellefonte, PA) and analyzed with a gas chromatograph equipped with flame ionization detector (AutoSystem XL, Perkin-Elmer, Eder Prairie, MN).

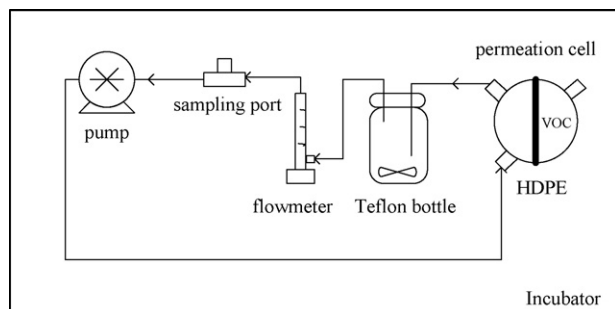


Fig. 1. Experimental setup of closed-loop permeation system.

### 3.3. Immersion test

For the immersion test, pieces of air-dried HDPE with a 5.08 cm (2 in.) diameter were cut giving the same surface area exposed as in the permeation cell. The HDPE samples were weighed using a highly sensitive electronic balance (AG245, Mettler Toledo, Switzerland) with an accuracy of 0.0001 g, and then completely immersed into screw-tight Teflon bottles containing organic solvent. The immersion tests were performed at 25 ± 1, 35 ± 1 and 45 ± 1 °C in an incubator.

After being taken from the sealed bottle at every 5-min interval, the HDPE sample was gently blotted to remove the surface liquid and was weighed immediately using the electronic balance. The HDPE sample was then returned to the screw-tight bottle and efforts were taken to minimize the time needed to weigh the sample. The samples were weighed until the mass of HDPE was constant (i.e., equilibrium sorption).

## 4. Results and discussion

### 4.1. Experimental diffusion and solubility coefficients

Permeation and immersion experiments were repeated four times for each organic solvent and temperature. Fig. 2 shows the concentrations of organic solvents in the collection medium for permeation experiments. The lag time  $t_l$  can be determined by the extrapolation of the steady state portion in Fig. 2, and the diffusion coefficients  $D_p$  were estimated using Eq. (3). The experimental steady state permeation rate,  $J_{s,p}$ , was calculated as follows

$$J_{s,p} = \alpha \frac{V}{A} \quad (8)$$

where  $\alpha$  is the slope of linear portion of the organic solvent concentrations in collection medium (ML<sup>-3</sup>T<sup>-1</sup>) as shown in Fig. 2;  $V$  the total volume of collection medium (730 mL);  $A$  is the area of HDPE exposed to the permeate (18.08 cm<sup>2</sup>) in the cell. Further, the solubility for permeation experiment,  $S_p$ , was obtained by substituting  $D_p$  and  $J_{s,p}$  into Eq. (4).

Fig. 3 shows the  $C_t - \sqrt{t}$  sorption curves of the organic solvents for the immersion test. The gradient of sorption

