

Estimation of Diffusion Coefficients and Solubilities for Organic Solvents Permeation through High-Density Polyethylene Geomembrane

Keh-Ping Chao¹; Ping Wang²; and Chia-Huei Lin³

Abstract: Experiments on the permeation of several chlorinated and aromatic hydrocarbons through high-density polyethylene (HDPE) geomembranes were conducted using the ASTM F-739 standard test method. The diffusion coefficients were estimated by a one-dimensional diffusion equation based on Fick's second law, and the solubilities of the solvents in HDPE were determined by the steady state permeation rates. The one-dimensional transient model was able to simulate the permeation concentrations and implied that equilibrium partition between organic solvent and HDPE geomembrane was not achieved during the initial permeation. The solubilities of organic solvents in the HDPE geomembranes obtained by immersion tests or weight gain methods of permeation experiments were not an appropriate boundary condition for the model simulation of permeation. It was found that the diffusion coefficients and solubilities of organic solvents correlated well with their molecular weights and dipole moment, respectively. The present work provides information on the extent of organic compounds permeations through HDPE geomembranes as applied in hazardous waste landfills.

DOI: 10.1061/(ASCE)0733-9372(2006)132:5(519)

CE Database subject headings: Diffusion; Geomembranes; Polymers; Sorption; Solvents.

Introduction

Current waste disposal regulations require municipal and hazardous waste landfills to be lined with geomembranes, such as high-density polyethylene (HDPE), to prevent the transport of leachate and contaminants from the landfill into the surrounding environment. Geomembranes are nonporous materials and are impermeable to liquids, but organic solvents in the leachate may permeate the geomembrane by diffusion, resulting in the contamination of groundwater and soil, which poses a risk to human health (Aminabhavi et al. 1996).

Permeation of organic solvents through the membrane is dependent on the molecular interactions between the solvent and polymer and involves various mass transfer mechanisms (Vergnaud 1991; Park and Nibras 1993; Park et al. 1996; Sangam and Rowe 2001). First, the permeant dissolves or partitions into the contact surface of membrane. Subsequently, the permeant diffuses through the membrane and is desorbed from the opposite surface. Permeation is mainly a function of solubility and diffusivity of solvents through the polymer with desorption playing an insignificant role (Zeller 1993).

The permeation of organic solvents through a polymer membrane can be described by Fick's first law (Crank 1975; Britton et al. 1989; Sangam and Rowe 2001; Vahdat and Sullivan 2001; Chao et al. 2003). The permeation rate per unit area, J [$\text{M L}^{-2} \text{T}^{-1}$], is given as

$$J = -D \frac{dC_z}{dz} \quad (1)$$

where D =Fick's law diffusion coefficient of the organic solvent in the polymer membrane [$\text{L}^2 \text{T}^{-1}$]; C_z =solvent concentration at some point Z in the polymer membrane [M L^{-3}]; and Z =distance along the direction of diffusion [L]. It is generally assumed that the diffusion coefficient is independent of the concentration C_z and position (i.e., Z) in the membrane (Crank 1975; Vahdat 1991; Aminabhavi et al. 1996; Chao et al. 2003). On the other hand, the diffusion coefficient may be dependent on the size, shape, and structure of the permeant molecule (Park and Nibras 1993; Sangam and Rowe 2001). For a polymer membrane of thickness L , the steady state permeation rate, J_s , can be expressed as follows:

$$J_s = D \frac{C_{z=0} - C_{z=L}}{L} \quad (2)$$

If the diffusing solvent does not accumulate on the opposite surface of the polymer membrane, $C_{z=L}$ is considered to be negligible and may be assumed to be equal to zero ($C_{z=L}=0$) (Park and Nibras 1993; Sangam and Rowe 2001; Chao et al. 2003). The steady state permeation rate can be determined using permeation experiments, such as the American Society for Testing and Materials Method F-739 (ASTM 1996). Thus, Eq. (2) may be represented by

$$J_s = D \frac{C_{z=0}}{L} \quad (3)$$

¹Associate Professor, Dept. of Occupational Safety and Health, China Medical Univ., Taichung, Taiwan, ROC. E-mail: kpchao@mail.cmu.edu.tw

²Associate Professor, Dept. of Civil Engineering, Ching-Yun Univ., Chungli, Taiwan, ROC.

³Graduate Student, Institute of Environmental Health, China Medical Univ., Taichung, Taiwan, ROC.

Note. Discussion open until October 1, 2006. Separate discussions must be submitted for individual papers. To extend the closing date by one month, a written request must be filed with the ASCE Managing Editor. The manuscript for this paper was submitted for review and possible publication on June 23, 2004; approved on July 26, 2005. This paper is part of the *Journal of Environmental Engineering*, Vol. 132, No. 5, May 1, 2006. ©ASCE, ISSN 0733-9372/2006/5-519-526/\$25.00.

Crank (1975) employed a diaphragm cell to investigate the diffusion of volatile organic compounds (VOC) vapor through the polymer film. The one-dimensional diffusion into the polymer film may be expressed by Fick's second law with a constant diffusion coefficient as follows:

$$\frac{\partial C_z}{\partial t} = D \frac{\partial^2 C_z}{\partial z^2} \quad (4)$$

Crank assumed that the boundary conditions were: $C_{z=L}$ equal to zero at any time, and $C_{z=0}$ equal to the solubility of the VOC in the polymer film. According to the solutions of Eq. (4), Crank proposed that the diffusion coefficient of VOC vapor in the polymer film could be modeled using

$$D = \frac{L^2}{6t_1} \quad (5)$$

where L =thickness of polymer film [L]; and t_1 =lag time [T], which is given by the extrapolation of the steady state permeation portion of the cumulative permeation curve to the time axis. Crank did not provide an estimation method for the solubility of the VOC in polymer film as it was not essential for Eq. (5).

