Sorption and Permeation of Organic Environmental Contaminants Through PVC Geomembranes

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ABSTRACT: The effect of penetrant diffusion on the barrier properties of PVC geomembranes have been determined for the following organic environmental contaminants: benzene, dichloromethane, and trichloroethylene. The membranes experienced swelling to a degree which depends on the type of penetrant used. Some dissolution may occur, and in general we are dealing with Case II transport. The experimental work was performed with an ASTM-cell, a Cahn balance, and an in-house built gravity (G-) cell. Those instruments generated comparable data on breakthrough times. The obtained diffusion coefficients as well as the breakthrough times obeyed an Arrhenius-type relation over the temperature range studied. Liquid sorption of the various penetrants modified the geomembrane structure. Membrane surface pretreatment with different contaminants influences the subsequent transport of organic penetrants through PVC geomembranes. That is to say: the induced swelling, as result of membrane contact with one penetrant, is likely to alter the system free volume, allowing for a different rate of mass transport for subsequent penetrants. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63**: 1189–1197, 1997

Key words: diffusion; geomembranes; contaminents; PVC

INTRODUCTION

Recent studies have evaluated the barrier properties of geomembranes.[1,2] Geomembranes are polymeric membranes used as liners for solid waste disposal facilities. Their role is to prevent waste leachate from contaminating the surrounding groundwater. Waste leachate may contain potential carcinogenic organic compounds such as benzene, vinyl chloride, dichloromethane, etc. PVC geomembranes contain poly(vinyl chloride) resin, additives, and a significant amount of plasticizer which can represent up to 30% of the geomembrane total weight.[3,4]

Migration of organic penetrants through a membrane involves molecular diffusion, penetreant/

membrane interactions, and possible cell container materials/penetrant interactions. Based on these considerations, one should take into account the suitability of the cell material and the possible geomembrane modifications resulting from the organic penetrant diffusion. Rowe, Hrapovic, and Kosaric[1] have examined cell container material/penetrant interactions during geomembrane diffusion tests. Comparison of stainless steel, polytetrafluoroethylene, and glass as cell container material indicated that only glass did not interfere with the diffusion study of dichloromethane in dilute aqueous solution through high density polyethylene geomembranes. Our observations involving other chemicals are different.

Transport of organic penetrants through polymeric materials is controlled by two mechanisms: chemical potential gradient driven diffusion associated with a companion stress evolution. The relative magnitude of these two processes will dic-

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tate which mechanism is predominant. When membrane swelling is not observed, the transport mechanism is mainly due to molecular diffusion and the advance of the penetrant front is proportional to t^n with $n \approx \frac{1}{2}$. This situation is referred to as a Case I mechanism. When membrane swelling is observed, the stress in the viscoelastic membrane is altered significantly and $n \approx 1$. This situation is referred to as a Case II mechanism.

In this study we report on the effect of organic penetrants diffusion on the barrier properties of PVC geomembranes. In particular, we consider the effect of membrane surface pretreatment, of temperature, and of concentration. Penetrants such as benzene, dichloromethane, and trichloroethylene have been selected for the permeation and sorption tests.

EXPERIMENTAL

Materials and Chemicals

A poly(vinyl chloride) geomembrane produced by Texcel, Beauce-Nord, Canada, was employed in this study. The monomer molecular weight, the density and the membrane thickness were 62.5 g/mol, 1.25 g/cm³, and 1.00 ± 0.03 mm, respectively. The measured density suggests the presence of additives and/or plasticizers. The degree of crystallinity is probably ~ 15%. No exact information could be obtained from the manufacturer. The organic penetrants considered were dichloromethane (DCM) and glass distilled grade benzene purchased from OmniSolv. In addition, A.C.S. Spectro, grade trichloroethylene (TCE) was obtained from Anachemia.