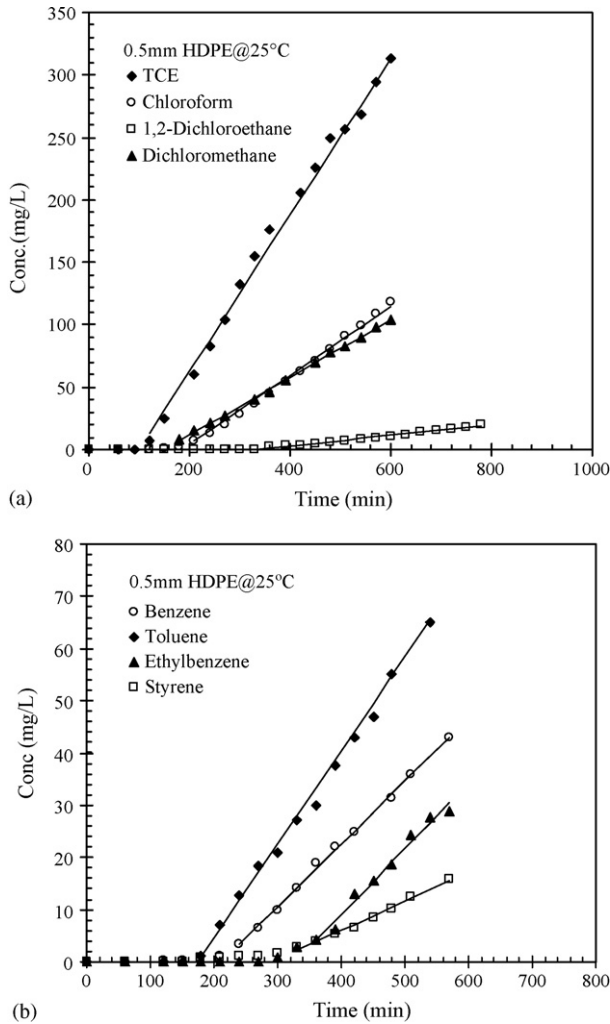


Fig. 2. Permeation concentrations of organic solvents in collection medium.

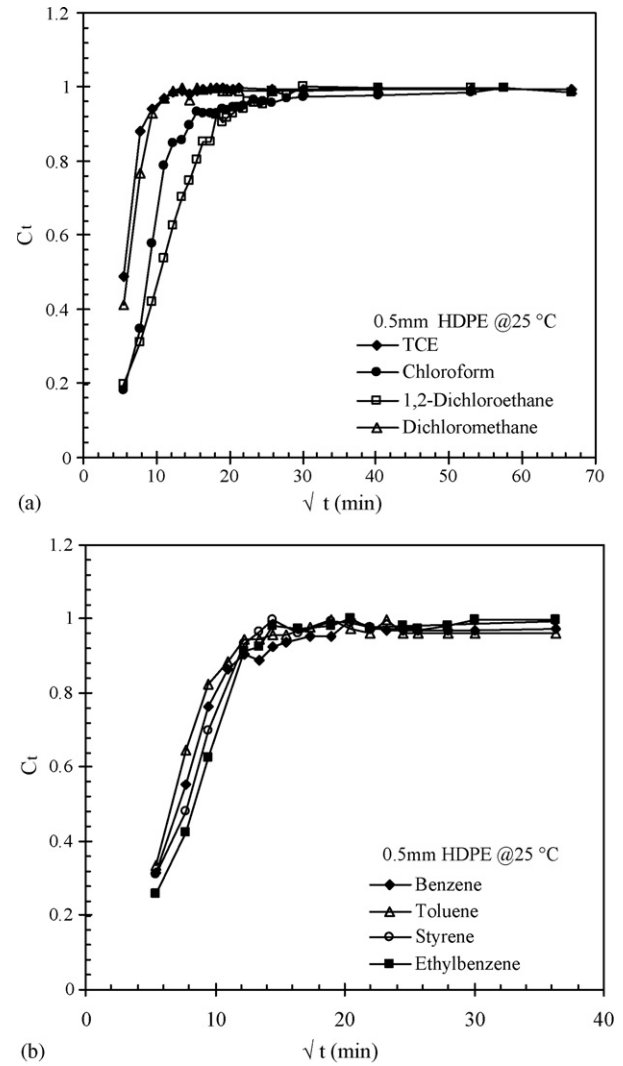


Fig. 3. Sorption curves for immersion tests.

curve  $\theta$  was obtained by the least square analysis of the initial period. The diffusion coefficients  $D_i$  and solubility  $S_i$  were determined using Eqs. (6) and (7), respectively. For the immersion test, the steady state permeation rate,  $J_{s,i}$  ( $\text{ML}^{-2}\text{T}^{-1}$ ), was assumed to be determined by substituting  $D_i$  and  $S_i$  into Eq. (4).

For the steady state, the solubility coefficient,  $K$  (dimensionless), of organic solvent in HDPE can be determined using the Nerst distribution function (Henry's law) as follows [2,9,10,16,18]:

$$K = \frac{S}{C_f} \quad (9)$$

where  $C_f$  is the equilibrium concentration of permeate ( $\text{ML}^{-3}$ ). In this study,  $C_f$  is the density of organic solvent. The solubility coefficients for permeation experiment ( $K_p$ ) and immersion test ( $K_i$ ) were obtained by substituting  $S_p$  and  $S_i$  into Eq. (9), respectively. Table 2 shows the average steady state permeation rates, diffusion and solubility coefficients of organic solvents in 0.5 mm HDPE at 25 °C.