Several researchers have similarly assumed $C_{z=0}$ as equal to the solubility of chemical in the polymer film. The solubility, S [ML⁻³], was determined using the equilibrium sorption of the chemical in the immersion test (Vahdat 1991; Zeller 1993; Vahdat and Sullivan 2001). According to Eq. (3), the diffusion coefficient could be determined as follows:

$$D = \frac{J_s L}{S} \quad (6)$$

Many studies have been conducted to estimate the diffusion coefficients of organic solvents in HDPE geomembranes by using the equilibrium sorption of the chemical in the immersion test (Haxo and Lahey 1988; Britton et al. 1989; Park and Nibras 1993; Aminabhavi and Naik 1999; Sangam and Rowe 2001). Although the sorption experiments are simpler to conduct than the permeation experiments as only the increase in weight of the organic solvent in HDPE geomembrane is measured, it is doubtful that the diffusion coefficient estimated by sorption/immersion experiments is suitable for the permeation of chemicals through the polymer film. Even though the previous two models have been used to estimate the diffusion coefficient of organic solvent in HDPE geomembrane (Aminabhavi and Naik 1999; Britton et al. 1989; Prasad et al. 1994; Park et al. 1996; Sangam and Rowe 2001), there is still a need to further understand the use of the solubility of the chemical in the membrane for modeling of permeation data.

In this study, permeation experiments using the ASTM F-739 (1996) method were conducted to estimate the diffusion coefficients and the solubility of eight organic solvents in HDPE geomembrane. The organic solvents were chlorinated and aromatic hydrocarbons. Using the diffusion equation of Fick's second law, the experimental results for the organic solvents permeation through HDPE geomembrane were predicted using different diffusion coefficients and solubilities of the chemicals. Finally, correlations between the VOC diffusion coefficients or solubilities and several physical and chemical properties of the organic solvents were investigated. The correlation analysis may provide an understanding in the permeation process of organic compounds in HDPE geomembrane.

Table 1. Properties of HDPE Geomembrane

Property	Test method	Data ^a
Thickness (mm)	ASTM D5199	0.50
Density (g/cm ³)	ASTM 1505/D792	0.94
Tear resistance (N)	ASTM D1004	87
Puncture resistance (N)	ASTM D4833	245
Carbon black content (%)	ASTM D1603	2.5
Carbon black dispersion	ASTM D5596	Catalog 1–2
Dimensional stability (%)	ASTM D1204 (100°C, 1 h)	±1

^aData from Hui-Kwang Chemical Co. (Tainan, Taiwan, ROC).

Materials and Methods

Chemicals and HDPE Membrane

The study was conducted using a 0.5 mm thick HDPE geomembrane produced by Hui-Kwang Chemical Co. (Tainan, Taiwan, ROC). The properties of HDPE geomembrane are summarized in Table 1. Before experimentation, a HDPE sample (diameter=8 cm) was rinsed with deionized water and air dried for 24 h at 25±1°C and a relative humidity of 50±20%. The average thickness of each sample was determined by measuring at four random locations using a dial thickness gauge (Teclock Co., Japan) to an accuracy of 0.001 cm.

Eight organic solvents used for this study were chlorinated hydrocarbons (dichloromethane, 1,2-dichloroethane, chloroform, and trichloroethylene) and aromatic hydrocarbons (benzene, toluene, styrene, and ethyl benzene). These organic solvents were selected as these are commonly found as leachates whereas pure solvents may be typically found in landfills where indiscriminate disposal is practiced (Aminabhavi and Naik 1999; Sangam and Rowe 2001). As shown in Table 2, these organic solvents exhibit a wide range of physical and chemical properties, i.e., molecular weights and octanol-water partition coefficient. The tested solvents were of reagent grade or higher purity (>98%) and were used without further purification.

Permeation Experiment

Permeation experiments were conducted using the ASTM F-739 (1996) liquid chemical permeation test method with a closed loop system. As shown in Fig. 1, the permeation cell (Pesce Laboratories, Kennett Square, Pa.) with a diameter of 5.08 cm was separated by the disk sample into the collection and challenge chambers. Deionized water was used as the collection medium and circulated through the collection chamber using a MasterFlex PTFE-Tubing Pump System (CZ-77912-00, Cole-Parmer, Vernon Hills, Ill.) at 60 mL/min (ASTM F739 suggesting 50–150 mL/min). The permeation cell and associated equipment were connected with Teflon tubing (Nalgene, Rochester, N.Y.) and were placed in an incubator at a temperature of 25±1°C.

During the experimental run, 4.5 mL aliquots of the collection medium were collected from the downstream sampling point at 30 min intervals using gas-tight syringes. The samples were immediately transferred to 4.0 mL glass vials sealed with open top caps equipped with Teflon lined septa. At the same time, 4.5 mL of deionized water was injected into the well-stirred Teflon bottle of the closed loop system (as shown in Fig. 1) to maintain the total volume of the collection medium in the system (approx-

Table 2. Physical and Chemical Properties of Organic Chemicals

Chemicals	Grade	MW	Density	VIS	MV	DM	WS	log K_{ow}	H	LDL
Chlorinated hydrocarbon										
Dichloromethane	LC (99.9%, Merck)	84.93	1.327	40.2	63.98	1.59	20,000	1.25	0.085	0.48
1,2-Dichloroethane	GR (99.5%, Merck)	98.97	1.253	83.5	79.01	1.90	8,690	1.45	0.063	0.59
Chloroform	GR (99.4%, Merck)	119.38	1.484	61.7	80.86	1.15	8,000	1.97	0.147	0.63
Trichloroethylene	GR (99.5%, Merck)	131.79	1.464	87.2	89.75	0.77	1,100	2.53	0.397	0.33
Aromatic hydrocarbon										
Benzene	ACS (99%, Merck)	78.11	0.877	80.1	89.05	0	1,780	2.13	0.232	0.59
Toluene	ACS (99%, Merck)	92.14	0.867	110.6	106.23	0.38	515	2.79	0.273	0.59
Styrene	GC (99.5%, Merck)	104.15	0.906	136.2	115.01	0.13	300	2.95	0.105	0.64
Ethyl benzene	GC (98%, Merck)	106.17	0.867	136.2	122.49	0.59	152	3.13	0.344	0.65

Note: Properties are at 25°C and abbreviations are as follows: MW=molecular weight (g/mol) (Lide 1994); density (g/cm³); VIS=viscosity (cp) (Lide 1994); MV=molar volume (cm³)=(MW/density); DM=dipole moment (debye) (Lide 1994); WS=water solubility (mg/L) at 20°C (LaGrega et al. 1994); K_{ow} =octanol-water partition coefficient (LaGrega et al. 1994); H =Henry's constant (LaGrega et al. 1994); and LDL=limit detection level (mg/L).

mately 730 mL), and minimize the effect of sampling on the permeated mass of organic solvent in collection chamber.