Liquid Sorption Test

A home made contamination-permeation cell (C-cell) was used for the liquid sorption tests. This cell made of aluminum is based on a modification of the cone standard gravimetric cell,[5] which allows liquid to contact only one side of the membrane. The liquid–membrane contact area is 20 cm², which is the same as for the standard ASTM permeation cell. To perform the liquid sorption test, a protocol similar to the immersion test as described by Aminabhavi and Aithal[6] and Aminabhavi et al.[7] was developed. That is to say: after the liquid was applied to the challenging side of the membrane for a required time interval, the liquid was decanted, the cell was quickly disassembled, and the extra liquid was wiped off from the membrane surface using filter paper. Then, the membrane was weighted using a Mettler model 240 balance to ±0.1 mg and the membrane thickness was measured using a micrometer to ±0.001 mm. The membrane was reinstalled and the above procedure was repeated. After the sorption test was completed, the desorption test was carried out by following the weight and thickness of the contaminated membrane with time under atmospheric conditions.

Vapor Sorption Test

Vapor sorption and desorption experiments have been carried out using a CAHN 2000 electrorecording microbalance. The weighting unit is enclosed in a glass vacuum bottle having a vacuum outlet and three hangdown tubes. The geomembrane sample and counterweight stirrup are suspended using wires and metal loops which are attached to the beam. The whole weighing unit is fitted inside a metallic box and the temperature is controlled by a Sargent-Welch thermomonitor and RMT cooling unit. Pressure control and measurement are achieved by a pressure control loop that consists of a valve controller, an electronic manometer, a pressure transducer, and a servo valve. The data acquisition part consists of an HP3421A data acquisition unit and a microcomputer. A computer program was developed to transfer the digitized output signals from the data acquisition unit to the HP–IB interface card. The program prints the following numerical values: sample weight, temperatures of both the sample and the chamber, and the pressure as a function of time. Further information on this experimental set up can be found in Guo and De Kee.[8]

A PVC 240 geomembrane sample of thickness 1.0 mm is cut into 5 × 5 mm² slabs weighing ~ 40 mg and loaded onto the sample pan of the balance. The system is degassed by a vacuum pump for 24 h at a pressure of 10^{-2} mmHg. After the temperature of the sample and the surrounding chamber achieved the test temperature, the sample was exposed to pure solvent vapor. The weight change of the geomembrane, the vapor pressure, and the temperatures of interest were recorded as a function of time. The sorption test is considered to be completed when the weight change during a 50 min interval is $<10^{-6}$ g. This does not imply that equilibrium conditions were achieved. When this criterion is satisfied, desorption is initiated by quickly applying vacuum to the weighing system. Again, once the weight change is less than 10^{-6} g in a 50 min interval,
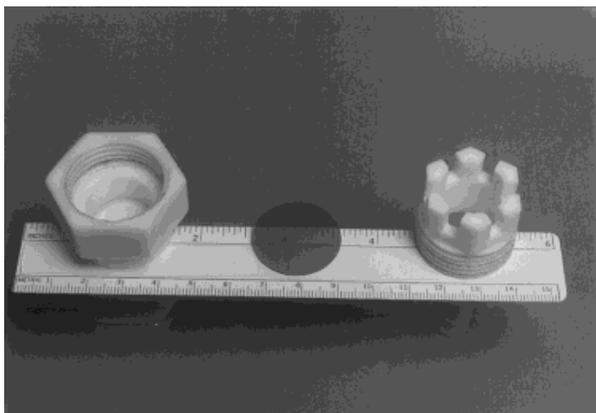
Figure 1 Photograph of the G-cell.

the desorption is considered to be completed. If required, another sorption/desorption cycle at another pressure can be initiated at this time.

Permeation Test

The gravimetric method as well as the ASTM method were used to study the permeation of organic liquids through geomembranes.