#### 4.2. Sorption kinetics of immersion test

As shown in Table 2, the maximum weights of organic solvents gained in the HDPE samples,  $W_\infty$ , were significantly correlated to the steady state permeation rate of immersion tests,  $J_{s,i}$ , with  $r^2 = 0.777$  ( $p = 0.004$ ). Therefore, the more mass was sorbed in HDPE, the less the resistance to organic solvents.

From the solubility parameter theory [19], two substances are soluble in one another if the internal energy change,  $\Delta E$  ( $\text{ML}^2\text{T}^{-2}$ ), is less. For interaction of the solvent and polymer, the internal energy change is defined as follows

$$\Delta E = v_s v_p (\delta_s - \delta_p)^2 = v_s v_p |\Delta \delta|^2 \quad (10)$$

where  $v$  is the volume fraction;  $\delta$  is the solubility parameter ( $\text{M}^{0.5}\text{LT}^{-1}$ ); subscript 's' and 'p' represent the solvent and polymer, respectively.

As shown in Eq. (10), if the solvent and polymer have similar solubility parameter (i.e., less  $\Delta \delta$ ), the solvent will be more soluble in the polymer. The solubility parameter for

Table 2  
Diffusion and solubility coefficients of organic solvents

Organic solvent	Immersion test					Permeation experiment		
	$D_i$	$K_i$	$J_{s,i}$	$W_\infty$	$n$	$D_p$	$K_p$	$J_{s,p}$
Dichloromethane	0.87	6.10	7.96	8.56	0.75	0.45	12.21	8.97
1,2-Dichloroethane	0.27	3.81	1.43	5.11	0.66	0.27	4.85	1.96
Chloroform	0.51	9.61	8.03	15.34	0.98	0.34	19.66	11.12
Trichloroethylene	1.18	11.99	23.08	18.88	0.83	0.79	20.98	26.60
Benzene	0.53	9.69	5.32	8.73	0.67	0.36	19.50	7.11
Toluene	0.61	10.35	6.26	9.42	0.67	0.41	19.95	7.98
Styrene	0.57	8.83	5.35	8.22	0.66	0.31	16.66	5.41
Ethyl benzene	0.45	10.20	4.59	9.29	0.78	0.25	15.4	4.05

Data for 0.5 mm HDPE at 25 °C;  $D_i$ , diffusion coefficient ( $10^{-7}$  cm<sup>2</sup>/s);  $K_i$ , solubility coefficient ( $10^{-2}$ );  $J_{s,i} = D_i S_i / L$  ( $\mu\text{g}/\text{cm}^2 \text{min}$ );  $J_{s,p}$ , determined by ASTM F739 experiments ( $\mu\text{g}/\text{cm}^2 \text{min}$ );  $W_\infty$ , maximum weight gain of HDPE ( $10^{-2}$  g);  $n$ , sorption kinetic.

polyethylene is  $7.93 (\text{cal}/\text{cm}^3)^{1/2}$  [18]. For immersion tests, the solubility coefficient of organic solvent in HDPE,  $K_i$ , was found to be significantly correlated to  $\Delta\delta$  with  $r^2 = -0.719$  ( $p = 0.008$ ). On the other hand, the steady state permeation rate,  $J_{s,i}$ , was poorly correlated to  $\Delta\delta$  with  $r^2 = -0.014$  ( $p = 0.782$ ). The correlation coefficient indicates that the solubility parameter theory is not available to describe the permeation of organic solvents through HDPE.

The diffusion mechanism can be classified by the value of  $n$  from the following relation [3,7,8,17]:

$$C_t = kt^n \quad (11)$$

where  $k$  and  $n$  are empirical parameters and can be determined by the least square analysis of  $\log C_t$  and  $\log t$ . The Fickian diffusion is characterized by  $n = 0.5$ , and non-Fickian or anomalous diffusion by  $n$  varying between 0.5 and 1.