Organic solvents were extracted using solid phase microextraction (SPME) fiber and analyzed with a gas chromatograph equipped with flame ionization detector (AutoSystem XL, Perkin Elmer, Eder Prairie, Minn.). The SPME fiber (polydimethylsiloxane, 57300-U PDMS, Supelco, Bellefonte, Pa.) was immersed in the 4.0 mL sample vials for 20 min and desorbed in the gas chromatograph injector port for 7 min. The capillary column used was DB-5 (J&W, Folsom, Calif.) and the oven temperature was kept at an initial temperature of 60°C for 1 min, and then ramped to 150°C at a rate of 8°C/min with a final hold of one minute. The temperatures of the injection port and detector were maintained at 200 and 250°C, respectively. Nitrogen was used as the carrier gas at a flow rate of 30 mL/min. Limit detection levels of eight organic solvents were shown in Table 2. Each experimental run was approximately 10 h to obtain steady state permeation rate and was repeated three times for each organic solvent.

Experimental Solubility

In this study, the solubility of organic solvent in HDPE geomembrane was determined using two experimental methods. Several researchers have used immersion tests to obtain the solubility of the solvent in the polymer (Vahdat 1991; Zellers 1993; Vahdat

and Sullivan 2001). HDPE geomembrane with the same surface area and conditioned as in the permeation test were weighed and immediately immersed in bottles filled with organic solvents at 25±1°C. The HDPE geomembrane was periodically taken out of the screw-tight bottle and wiped gently to remove the organic solvent from the sample surface. The sample was weighed using an electronic analytical balance (AG245, Mettler Toledo, Switzerland) with a sensitivity of 0.0001 g. The HDPE geomembrane typically reached a constant weight after 5 days. The solubility, S_1 , is defined as the weight of organic solvent uptake per unit volume of dry sample. Immersion tests to obtain the solubility were conducted in triplicate for each solvent.

For the second approach, the solubility, S_2 , is defined as the mass of organic solvent uptake per unit volume of dry HDPE sample and was obtained by measuring the weight gain by the HDPE sample in permeation experiments after steady state conditions have been established (i.e., at the end of the permeation experiment). S_2 represents the sorption of the organic solvent onto the HDPE sample under steady state permeation conditions.

Results and Discussion

Solubility and Diffusion Coefficient

At the end of the permeation experiments, the HDPE geomembrane samples were found to increase in average thickness by less than 12 and 10% for aromatic and chlorinated hydrocarbons, respectively. One of the reasons for the swelling is that the structure of HDPE samples was softened by the solvent and the molecular chains were subjected to large molecular forces (Munk 1989). However, the swelling of the HDPE geomembrane in the permeation test was negligible which is similar to work conducted by others (Park and Nibras 1993; Prasad et al. 1994; Park et al. 1996; Sangam and Rowe 2001).

As shown in Fig. 2, it was found that the average thickness of HDPE geomembrane increased with increasing molecular weight ($r=0.795$, $p=0.205$) and molar volume ($r=0.571$, $p=0.429$) for

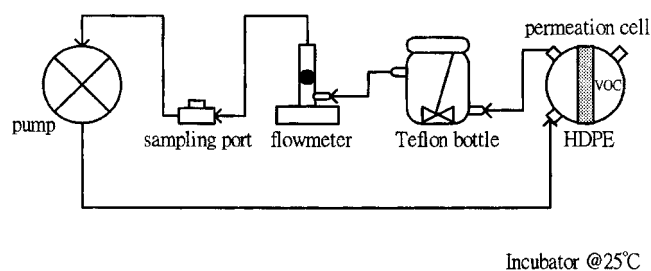


Fig. 1. Sketch of closed-loop permeation cell system

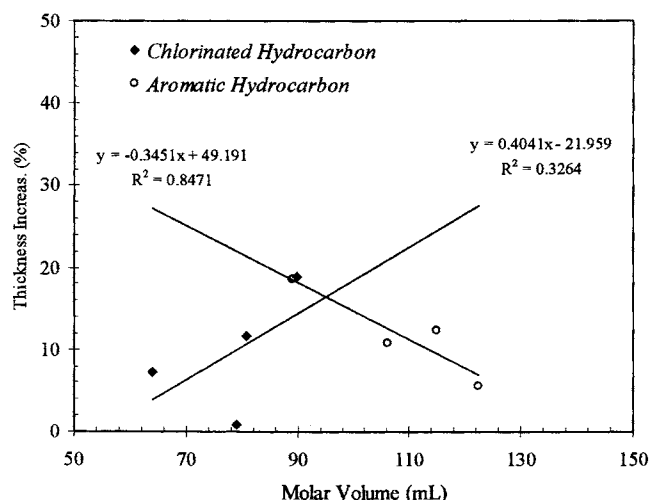
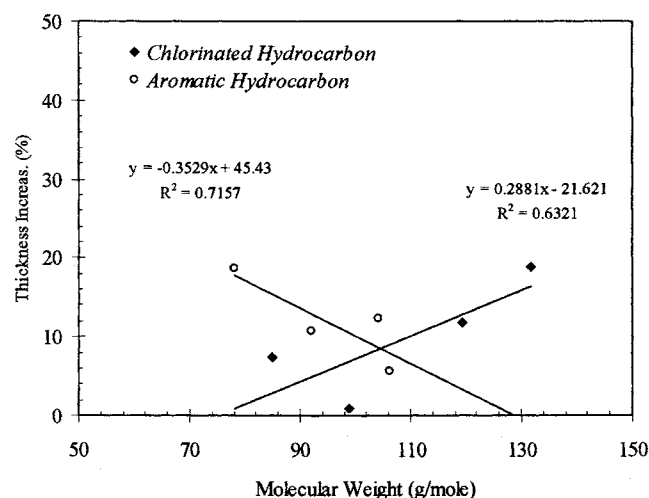


Fig. 2. Correlation of increase in average thickness of HDPE samples with molecular weight and molar volume

chlorinated hydrocarbons. On the other hand, the increase in average thickness for HDPE was found to be inversely proportional to the molecular weight ($r = -0.846$, $p = 0.154$) and molar volume ($r = -0.921$, $p = 0.08$) of aromatic hydrocarbons. This implies that the swelling of HDPE is dependent on the molecule sizes of organic solvents with similar structure under the experimental conditions of this study.