The gravimetric method made use of a homemade gravity cell (G-Cell). A detailed description can be found in Guo, De Kee, and Harrison.[9] This cell, made of Teflon, is basically a liquid container with a sample (membrane) sealed on its top. The bottom part of the cell is essentially a liquid container. The inside diameter of the container is 1.79 cm and its depth is 1.00 cm. The top part, which has the same inside diameter as the bottom container, helps to secure the membrane on the liquid container. The inside diameter of the cell accurately defines the permeation area of the membrane. The top part of the cell is cut in the form of a gear, as shown in Figure 1. This has a dual purpose: (1) when the cell is turned upside down, the liquid is in contact with the membrane and the gear spacing allows for a quick removal of permeated vapor; (2) the weight of the cell is reduced and a more sensitive balance (Mettler AE240) weighting range can be accessed. The use of Teflon also helps in reducing the weight and introduces negligible errors due to chemical interactions, since the concentrations of the chemicals are such that the tests require a few hours as opposed to a few weeks when working with very dilute solutions.[1] In addition, a permeation test using DCM as the penetrant and a Teflon sheet did not show any detectable weight loss over a 24 h period.

In the ASTM method, an open loop assembly was developed. The standard ASTM permeation cell (F-739-85) was connected to a gas chromatograph (Hewlett Packard, model 5790A series) through a Valco programmer valve. Nitrogen at a flow rate of 100 mL/min^{-1} was used as the carrier gas. The ASTM cell was immersed in a water bath with temperature controlled at 30 ± 0.5°C. The penetrant which had diffused through the membrane was automatically sampled with the Valco programmed valve and analyzed by a GC flame-ionization detection (FID) system. The sensitivity of the detector was regularly calibrated using the standard diffusion capillary tubes at the same condition as for the permeation tests.

RESULTS AND DISCUSSION

Sorption/Desorption Study

Both thickness and weight of the membrane during liquid sorption and desorption were examined. Figure 2 presents changes of both weight and thickness (l) of a PVC240 membrane upon sorption/desorption of various chemicals at 303 K. The desorption was initiated after 100 min. For the DCM/PVC system, the membrane swells rapidly, reaches a maximum thickness after 15 min, and then slowly retracts. Meanwhile, its weight change follows a similar pattern. In the case of benzene, a maximum thickness is approached only after 40 min, and the retraction during the
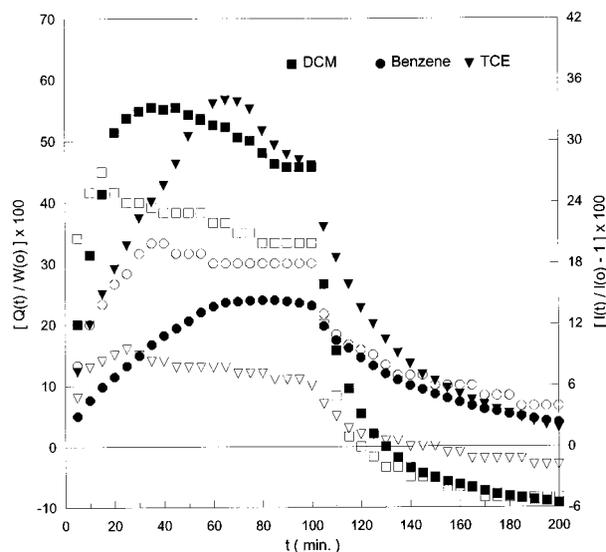
Figure 2 Changes of thickness (open symbols) and weight (closed symbols) of a PVC 240 membrane with time during liquid sorption and desorption at 303 K using a C-cell.

sorption process is also much less significant than that for the DCM sorption. For TCE, the maximum thickness is obtained after 25 min, however, the change in thickness during the sorption process is smaller than for either DCM or benzene even though the weight change is similar to the DCM sorption case. In the case of the desorption process, we note that the thickness and weight of the membrane in contact with DCM is smaller than their initial values. In the case of TCE transport through the membrane, only the membrane thickness becomes smaller than its initial value, whereas in the case of benzene contamination, both the membrane thickness and weight after 200 min are larger than their initial values (see Fig. 2).