As shown in Table 2, the values of empirical parameter  $n$  for the experimental solvents were calculated to be 0.66–0.98 using the initial sorption data of immersion tests. Therefore, the diffusion kinetic of these organic solvents in 0.5 mm HDPE was non-Fickian. This was the reason that the sorption curves were slightly sigmoidal in shape during the initial period as shown in Fig. 3. Non-Fickian diffusion probably occurs due to the swelling of polymer and relaxation of internal stresses [16,17].

For the immersion tests, the thickness of HDPE was increased less than 5% for the eight organic solvents. The swelling of HDPE was not obvious in this study.

#### 4.3. Effect of temperature

Table 3 shows the results of immersion and permeation experiments for 1 mm HDPE at  $25 \pm 1$ ,  $35 \pm 1$  and  $45 \pm 1$  °C, respectively. Because the chains of HDPE became more flexible and free volume was increased at higher temperature [7]. Either diffusion or solubility coefficients were increased with increasing temperature for 1,2-dichloroethane, chloroform and trichloroethylene. Therefore,  $J_{s,i}$  and  $J_{s,p}$  were significantly increased with temperature. As shown in Table 3, the steady state permeation rates increased by about twice for every increase of 10 °C. This implies that the resistance of organic solvents to HDPE will decrease with an increase in temperatures. As presented in Table 3, the values of  $n$  range between 0.61 and 0.9 for different temperatures indicating non-Fickian diffusion kinetic. It is noted that the value of  $n$  varies as:  $35^\circ\text{C} > 25^\circ\text{C} > 45^\circ\text{C}$ .

The permeation coefficient,  $P$  ( $\text{L}^2\text{T}^{-1}$ ), is calculated as follows [2,3,7,10]:

$$P = KD \quad (12)$$

Table 3  
Results of immersion tests and permeation experiments at different temperatures

Organic solvent	Temperature (°C)	Immersion test					Permeation experiment			
		$D_i$	$K_i$	$P_i$	$J_{s,i}$	$n$	$D_p$	$K_p$	$P_p$	$J_{s,p}$
1,2-Dichloroethane	25	0.38	3.69	1.40	1.06	0.65	0.45	1.81	0.81	0.60
	35	0.77	4.62	3.56	2.70	0.89	0.70	2.68	1.88	1.62
	45	1.33	5.70	7.58	5.80	0.61	1.43	3.14	4.49	3.87
Chloroform	25	0.66	9.12	6.02	5.45	0.89	0.40	13.44	5.38	4.74
	35	1.49	11.10	16.54	14.90	0.9	0.79	16.90	13.35	14.80
	45	2.31	13.10	30.26	27.40	0.71	1.66	23.85	39.59	34.58
Trichloroethylene	25	1.02	11.22	11.44	10.02	0.87	0.89	15.32	13.63	11.68
	35	2.33	13.95	32.50	25.85	0.90	1.37	19.46	26.66	25.32
	45	3.13	16.70	52.27	46.73	0.73	2.29	21.19	48.53	38.45

Data for 1 mm HDPE;  $D_i$ , diffusion coefficient ( $10^{-7}$  cm<sup>2</sup>/s);  $K_i$ , solubility coefficient ( $10^{-2}$ );  $P_i$ , permeation coefficient ( $10^{-9}$  cm<sup>2</sup>/s);  $J_{s,i} = D_i S_i / L$  ( $\mu\text{g}/\text{cm}^2 \text{min}$ );  $J_{s,p}$ , determined by ASTM F739 experiments ( $\mu\text{g}/\text{cm}^2 \text{min}$ );  $n$ : sorption kinetic.

Table 4  
Arrhenius and van't Hoff parameters for immersion and permeation experiments

Organic solvent	$E_D$ (kJ/mol)	$E_P$ (kJ/mol)	$\Delta H_s$ (kJ/mol)
Immersion test			
1,2-Dichloroethane	49.40	66.57	17.17
Chloroform	41.88	58.17	14.28
Trichloroethylene	44.38	60.07	15.69
Permeation experiment			
1,2-Dichloroethane	45.41	67.43	20.26
Chloroform	56.55	78.55	22.53
Trichloroethylene	37.39	46.77	9.60