Fig. 3 shows the permeation results for the experiments conducted. In most experiments, the solvent concentrations in the collection medium were close to negligible for the first 2 h. Once breakthrough has occurred, the solvent concentrations in the collection medium were found to increase linearly. In general, breakthrough times for chlorinated hydrocarbons were less than that of aromatic hydrocarbons used in this study. According to ASTM F-739 (1996), steady state permeation rates, J_s , were estimated using the rate of increase of the permeated concentrations in the collection medium

$$J_s = \frac{\alpha V}{A} \quad (7)$$

where A = area of HDPE geomembrane exposed to the permeate (18.08 cm^2) in the cell; V = total volume of collection medium (730 mL) in the closed system; and α = slope of the linear portion

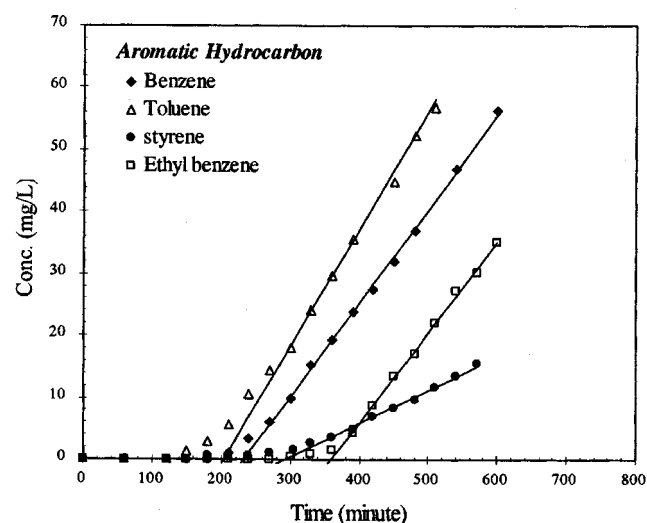
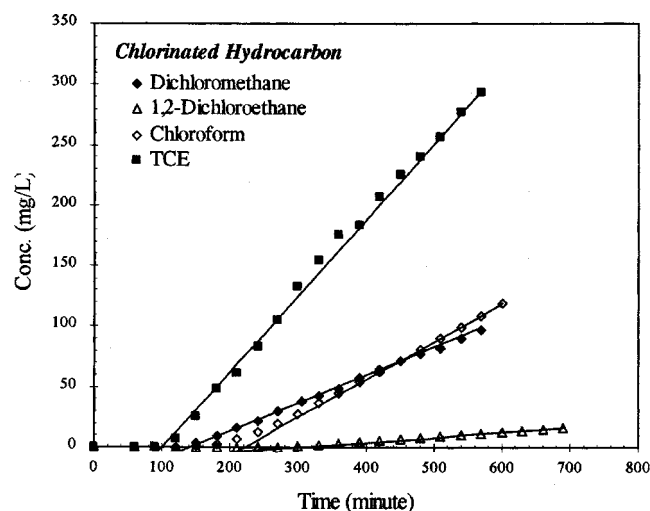


Fig. 3. Permeation concentrations of organic solvents in collection medium

of the permeated concentrations in collection medium [$\text{ML}^{-3} \text{T}^{-1}$], as shown in Fig. 3.

The steady state permeation rates J_s of the eight organic solvents in HDPE are presented in Table 3. The order of steady state permeation rate from highest to lowest were $\text{TCE} > \text{chloroform} > \text{dichloromethane} > 1,2\text{-dichloroethane}$, for chlorinated hydrocarbons, and $\text{toluene} > \text{benzene} > \text{ethylbenzene} > \text{styrene}$, for aromatic hydrocarbons. For the eight organic solvents of this study, the results of lag time and steady state permeation rates J_s indicate that aromatic hydrocarbons are less permeable through the HDPE geomembrane than chlorinated hydrocarbons. Further, it was found that the steady state permeation rates of eight organic solvents were correlated well to their molecular weight ($r = 0.668$, $p < 0.001$) and Henry's law constants ($r = 0.622$, $p < 0.001$).

Table 3 also shows the solubilities S_1 and S_2 for the eight organic solvents. In the permeation experiments, only one surface of the HDPE sample was exposed to organic solvent. Although for the immersion test, both surfaces of the sample were in contact with the solvent. Both S_1 and S_2 represent the steady state sorption of organic compounds in HDPE geomembrane. As shown in Table 3, S_1 and S_2 were found to be highly correlated

Table 3. Comparisons of Steady State Permeation Rate, Solubility and Diffusion Coefficients

Chemical	J_s ($\mu\text{g}/\text{cm}^2/\text{min}$)	S_1 ($10^{-2} \text{ g}/\text{cm}^3$)	D_{S_1} ($10^{-7} \text{ cm}^2/\text{s}$)	S_2 ($10^{-2} \text{ g}/\text{cm}^3$)	D_{S_2} ($10^{-7} \text{ cm}^2/\text{s}$)	D ($10^{-7} \text{ cm}^2/\text{s}$)	S ($10^{-2} \text{ g}/\text{cm}^3$)
Chlorinated hydrocarbon							
Dichloromethane	8.96 ± 1.21	7.63 ± 0.32	1.02 ± 0.14	10.0 ± 0.89	0.78 ± 0.11	0.45 ± 0.01	15.1 ± 0.83
1,2-Dichloroethane	1.64 ± 0.05	6.51 ± 3.36	0.26 ± 0.11	5.91 ± 0.51	0.25 ± 0.03	0.24 ± 0.01	5.93 ± 0.28
Chloroform	12.0 ± 1.75	13.3 ± 1.00	0.79 ± 0.15	16.4 ± 1.63	0.64 ± 0.13	0.34 ± 0.02	31.1 ± 4.46
Trichloroethylene	27.3 ± 0.25	16.8 ± 1.26	1.60 ± 0.50	22.8 ± 2.17	0.67 ± 0.06	0.79 ± 0.01	31.7 ± 0.18
Aromatic hydrocarbon							
Benzene	6.03 ± 0.57	7.41 ± 0.30	0.71 ± 0.09	10.2 ± 0.30	0.51 ± 0.06	0.32 ± 0.01	16.6 ± 1.09
Toluene	7.76 ± 0.60	7.41 ± 0.26	0.96 ± 0.03	12.1 ± 0.39	0.59 ± 0.03	0.42 ± 0.01	16.9 ± 1.28
Styrene	2.17 ± 0.02	8.04 ± 2.11	0.25 ± 0.06	9.04 ± 1.70	0.22 ± 0.05	0.27 ± 0.01	7.17 ± 0.18
Ethyl benzene	5.69 ± 0.55	7.32 ± 0.31	0.68 ± 0.07	11.2 ± 1.43	0.45 ± 0.03	0.21 ± 0.01	23.4 ± 2.61