Generally, transport of molecules through polymeric materials has been expressed by an equation of the form[10]

$$\frac{Q(t)}{Q(\infty)} = kt^n \tag{1}$$

Where

$$Q(t) = W(t) - W(o \tag{2}$$

$W(o)$ is the weight of the dry membrane and $W(t)$ is the weight of the membrane plus penetrant at time t; k is a constant and the exponent n is associated with the type of transport mechanism. For a Fickian diffusion, the value of n is 0.50. For Case II diffusion, where the rate of diffusion is much faster than the rate of the relaxation process, values of n are reported to be around unity.[11] Our results, as shown in Figure 2, indicate that a nearly linear relationship exists for the initial weight gain and time for all contaminants investigated, implying that the overall process of the liquid sorption is a Case II transport.

Figure 3(a) presents vapor sorption as a function of DCM vapor pressure ranging from 6.5 to 100 mm Hg. As the pressure increases, a linear relation is observed between the initial weight gain and time, suggesting that Case II transport is predominant. Graphs of the initial weight gain versus the square root of time suggest that a change in mechanism from Case II toward Fickian transport occurs with decreasing vapor pressure. Such a change in mechanism with vapor activity has been experienced in many polymer-penetrant systems.[11]

Figure 3(b) shows weight changes of the membrane during desorption. The desorption curves follow a similar pattern independent of the initial pressure, suggesting a unique desorption mechanism. At each pressure, the desorption curve describes three different regions. Immediately after the onset of desorption, the amount of the penetrant is quickly decreasing; then there is a much slower decrease (or a transition region) which is finally followed by a tail. We choose the onset of the tail as the transition time t^* [see Fig. 3(b)]. Normalizing $Q(t)$ via $Q(t^*)$ and measuring time in relative units of t^* generates a master curve, as shown in Figure 3(c). Stastna, De Kee, and Harrison[12] analyzed this situation in terms of a continuous random walk diffusion model.

Permeation Study

Comparison of Test Methods

The permeation flux, F (g cm^{-2} s^{-1}), of organic penetrants through geomembranes was measured using the G-cell and the ASTM-cell, described earlier. Generally, the ASTM technique is more sensitive and more accurate, but is more expensive to operate, as it involves a gas chromatograph, a valve selector for sampling, etc. The G-cell (gravimetric method) relies on a more simple procedure, is considerably less expensive to operate, but is not suitable to study multicomponent permeation. Both systems allow for the determination of the breakthrough time (t_b) and the permeation flux. The breakthrough time is the time required for the penetrant to be detected on the opposite side of the membrane. This value depends on the sensitivity of the measuring system. Figure 4 presents typical permeation results of DCM, TCE, and benzene through a PVC 240 geomembrane. It shows that the estimation of t_b via the two techniques is quite comparable.