The effect of temperature on the permeation process can be related using Arrhenius and van't Hoff relations as follows [2,3,7,8,10,20]:

$$K = K_0 e^{-\Delta H_s/RT} \quad (13)$$

$$D = D_0 e^{-E_D/RT} \quad (14)$$

$$P = P_0 e^{-E_P/RT} \quad (15)$$

where  $\Delta H_s$  is the heat of sorption ( $\text{ML}^2\text{T}^{-2}$ ),  $E_D$  and  $E_P$  are the activation energy of diffusion and permeation, respectively ( $\text{ML}^2\text{T}^{-2}$ );  $R$  the universal gas constant ( $\text{ML}^2\text{T}^{-3}$ );  $T$  absolute temperature;  $K_0$ ,  $D_0$  and  $P_0$  represent the pre-exponential factor.

The  $\Delta H_s$  value was determined from least squares method by fitting the  $\ln K$  versus  $1/T$ . Similarly,  $E_D$  and  $E_P$  can be obtained. The plots of Arrhenius and van't Hoff relations were highly linear ( $r^2 = 0.939-1$ ,  $p < 0.5$ ) for both immersion and permeation experiments. The estimated values of  $\Delta H_s$ ,  $E_D$  and  $E_P$  are shown in Table 4. The positive values of  $\Delta H_s$ , ranged between 9.6 and 22.53 kJ/mol, indicate that the process of organic solvents permeation through HDPE is the endothermic reaction and Henry's law sorption mode [7,8]. There is no systematic difference in  $\Delta H_s$ ,  $E_D$  and  $E_P$  between immersion and permeation experiments.

#### 4.4. Correlation of immersion test to permeation experiment

Fig. 4a shows the correlation of diffusion coefficients for permeation and immersion results presented in Tables 2 and 3. As shown in Fig. 4a,  $D_i$  was greater than  $D_p$ , but they were of the same magnitude.  $D_i$  and  $D_p$  were found to be significantly correlated with  $r^2 = 0.904$  ( $p < 0.001$ ). It is reasonable because they were derived from the Fick's second law but with different boundary conditions. On the other hand, Fig. 4b shows that  $K_p$  was correlated well to  $K_i$  ( $r^2 = 0.694$ ,  $p < 0.001$ ) and  $K_p$  was approximately 50% greater than  $K_i$ .

For ASTM F739 method, the steady state permeation rate is required to be documentary as the resistance of polymer to permeation. Fig. 4c shows that  $J_{s,i}$  and  $J_{s,p}$  were significantly correlated with  $r^2 = 0.973$  ( $p < 0.001$ ). In general, the steady state permeation rates obtained from immersion tests were lower than the permeation experiments, but  $J_{s,i}$  and  $J_{s,p}$  were