Note: Mean $\pm$ SD. J_s was determined using Eq. (7). $D_{S_1} = J_s L / S_1$; $D_{S_2} = J_s L / S_2$; $D = L^2 / 6t_1$; and $S = J_s L / D$.

($r=0.948$, $p<0.001$) even though they were determined using different approaches, immersion and permeation tests. Table 4 compares some of the solubilities S_1 found in this study and the solubilities estimated by others using the immersion tests (Haxo and Lahey 1988; Britton et al. 1989; Park and Nibras 1993). It appears that the solubilities S_1 found in this study were consistent with the literature data.

In Table 3, the diffusion coefficients D_{S_1} and D_{S_2} were determined by J_s , S_1 , and S_2 using Eq. (6). Because the values of S_2 were higher than S_1 , the diffusion coefficients D_{S_1} were greater than D_{S_2} . The diffusion coefficients D estimated by Eq. (5) are also presented in Table 3. The solubility S was obtained by substituting D into Eq. (6). It is observed that except for TCE and styrene, the diffusion coefficients D were less than the values of D_{S_1} and D_{S_2} but were of the same magnitude.

Simulation of Permeation Concentration in Collection Medium

Using the boundary conditions, $C_Z(0,t)=S$ and $C_Z(L,T)=0$, and the initial condition, $C_Z(Z,0)=0$, as assumed by Crank (1975), the concentration profile C_Z in the membrane is as follows by solving Eq. (4):

$$C_Z(Z,t) = S \left(1 - \frac{Z}{L} \right) - \sum_{n=1}^{\infty} \frac{2S}{n\pi} \exp \left(-D \left(\frac{n\pi}{L} \right)^2 t \right) \sin \left(n\pi \frac{Z}{L} \right) \quad (8)$$

Table 4. Comparisons of Solubilities Determined by Immersion Test and Others

Chemicals	Solubility S_1	Literature		
		Park and Nibras (1993)	Haxo and Lahey (1998)	Britton et al. (1989) ^a
1,2-Dichloroethane	6.51 ± 3.36			5.70
Trichloroethylene	16.8 ± 1.26	13.6 ± 0.15	15.8	
Benzene	7.41 ± 0.30		6.33	8.44
Toluene	7.41 ± 0.26	7.80 ± 0.08	6.33	9.07
Styrene	8.04 ± 2.11			8.12
Ethyl benzene	7.32 ± 0.31	8.67 ± 0.17		

Note: $10^{-2} \text{ g}/\text{cm}^3$.

^aDetermined at 22°C .

By taking the mass balance for the collection medium, the permeation concentration, C [M L^{-3}], in the closed loop system was determined as follows:

$$V \frac{dC}{dt} = -AD \left. \frac{\partial C_Z}{\partial Z} \right|_{Z=L} = -ADf(t) \quad (9)$$

where $f(t) = (\partial C_Z / \partial Z)|_{Z=L}$. C can be solved from Eq. (9) as follows:

$$C = -\frac{AD}{V} \int f(t) dt + C^* \quad (10)$$

With the initial condition of $C(0)=0$, the integration constant C^* can be further determined.

Using S and D values as determined earlier, the permeation concentration with respect to time in Eq. (10) can be solved using Maple software (Waterloo Maple Inc., Waterloo, Ont., Canada). Fig. 4 shows the simulation results of eight organic solvents using diffusion coefficient D and solubility S for the permeation experiments. Despite some scatter of the initial data, it can be seen that the diffusion coefficient D estimated from Eq. (5) was able to approximately simulate the permeation results with S as the boundary condition.

At the initiation of the permeation, the simulated results were found to be greater than the experimental concentrations. This observed slight deviation is probably due to the effects of increase in thickness of HDPE sample, and sorption and/or desorption on the permeation process. Several researchers have assumed that the partition between geomembrane and organic solvent was in equilibrium during sorption (Vergnaud 1991; Park and Nibras 1993; Aminabhavi and Naik 1998; Sangam and Rowe 2001). This assumption may not be appropriate for all organic solvents during the initial period of the permeation experiment. As shown in Fig. 4, the simulation curves did not match well with the experimental data for organic solvents of lower polarity (i.e., solvents with large values of $\log K_{ow}$). For example, the model simulations for chlorinated hydrocarbons were better than that for aromatic hydrocarbons.

Fig. 5 shows the simulated concentration profile for chloroform by using different diffusion coefficients and solubilities. As seen in Fig. 5, Eq. (10) was unable to model the permeation concentration data using either S_1 or S_2 as the boundary conditions. Similar results were also found for the other organic solvents of this study. Fig. 5 indicates that the experimental solu-