Table I lists the measured results for t_b and for the maximum flux, illustrating the relation between t_b and the time required to achieve maximum swelling. We further note that, as expected, the breakthrough time corresponds to the time required for the membrane to reach its maximum thickness (see Fig. 2). Also, following the breakthrough time, the permeation flux (F) increases to reach a maximum value and then gradually decreases toward a steady state value, provided a sufficient supply of penetrant is available. We assume the existence of a sharp boundary, separating a downstream glassy zone from an upstream swollen rubbery zone, as the penetrant front moves through the membrane. Maximum swelling is achieved once the front traveled
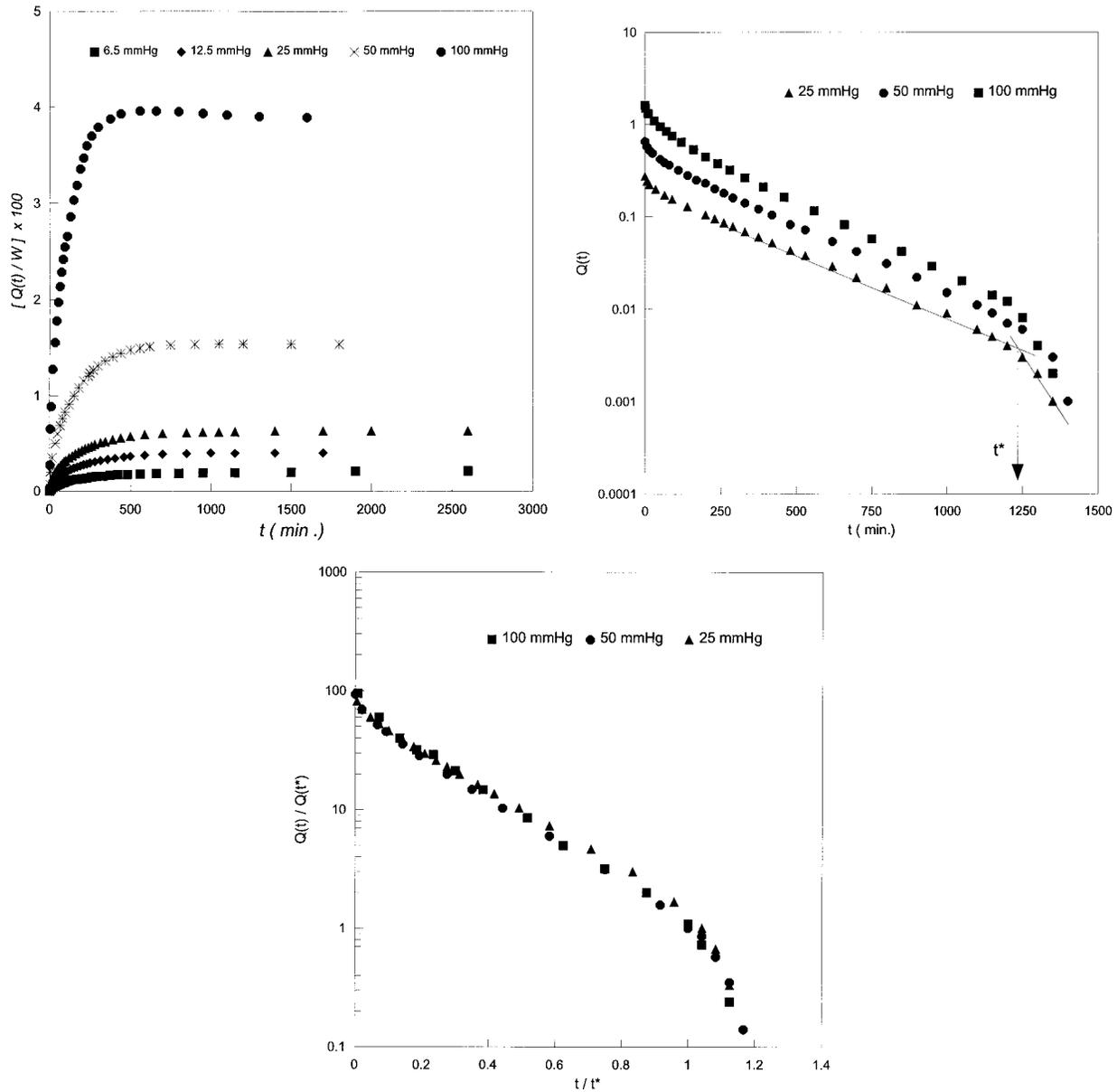
Figure 3 (a) Vapor sorption curves for the DCM/PVC 240 system at 303 K. (b) Vapor desorption curves for the DCM/PVC 240 system at 303 K. (c) Normalized vapor desorption curve for DCM in PVC 240 at 303 K.

through the membrane. At this (breakthrough) time, the membrane experiences its maximum thickness (see Table I), the desorption process is initiated, and with time, the membrane tries to regain its original shape, presumably as a result of structural changes associated with a relaxation process.