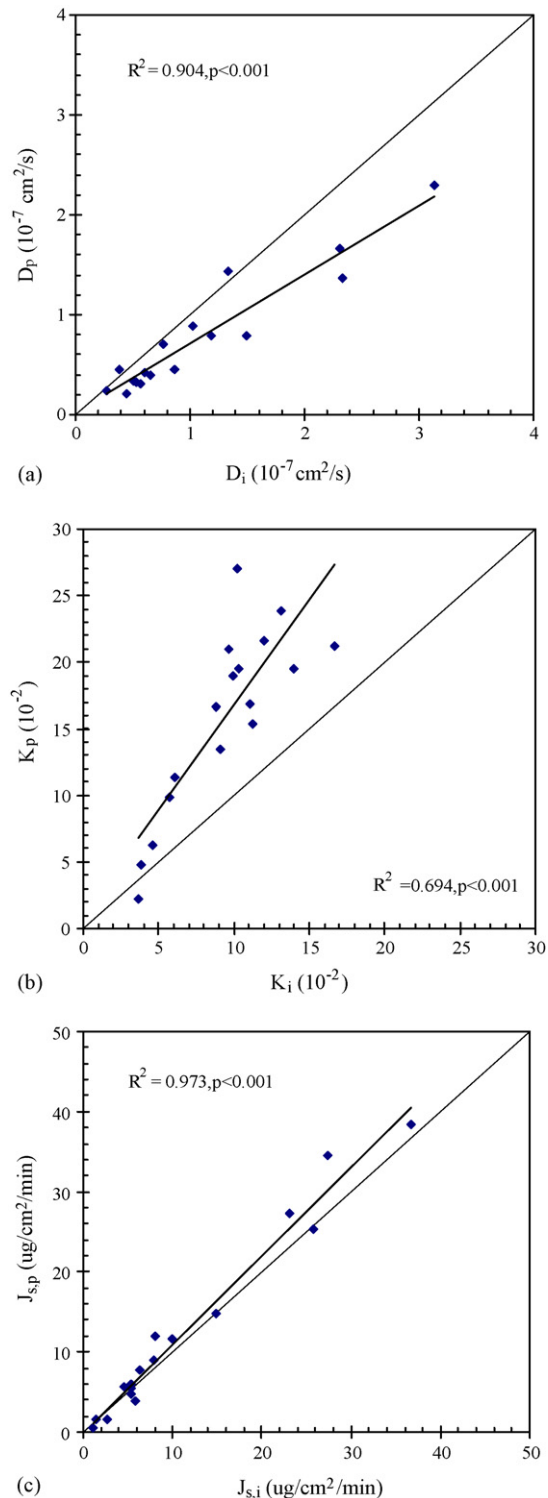


Fig. 4. Comparisons of steady state permeation rates, solubility and diffusion coefficients determined by ASTM F739 experiments and immersion test.

very close to 1:1 line indicating good agreement between ASTM F739 and immersion experiments. In comparison with ASTM F739 method, the immersion test could be a much simpler approach to measure the steady state permeation rate.

#### 4.5. Simulation of permeation results

For HDPE with thickness of  $L$ , the boundary and initial conditions in Eq. (2) were assumed as follows:

$$C_Z(0, t) = S = KC_f \quad t > 0$$

$$C_Z(L, t) = 0 \quad t > 0$$

$$C_Z(Z, 0) = 0$$

The concentration profile  $C_Z$  in HDPE is given as

$$C_Z(Z, t) = KC_f \left( 1 - \frac{Z}{L} - \sum_{n=1}^{\infty} \left( \frac{2}{n\pi} e^{-D(n\pi/L)^2 t} \sin\left(\frac{n\pi}{L} Z\right) \right) \right) \quad (16)$$

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

$$V \left( \frac{dC}{dt} \right) = -AD \left. \frac{\partial C_Z(Z, t)}{\partial Z} \right|_{Z=L} \quad (17)$$

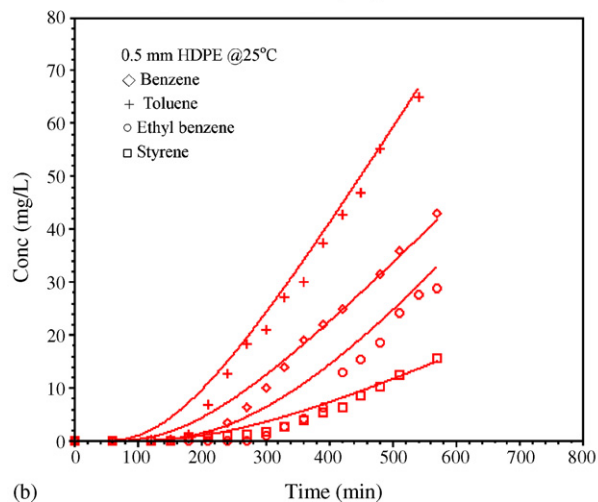
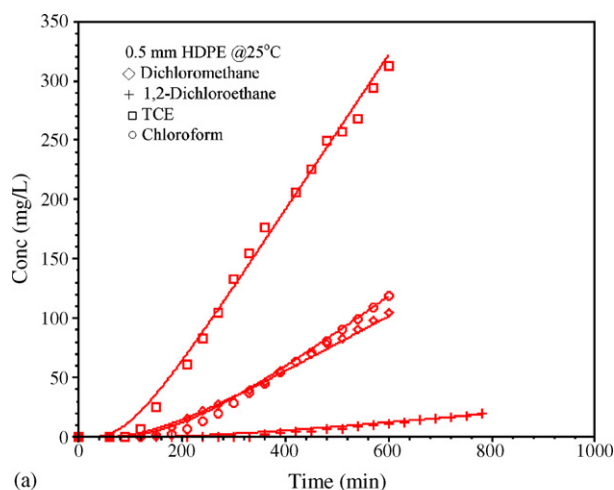


Fig. 5. Simulations of organic solvent concentrations in permeation experiments using  $K_p$  and  $D_p$ .