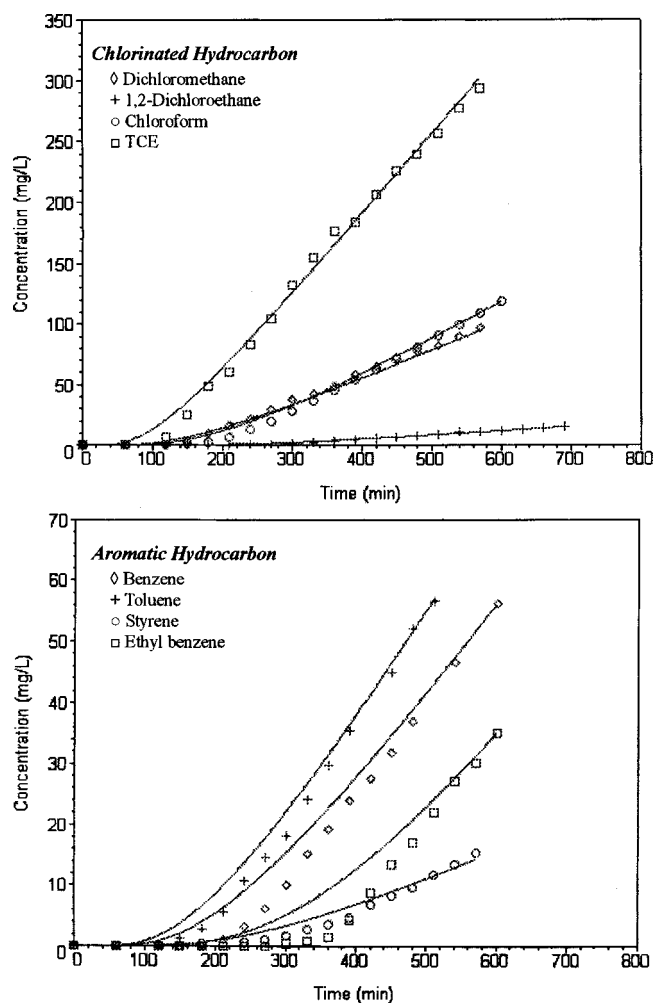


Fig. 4. Simulations of organic solvent concentrations in collection medium using permeation experiment determined diffusion coefficient D and solubility S

bility S_1 and S_2 determined by sorption using immersion tests or permeation experiments may not be the appropriate boundary conditions for diffusion in Eq. (4).

Correlation Analysis of Solubility and Diffusion Coefficient

Several correlation analyses of permeation parameters have been proposed to comprehend the diffusion process of organic compounds in polymer membranes using immersion test (Park and Nibras 1993; Aminabhavi and Naik 1998; Sangam and Rowe 2001). In this study, the diffusion coefficient D and solubility S of eight organic solvents were correlated to their physical and chemical properties summarized in Table 2.

From the immersion test, Aminabhavi and Naik (1998) indicated that the diffusion coefficients in the polymer decrease with increasing molecular weight and molar volume of organic solvent. As presented in Table 5, it is interesting to note that the diffusion coefficients were proportional to the molecular weights of chlorinated hydrocarbons ($r=0.576$, $p<0.05$), whereas an inversely proportional trend was observed for aromatic hydrocarbons ($r=-0.592$, $p<0.05$). Table 5 also shows that the diffusion coefficients had a logarithmic relationship with the molar volume

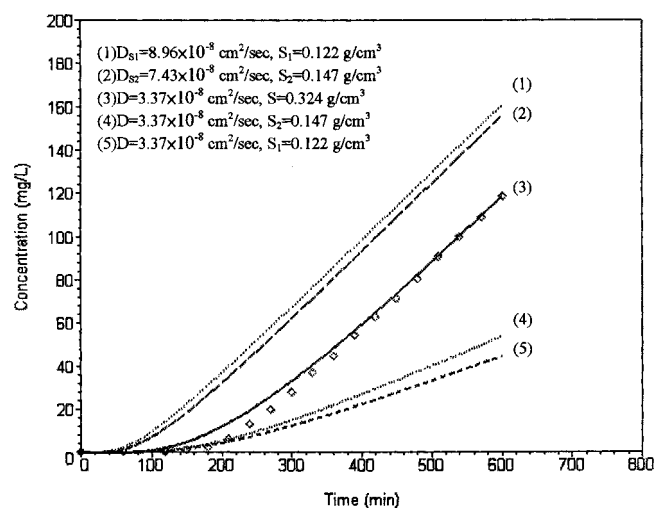


Fig. 5. Comparisons of simulation for chloroform concentrations using various diffusion coefficients and solubilities

($r=-0.595$, $p<0.05$) for aromatic hydrocarbons, but were not well correlated for chlorinated hydrocarbons ($r=0.28$, $p>0.05$).

In the study of Sangam and Rowe (2001), the diffusion coefficients of organic solvents were unsuccessfully correlated to their molecular weights. Unlike work done herein, solvents were not grouped in different categories, i.e., chlorinated and aromatic hydrocarbons, for correlation analysis of Sangam and Rowe (2001). However, molecular weight can be a good basis to understand the diffusivity of organic solvents in HDPE geomembrane.

The diffusion coefficients for chlorinated hydrocarbons was found to correlate best with the Henry's law constant ($r=0.925$, $p<0.05$). The diffusion coefficients were correlated well to dipole moment ($r=-0.809$, $p<0.05$) and $\log K_{ow}$ ($r=0.731$, $p<0.05$) of chlorinated hydrocarbons. This result may imply that polarity is an important property for chlorinated hydrocarbon diffusion in HDPE geomembrane. In the immersion study of HDPE geomembrane, Sangam and Rowe (2001) found that diffusion coefficients of organic solvents were proportional to $\log K_{ow}$ but decreased for hydrocarbons of high $\log K_{ow}$ values. Similar results were found in this study. As shown in Table 5, the diffusion coefficients were inversely proportional to $\log K_{ow}$ ($r=-0.432$, $p>0.05$) for aromatic hydrocarbons that have higher values of $\log K_{ow}$.

Table 6 shows the correlation of the estimated solubility S with the different physical-chemical properties of the organic solvents. Several researchers have indicated that the lower the polarity (i.e., higher value of $\log K_{ow}$), the stronger the sorption of the chemical in HDPE geomembrane (Prasad et al. 1994; Sangam and Rowe 2001). In this study, the solubility of chlorinated hydrocarbons was significantly correlated to their dipole moment ($r=-0.942$, $p<0.05$) $\log K_{ow}$ ($r=0.819$, $p<0.05$). However, the solubility of aromatic hydrocarbons was well proportional to the dipole moment ($r=0.659$, $p<0.05$) and correlated to $\log K_{ow}$ only with a regression coefficient $r=0.08$.