Estimation of Diffusion Coefficient

Rogers[13] related the penetrant flux $F(t)$ to the diffusion coefficient D by

$$F(t) = -D\left(\frac{\partial c}{\partial x}\right)\bigg|_{x=l}$$

$$= 2c_1\left(\frac{D}{\pi t}\right)^{1/2} \sum_{m=0}^{\infty} \exp\left[-\frac{(2m+1)^2 l^2}{4Dt}\right] \quad (3)$$

Where l is the thickness of the membrane, c_1 is the penetrant concentration at $x = 0$, and D is a constant diffusion coefficient. For small times, only the first term of the series is important and the equation reduces to:
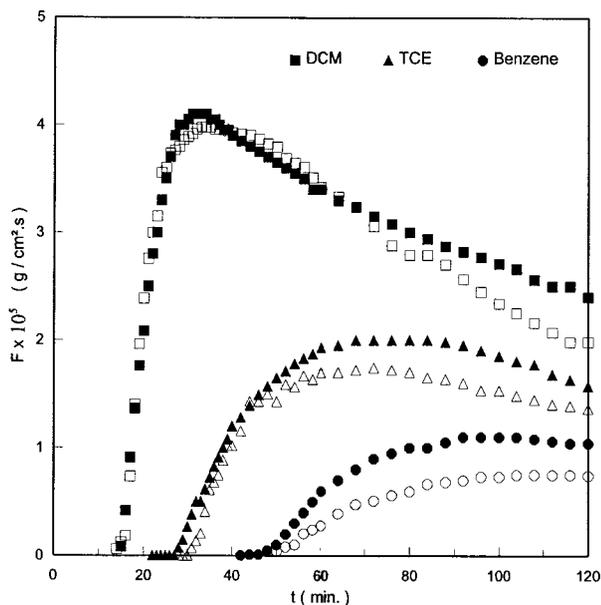
Figure 4 Permeation of organic solvents through PVC 240 at 303 K using an ASTM-cell (closed symbols) and a G-cell (open symbols).

$$\ln(t^{1/2}F) = \ln\left[2c_1\left(\frac{D}{\pi}\right)^{1/2}\right] - \frac{l^2}{4Dt} \qquad (4)$$

A graph of $\ln(t^{1/2}F)$ against $(1/t)$ yields a straight line with slope $-l^2/4D$ from which the value of D can be estimated. One actually estimated D_0, the limiting diffusion coefficient at zero concentration, since the concentration of penetrant in the membrane is small when $t \rightarrow 0$.

Effect of Concentration, Temperature, and Contamination on Permeation

Membranes and Penetrants. Estimated diffusion coefficients of penetrants through different membrane samples are summarized in Table II. The data in Table II confirm the information dis-

Table II Diffusion Coefficients of Penetrants through Different PVC Membranes

Penetrant/Membrane at 303 K	Diffusion Coefficients $D_0 \times 10^7$ (cm^2/s)
DCM/PVC220 (thickness: 0.51 ± 0.02 mm)	3.4
DCM/PVC240	2.7 (2.4)[a]
TCE/PVC240	0.80 (0.69)[a]
Benzene/PVC240	0.36 (0.52)[a]

[a] Diffusion coefficient obtained from G-cell data.

played in Figure 4. That is to say: DCM has the highest diffusion coefficient, associated with the largest flux (Fig. 4). This is followed by TCE and by benzene. Table II reveals a diffusion coefficient of 2.7×10^{-7} cm^2/s for the 1.00 mm thick PVC membrane and a diffusion coefficient of 3.4×10^{-7} cm^2/s for the 0.51 mm thick sample. This is most likely due to the nature of the additives present. The different colors of the PVC 220 and PVC 240 samples lend support to this observation.