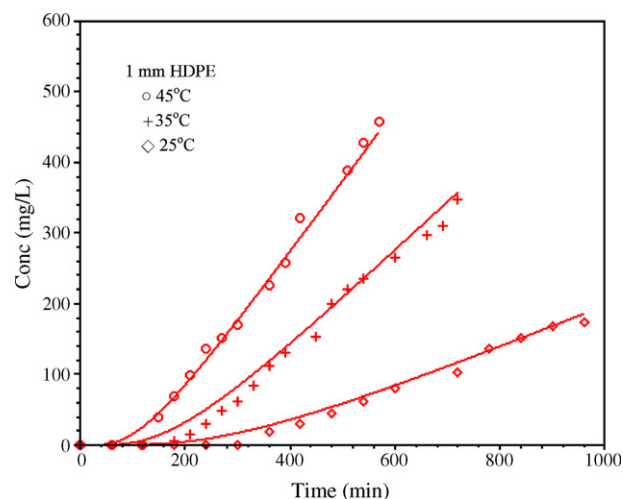


Fig. 6. Simulations of TCE permeation concentration using  $D_p$  and  $K_p$  at different temperatures.

The analytical solution for Eq. (17) can be obtained with initial condition  $C(0) = 0$ . Fig. 5 shows the simulation results of Eq. (17) using diffusion coefficient  $D_p$  and solubility coefficient  $K_p$  determined from the permeation experiments. For the eight organic solvents,  $D_p$  estimated from Eq. (3) was able to appropriately simulate the permeation results with  $K_p$  as the boundary condition on exposed surface, especially for the steady state conditions.

As shown in Fig. 5, the simulated concentrations were little greater than the experimental results during the initial period. This deviation may be as a result of the non-Fickian diffusion for organic solvent permeation through HDPE. At the end of the permeation experiments, the thickness of HDPE samples was found to increase by less than 12%. The other possible reason can be the effects of sorption on the permeation process. The higher concentrations of modeling results implied that the HDPE sample may be not in equilibrium with the organic solvents during the initial period of permeation. However, the swelling of HDPE can have an effect on the partition of organic solvent to HDPE [21].

Fig. 6 shows the simulated results of TCE permeation through 1 mm HDPE at different temperatures using  $D_p$  and  $K_p$  in Eq. (16). During the initial period, the simulation results were slightly higher than the experimental data, and the deviation varies as:  $35^\circ\text{C} > 25^\circ\text{C} > 45^\circ\text{C}$ . This is consistent with the results of diffusion kinetic (i.e.,  $n$  value) obtained in immersion tests. Similar results were found for chloroform and 1,2-dichloroethane.

Fig. 7 shows the simulations of chlorinated hydrocarbons permeation through 0.5 mm HDPE using  $D_i$  and  $K_i$  in Eq. (16). It is interesting to note that in Fig. 7,  $D_i$  and  $K_i$  were able to appropriately simulate the permeation concentrations, except for chloroform. However, Fig. 8 shows that Eq. (16) predicted the observably higher concentrations for aromatic hydrocarbons permeation through 0.5 mm HDPE using  $D_i$  and  $K_i$ .

In this study, the correlation coefficient of steady state permeation rates between permeation and immersion tests was as high as  $r^2 = 0.973$  ( $p < 0.001$ ). However, the simulation results

