Estimation of Permeability for Organic Compounds through PVC Pipes

Bing-Hsien Wang, Miao-Ling Huang and Keh-Ping Chao

ABSTRACT

A pipe-bottle model with a volume of 125 mL was proposed to estimate the permeability of benzene and toluene for the polyvinyl chloride (PVC) water pipes. The concentrations of permeant in pipe-water were directly sampled using the solid phase microextraction (SPME) technique. The permeability coefficients of benzene and toluene were 0.07 and 0.025 μg/cm/hr, respectively, indicating toluene is less permeable through the PVC pipe. Using a transient mass diffusion equation and appropriate initial and boundary conditions, the simulation studies of the concentration profiles of benzene in pipe-water implied that swelling of the PVC pipe wall might have a significant effect on the permeation experiments. The new pipe-bottle model is a less time-consuming and more sensitive means to determine the chemical resistance of polymeric pipes to permeation by organic solvents.

INTRODUCTION

Several studies have indicated that organic chemical pollutants in soil or groundwater might permeate through the plastic water pipes and contaminate the drinking water lines [1-2]. For the practical purposes, there is a need to investigate the permeability of organic compounds through the plastic pipes used in water supply systems. Although several researchers have conducted the immersion method [3] and pipe-bottle experiments to measure the permeation of organic compounds for polyvinyl chloride (PVC) and polyethylene (PE) pipes [3-5], the sampling procedures are time-consuming and complex. For example, Mao [5] developed a 1-L pipe-bottle, as shown in Fig. 1, to determine the permeability of hydrocarbons through PVC pipes. After each sampling of pipe-water, the test pipe was flushed with deionized water, and then fresh deionized water was refilled into the pipe to continue the permeation experiment. This effort was made to well-mix the water samples inside the test pipe for the analysis of permeant. However, refilling fresh deionized water for each sampling could result in an overestimation...
of the permeability for permeants through the test pipe wall. The objective of this study was to develop a new pipe-bottle model, coupling with the solid phase microextraction (SPME) technique, for the permeation tests of PVC pipes. The results of this study can facilitate the measurements on the permeability of organic compounds through plastic water pipe walls.

### METHOD

The PVC water pipes (model B27) used for this study were made by the Nan-Ya Plastics Corp. (Taiwan, ROC). The outside diameter, inside diameter and thickness of the PVC pipe were 3.4, 2.7 and 0.31 cm, respectively. The PVC pipe samples, cut with a length of 5.8 cm, were rinsed with deionized water and air dried for 24 hr at 25±1°C. The organic solvents conducted for the permeation experiments were benzene and toluene (Merck Co., Darmstadt, Germany), which were ACS Grade (>99%).

Fig. 2 shows the pipe-bottle model developed in this study for the permeation test, which was composed of a polyformaldehyde (POM) bottle cap and a stainless steel base. There was a 10 mm long sampling port in the bottle cap, and the bottle cap has an embedded O-ring. The stainless steel base was a circular groove in outside diameter of 47 mm, inside diameter of 36 mm and depth of 3.5 mm, respectively. A PTFE film with a thickness of 1 mm was placed in the groove, and the pipe sample was tightly connected by the stainless steel base and the POM bottle cap using three screws.
A stir bar and 30 mL DI water were added into the PVC pipe from the sampling port in the bottle cap, and the sampling port was capped with PTFE-faced silicone septa. The headspace in the PVC pipe was approximately zero to minimize volatilization of permeant from pipe-water. The 125 mL glass bottle was filled with 70 mL test organic solvent. The assembled POM bottle cap and PVC pipe were immersed in the organic solvent, and the bottle cap was screwed down the glass bottle. The wall of PVC pipe was completely contacted with the test solvent in the glass bottle. The pipe-bottle model and magnetic stirrer were inserted into a low temperature incubator at a temperature of 25±1°C for the permeation experiment. The pipe-bottle model was placed onto the magnetic stirrer at a stirring speed of 200 rpm. During the permeation experiment, the SPME device (100 μm PDMS, Supelco, USA) was injected into the sampling port of the POM bottle cap to adsorb DI water sample for different periods of time. After sampling for 15 min, the SPME fiber was then taken out and injected into the GC-FID (Auto-System XL, Perkin Elmer, Norwalk, Conn.) for 5 min to analyze the concentrations of organic solvents. The temperature of the capillary GC column (Equity™-5, Supelco, Bellefonte, PA) was kept at 200°C for 10 min, and the temperatures of GC injector and detector were 220°C and 250°C, respectively. The GC calibration was performed using the pipe-bottle model but without adding solvents into the glass bottle. Standard solutions of different solvent concentrations were loaded into the PVC pipe of the assembled pipe-bottle model. The linear regression coefficients for all calibration curves were R²>0.997. The Limit Detection Levels (LDL) of benzene and toluene were 0.0031 and 0.0027 mg/L, respectively.