On the other hand, Sangam and Rowe (2001) proposed that the sorption of organic solvents was dependent on their chemical structures and increased with an increase in molecular weights. As seen in Table 6, a good correlation ($r=0.801$, $p<0.05$) between solubility and molecular weights was only found for the chlorinated hydrocarbons. Tables 5 and 6 also show the multiple

Table 5. Correlation and Relationship of Diffusion Coefficients

Variable	Correlation and relationship	
Chlorinated hydrocarbon		
MW	$D=-2.665\times10^{-8}+6.651\times10^{-10}$ MW ($r=0.576$, $p<0.05$)	$D=10^{-9.746}$ MW ^{1.164} ($r=0.454$, $p>0.05$)
MV	$D=-3.38\times10^{-8}+1.014\times10^{-9}$ MV ($r=0.450$, $p>0.05$)	$D=10^{-9.256}$ MV ^{-0.991} ($r=0.280$, $p>0.05$)
DM	$D=9.89\times10^{-8}-3.934\times10^{-8}$ DM ($r=-0.809$, $p<0.05$)	$D=10^{-7.27}$ DM ^{-1.053} ($r=-0.834$, $p<0.05$)
WS	$D=5.874\times10^{-8}-1.381\times10^{-12}$ WS ($r=-0.449$, $p>0.05$)	$D=10^{-6.332}$ WS ^{-0.277} ($r=-0.679$, $p<0.05$)
log K_{ow}	$D=-9.604\times10^{-9}+3.072\times10^{-8}$ log K_{ow} ($r=0.731$, $p<0.05$)	$D=10^{-7.611}$ log $K_{ow}^{0.956}$ ($r=0.601$, $p<0.05$)
VIS	$D=2.603\times10^{-8}+2.884\times10^{-10}$ VIS ($r=0.261$, $p>0.05$)	$D=10^{-7.518}$ VIS ^{0.074} ($r=0.053$, $p>0.05$)
H	$D=2.057\times10^{-8}+1.452\times10^{-7}$ H ($r=0.925$, $p<0.05$)	$D=10^{-6.916}$ H ^{0.532} ($r=0.860$, $p<0.05$)
H, MW*	$D=10^{-1.620}$ H ^{1.021} MW ^{-2.397} ($r=0.996$, $p<0.05$)	
H, MW, log K_{ow}^a	$D=10^{11.539}$ H ^{0.204} MW ^{-10.007} log $K_{ow}^{6.591}$ ($r=1.000$, $p<0.05$)	
Aromatic hydrocarbon		
MW	$D=6.881\times10^{-8}-4.02\times10^{-10}$ MW ($r=-0.592$, $p<0.05$)	$D=10^{-5.085}$ MW ^{-1.237} ($r=-0.610$, $p<0.05$)
MV	$D=6.802\times10^{-8}-3.462\times10^{-10}$ MV ($r=-0.568$, $p>0.05$)	$D=10^{-5.019}$ MV ^{-1.235} ($r=-0.595$, $p<0.05$)
DM	$D=3.272\times10^{-8}-7.837\times10^{-9}$ DM ($r=-0.234$, $p>0.05$)	
WS	$D=2.788\times10^{-8}+3.912\times10^{-12}$ WS ($r=0.332$, $p>0.05$)	$D=10^{-7.99}$ WS ^{0.174} ($r=0.632$, $p<0.05$)
log K_{ow}	$D=5.446\times10^{-8}-8.687\times10^{-9}$ log K_{ow} ($r=-0.432$, $p>0.05$)	$D=10^{-7.19}$ $K_{ow}^{-0.778}$ ($r=-0.462$, $p>0.05$)
VIS	$D=5.182\times10^{-8}-1.836\times10^{-10}$ VIS ($r=-0.558$, $p>0.05$)	$D=10^{-6.231}$ VIS ^{-0.631} ($r=-0.553$, $p>0.05$)
H	$D=3.1\times10^{-8}-1.832\times10^{-9}$ H ($r=-0.021$, $p>0.05$)	$D=10^{-7.516}$ H ^{0.018} ($r=0.033$, $p>0.05$)
WS, log K_{ow}^a	$D=10^{-12.654}$ WS ^{1.040} log $K_{ow}^{5.436}$ ($r=0.949$, $p<0.05$)	
MV, log K_{ow}^a	$D=10^{12.32}$ log $K_{ow}^{8.52}$ MV ^{-11.596} ($r=0.996$, $p<0.05$)	
WS, MV log K_{ow}^a	$D=10^{13.648}$ WS ^{-0.06} log $K_{ow}^{8.64}$ MV ^{-12.196} ($r=0.996$, $p<0.05$)	

^aStepwise (95% confidence limit).

regression analyses of D and S using stepwise regression with 95% confidence limits. Further study will be needed to assess its validity.

The results of correlation analysis can provide a fundamental to environmental engineers and geoenvironmental engineers to evaluate the resistance of HDPE geomembrane liners to permeation by organic compounds in hazardous waste application. Particularly for the less developed countries, the indiscriminate dumping of solvents in landfills may be not restricted.

Conclusions

In this study, a one-dimensional diffusion equation based on Fick's second law was used to simulate the results of permeation experiments. The diffusion coefficients, estimated by Crank's equation, were found to simulate well the experimental data using a solubility boundary condition that was determined by its steady state permeation rate. The simulation results indicated that partition between organic solvent with a higher polarity and HDPE