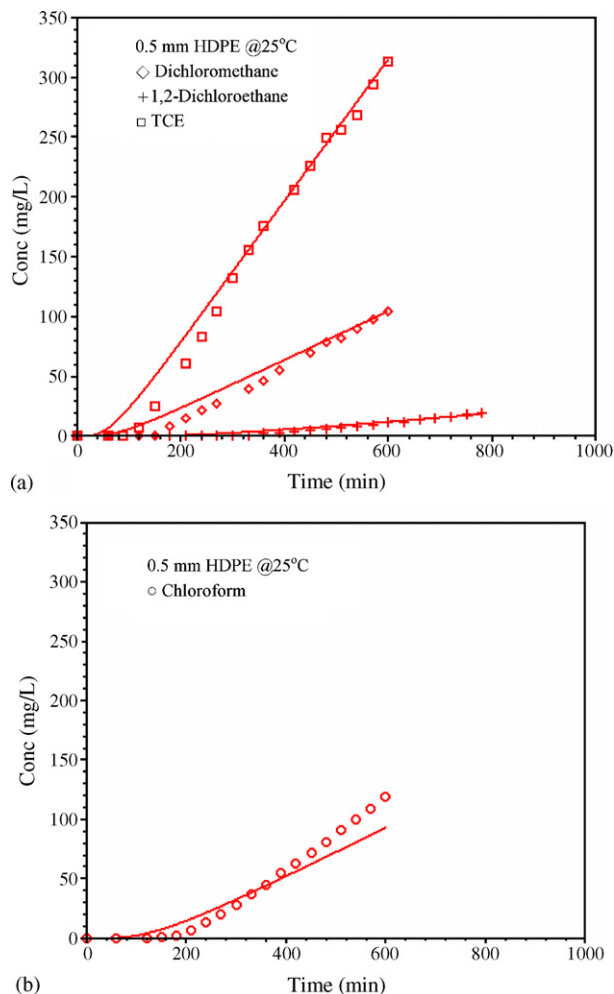


Fig. 7. Simulations of chlorinated hydrocarbons permeation through HDPE using  $K_i$  and  $D_i$ .

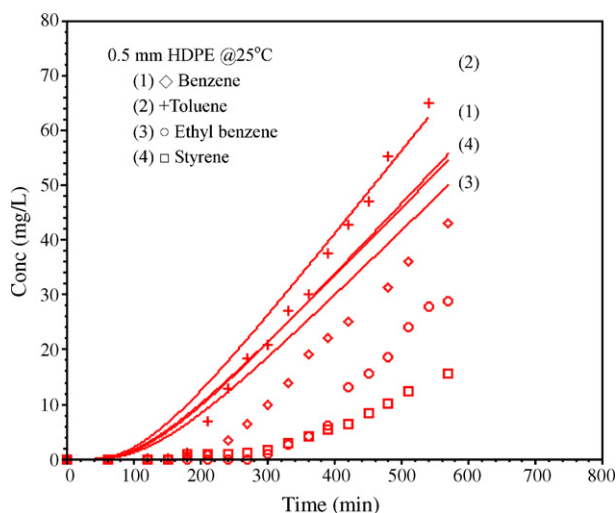


Fig. 8. Simulations of aromatic hydrocarbons permeation through HDPE using  $K_i$  and  $D_i$ .

(i.e., Figs. 7 and 8) indicate that the immersion test may be an inappropriate method to determine the diffusion and solubility coefficients of organic solvent permeation through HDPE geomembrane in the field.

## 5. Conclusion

Fick's diffusion coefficients and solubility coefficients of aromatic and chlorinated hydrocarbons in HDPE were obtained using the steady state permeation and sorption data from ASTM F739 and immersion methods, respectively. It was found that the diffusion kinetic of the experimental organic solvents in HDPE was non-Fickian type, and the solubility coefficients can be consistent with the solubility parameter theory. The diffusion and solubility coefficients follow the Arrhenius and van't Hoff relationships with temperature.

Although the HDPE samples were exposed to organic solvents under different conditions, the steady state permeation rates, diffusion and solubility coefficients were found to be significantly correlated for these two methods. The immersion test can be an expedient technique for providing information on the chemical resistance of HDPE geomembrane, especially for steady state permeation rates.

A one-dimensional Fick's diffusion equation was found to simulate well the ASTM F739 experimental results using diffusion coefficient  $D_p$  and solubility coefficient  $K_p$  as the boundary condition. On the other hand, the diffusion coefficient  $D_i$  and solubility coefficient  $K_i$  obtained from the immersion tests were inappropriate in simulating the results of ASTM F739 experiments. For practical purposes, it is suggested that an investigation should be conducted to obtain the diffusion and solubility coefficients using ASTM F739 method which closely simulates the conditions of HDPE used as barrier.

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