RESULTS AND DISCUSSION

Fig. 3 shows the permeation results for the experiments of benzene and toluene to PVC pipes. Once breakthrough was occurred, the cumulative mass of organic solvents in pipe-water was found to increase linearly. The steady state permeation rate, \( J_s \) (ML\(^{-2}\)T\(^{-1}\)), was obtained using the rate of increase of the permeated mass in pipe-water as follows:

\[
J_s = \alpha \frac{V}{A}
\]  

where \( \alpha \) is the slope of the linear portion, i.e. steady state permeation, of the permeant concentrations in pipe-water (MT\(^{-1}\)); \( V \) is the volume of deionized water in the test pipe (L\(^3\)), i.e. 30 mL; and \( A \) is the area of PVC pipe wall exposed to the permeant, i.e. 61.95 cm\(^2\).
In addition, the permeability coefficient, $P$ (ML$^{-1}$T$^{-1}$), of the permeant through the pipe wall can be determined as follows [6]:

$$P = J_s L$$  (2)

where $L$ (L) is the thickness of the PVC pipe wall. For the test PVC pipes, the permeability coefficients of benzene and toluene are 0.07 and 0.025 µg/cm/hr, respectively. This result indicates toluene is less permeable through the PVC pipe than benzene.

Permeation of organic solvents through the polymeric membrane is dependent on the molecular interactions between the solvent and polymer. First, the permeant dissolves or partitions onto the contact surface of the membrane. Subsequently, the permeant diffuses through the membrane and finally is desorbed from the opposite surface of the membrane. Permeation is mainly a function of solubility and diffusivity of solvents through the membrane, with desorption playing an insignificant role [7]. One-dimensional diffusion of the permeant into the polymeric membrane can be expressed by Fick’s second law as follows:

$$\frac{\partial C_s}{\partial t} = D \frac{\partial^2 C_s}{\partial Z^2}$$  (3)

where $D$ is the diffusion coefficient of the permeant in the polymeric membrane (L$^2$T$^{-1}$); $C_s$ is the permeant concentration at some point $Z$ in the membrane (ML$^{-3}$); and $Z$ is the distance along the direction of diffusion (L). It is generally assumed that the diffusion coefficient is independent of the concentration $C_s$ and position (i.e., $Z$) in the membrane [6-7].

In this study, the concentrations of benzene and toluene in pipe-water, below 40 mg/L, are significantly lower than their densities. Therefore $C_s|_{Z=L}$ can be assumed to be insignificant as compared to $C_s|_{Z=0}$. The boundary and initial conditions of Eq. (3) were assumed as follows:

$$C_s(0, t) = S$$
$$C_s(L, t) = 0$$
$$C_s(Z, 0) = 0$$
where $S$ is the solubility of the permeant in the PVC pipe wall (ML$^{-3}$).

By solving Eq. (3), the concentration profile $C_Z$ into the PVC pipe wall was given as follows:

$$C_Z(Z,t) = S \left( 1 - \frac{Z}{L} \right) - \sum_{n=1}^{\infty} \frac{2S}{n\pi} \exp \left( -D \frac{n\pi}{L} t \right) \sin \left( n\pi \frac{Z}{L} \right) \quad (4)$$

For the steady state, i.e. $t \rightarrow \infty$, the concentration profile $C_Z$ was described as follows:

$$C_Z(Z,t) = S \left( 1 - \frac{Z}{L} \right) \quad (5)$$

By taking the mass balance for pipe-water, the concentration of permeant, $C$ (ML$^{-3}$), in pipe-water was determined as follows:

$$V \frac{dC}{dt} = -AD \frac{\partial C_Z}{\partial Z} \bigg|_{Z=L} \quad (6)$$

The concentration of permeant in pipe-water can be solved from Eq. (6) as follows:

$$C = -\frac{AD}{V} \int f(t) dt + C^* \quad (7)$$

where $f(t) = \frac{\partial C_Z}{\partial Z} \bigg|_{Z=L}$. With the initial condition of $C(0)=0$ for Eq. (7), the integration constant $C^*$ can be determined.

According to the solutions of Eq. (4), the diffusion coefficient and solubility of permeant in the PVC pipe wall can be experimentally obtained by [6-7]:

$$D = \frac{L}{6 t_l} \quad (8)$$

$$S = \frac{P}{D} \quad (9)$$

where $t_l$ is the lag time (T) of the permeation curve.

The diffusion coefficients of benzene and toluene in the PVC pipe walls were 6.32 and 9.63 ×10$^{-8}$ cm$^2$/s, respectively. In addition, their solubilities were 306 and 7.22 mg/L. The permeation concentration with respect to time in Eq. (7) can be solved using Maple software (Waterloo Maple Inc., Waterloo, Ontario, Canada). Fig. 4 indicates the simulation results of test solvents using diffusion coefficient $D$ and solubility $S$ for the permeation experiments. It can be seen that the diffusion coefficient $D$ estimated from Eq. (8) was able to approximately simulate the permeation results by Fick’s second law with the assumptions of the boundary and initial conditions. However, Fig. 4 shows the simulated benzene concentrations were slightly higher than the experimental results at the period of breakthrough time. This deviation may be the result of neglecting the effects of swelling of the
test sample in the simulation equations. The thickness of PVC pipe walls was increased by approximately 20% for the permeation experiments.

![Figure 4](image)

**CONCLUSION**

In this study, a pipe-bottle model coupled with SPME sampling was proposed to test the permeability of PVC pipes under conditions of continuous contact with the organic solvent. During the permeation run, the concentrations of permeant in pipe-water were directly sampled using SPME. The availability of SPME to the test solvents was validated by conducting the calibration of GC-FID using the pipe-bottle model. The permeability coefficients of benzene and toluene were 0.07 and 0.025 µg/cm/hr, respectively, in the PVC pipe walls. The new pipe-bottle model provides a less time-consuming and more sensitive means to measure the mass of permeant in pipe-water for the permeation experiment. However, the effect of swelling of the PVC pipe walls could not be neglected to determine their resistance to permeation by organic solvents.

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