Table 6. Correlation and Relationship of Solubility

Variable	Correlation and relationship	
Chlorinated hydrocarbon		
MW	$S=-0.325+4.909\times10^{-3}$ MW ($r=0.801$, $p<0.05$)	$S=10^{-6.159}$ MW ^{2.657} ($r=0.656$, $p<0.05$)
MV	$S=-0.298+6.475\times10^{-3}$ MV ($r=0.541$, $p>0.05$)	$S=10^{-4.505}$ MV ^{1.978} ($r=0.354$, $p>0.05$)
DM	$S=0.538-0.243$ DM ($r=-0.942$, $p<0.05$)	$S=10^{-0.579}$ DM ^{-1.740} ($r=-0.871$, $p<0.05$)
WS	$S=0.289-8.427\times10^{-6}$ WS ($r=-0.515$, $p>0.05$)	$S=10^{0.425}$ WS ^{-0.313} ($r=-0.486$, $p>0.05$)
log K_{ow}	$S=-0.12+0.183$ log K_{ow} ($r=0.819$, $p<0.05$)	$S=10^{-1.198}$ log $K_{ow}^{1.809}$ ($r=0.720$, $p<0.05$)
VIS	$S=0.174+5.121\times10^{-4}$ VIS ($r=0.087$, $p>0.05$)	$S=10^{-0.511}$ VIS ^{-0.14} ($r=-0.063$, $p>0.05$)
DM, WS ^a	$S=10^{-2.569}$ DM ^{-3.223} WS ^{0.556} ($r=0.990$, $p<0.05$)	
DM, WS, VIS ^a	$S=10^{-4.85}$ DM ^{-3.821} WS ^{0.872} VIS ^{0.651} ($r=0.995$, $p<0.05$)	
Aromatic hydrocarbon		
MW	$S=0.181-2.23\times10^{-4}$ MW ($r=-0.042$, $p>0.05$)	$S=10^{0.561}$ MW ^{-0.706} ($r=-0.196$, $p>0.05$)
MV	$S=0.104+5.14\times10^{-4}$ MV ($r=0.109$, $p>0.05$)	$S=10^{-0.393}$ MV ^{-0.217} ($r=-0.059$, $p>0.05$)
DM	$S=0.113+0.171$ DM ($r=0.659$, $p<0.05$)	
WS	$S=0.16-3.271\times10^{-7}$ WS ($r=-0.004$, $p>0.05$)	$S=10^{-0.811}$ WS ^{-0.008} ($r=-0.017$, $p>0.05$)
log K_{ow}	$S=0.126+1.242\times10^{-2}$ log K_{ow} ($r=0.080$, $p>0.05$)	$S=10^{-0.738}$ $K_{ow}^{-0.219}$ ($r=-0.073$, $p>0.05$)
VIS	$S=0.19-2.611\times10^{-4}$ VIS ($r=-0.102$, $p>0.05$)	$S=10^{0.167}$ VIS ^{-0.487} ($r=-0.240$, $p>0.05$)

^aStepwise (95% confidence limit).

geomembrane was not in equilibrium during the initial period of the permeation experiment. The solubilities of solvents in HDPE obtained by immersion test were found to be inappropriate in the simulation of organic solvents permeation through HDPE geomembrane.

For organic solvents with similar structure, the diffusion coefficients correlated well with their molecular weights, and the solubilities were correlated well to their polarity. Further study will be considered necessary to investigate the permeation of aqueous solution, or leachate from landfill, through HDPE geomembrane.

Acknowledgments

The study was financially supported by National Science Council, Taiwan, ROC (NSC92-2211-E-039-001) and China Medical University (CMU92-OSH-07). The writers are grateful to Hui-Kwang Chemical Co. (Taiwan, ROC) for a supply of HDPE geomembranes.

References

- American Society for Testing and Materials (ASTM). (1996). "Resistance of protective clothing materials to permeation by liquids or gases under conditions of continuous contact (F739)." *ASTM F-739-96*, Philadelphia.
- Aminabhavi, T. M., Munnolli, R. S., and Ortego, J. D. (1996). "Molecular migration of some industrial solvents into fluoropolymer membranes." *Waste Manage.*, 16(4), 277–287.
- Aminabhavi, T. M., and Naik, H. G. (1998). "Chemical compatibility study of geomembranes-sorption/desorption, diffusion and swelling phenomena." *J. Hazard. Mater.*, 60(2), 175–203.
- Aminabhavi, T. M., and Naik, H. G. (1999). "Sorption/desorption, diffusion, permeation and swelling of high density polyethylene geomembrane in the presence of hazardous organic liquid." *J. Hazard. Mater.*, 64(3), 251–262.
- Britton, L. N., Ashman, R. B., Aminabhavi, T. M., and Cassidy, P. E. (1989). "Permeation and diffusion of environmental pollutants through flexible polymers." *J. Appl. Polym. Sci.*, 38(2), 227–236.
- Chao, K. P., Lee, P. H., and Wu, M. J. (2003). "Organic solvents permeation through protective nitrile gloves." *J. Hazard. Mater.*, 99(2), 191–201.
- Crank, J. (1975). *The mathematics of diffusion*, Oxford University Press, New York.
- Haxo, H. E., and Lahey, T. P. (1988). "Transport of dissolved organics from dilute aqueous solutions through flexible membrane liners." *Hazard. Waste Hazard. Mater.*, 5(4), 275–294.
- LaGrega, M. D., Buckingham, P. L., and Evans, J. C. (1994). *Hazardous waste management*, McGraw-Hill, New York.
- Lide, D. R. (1994). *Handbook of chemistry and physics*, CRC Press, Boca Raton, Fla.
- Munk, P. (1989). *Introduction to macromolecular science*, Wiley, New York.
- Park, J. K., and Nibras, M. (1993). "Mass flux of organic chemicals through polyethylene geomembranes." *Water Environ. Res.*, 65(3), 227–237.
- Park, J. K., Sakti, J. P., and Hoopes, J. A. (1996). "Transport of organic compounds in thermoplastic geomembranes. I: Mathematical model." *J. Environ. Eng.*, 122(9), 800–806.
- Prasad, T. V., Brown, K. W., and Thomas, J. C. (1994). "Diffusion coefficients of organics in high density polyethylene (HDPE)." *Waste Manage. Res.*, 12, 61–71.
- Sangam, H. P., and Rowe, R. K. (2001). "Migration of dilute aqueous organic pollutants through HDPE geomembranes." *Geotext. Geomembr.*, 19(6), 329–357.
- Vahdat, N. (1991). "Estimation of diffusion coefficient for solute-polymer systems." *J. Appl. Polym. Sci.*, 42(12), 3165–3171.
- Vahdat, N., and Sullivan, V. D. (2001). "Estimation of permeation rate of chemicals through elastometric materials." *J. Appl. Polym. Sci.*, 79(7), 1265–1272.
- Vergnaud, J. M. (1991). *Liquid transport processes in polymeric materials: Modeling and industrial applications*, Prentice-Hall, Englewood Cliffs, N.J.
- Zellers, E. T. (1993). "Three-dimensional solubility parameters and chemical protective clothing permeation. I. Modeling the solubility of organic solvents in viton gloves." *J. Appl. Polym. Sci.*, 50(3), 513–530.