Temperature. Temperature plays a very important role in the diffusion of penetrant molecules through polymeric membranes. As observed elsewhere,[14] the diffusion coefficient increases with increasing temperature. As a result, the permeation flux increases with increasing temperature resulting in a shorter breakthrough time. The breakthrough time (t_b) as well as the diffusion coefficient (D_0) follow an Arrhenius type relation given by

$$t_b = B_0\exp(E_B/RT) \qquad (5)$$

and

$$D_0 = d\,\exp(-E_D/RT) \qquad (6)$$

Table I Comparison of Different Tests Using PVC 240 Geomembrane

| Penetrant | Liquid Sorption Contact Time (min) to Achieve Maximum Thickness | Permeation Tests | | | |
| | | t_b (min) | | $F \times 10^5$ (g/cm^2/s)[a] | |
		G-cell	ASTM	G-cell	ASTM
DCM	15	15	15	4	4.1
TCE	25	30	28	1.7	2
Benzene	40	48	42	0.8	1.1

[a] Maximum permeation flux.
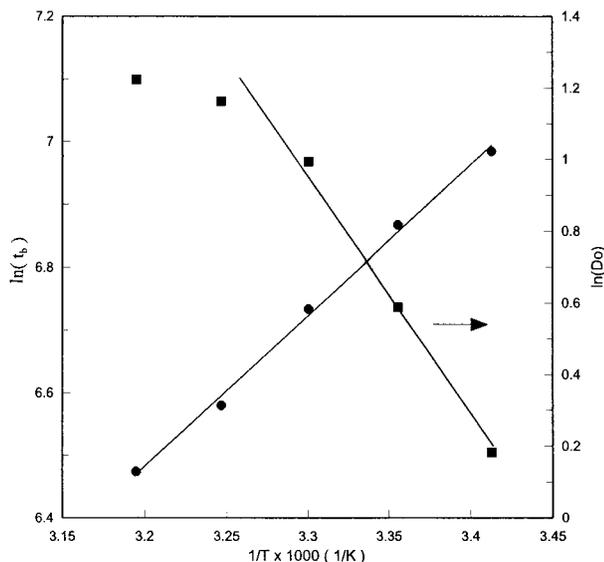
Figure 5 Effect of temperature on t_b and D_0 for a DCM/PVC 240 system.

over the temperature range studied (see Fig. 5).

In those equations, B_0 and d are constants, E_B and E_D are the (nominal) activation energies for breakthrough and diffusion. They have been found to be 21 kJ/mol and 54 kJ/mol, respectively, for DCM transport through a PVC 240 membrane (see Fig. 5). The values of the estimated activation energies are of an order of magnitude, comparable to those obtained by Hofenberg[11] involving a study of n-pentane transport through a polystyrene membrane. We note, however, that the membrane materials are different so that a comparison may not be strictly valid.

Penetrant Concentration. The permeation of aqueous DCM solutions in the concentration range of 100 to 1000 ppm through PVC membranes was measured via the ASTM method. Detection limits made it unrealistic to determine a permeation flux of solutions of concentration lower than 150 ppm in our open loop system involving a carrier gas. In recent studies, Rowe, Hrapovic, and Kosaric[1] and Park, Sakti, and Hoopes[2] used a closed-loop system which allowed them to study more dilute solutions. Such a system allows for the measurement of accumulated concentrations. We note, however, that open loop systems are more representative for actual landfill situations.

Figure 6 depicts permeation profiles of aqueous DCM solutions through PVC 240. One observes that the permeation flux at equilibrium (Fe) is

proportional to the DCM concentration. Such a relationship is to be expected since water has no effect on the membrane barrier properties, as will be discussed in the following section.

Effect of Contamination. The effect of geomembrane pretreatment with other chemicals on the permeation flux of various components was also evaluated. One test involved pretreating the membrane by immersion in water for 72 h. Another test involved applying a vacuum for 72 h, in order to remove undesired surface components. A combination of these two treatments was also examined. Subsequent permeation tests with DCM showed no effect on the breakthrough time following these pretreatments. However, this was not the case when contaminants other than water were used.

Figure 7 illustrates that immersion of a PVC 240 membrane in benzene for 1 h, followed by applying a vacuum (10^{-2} mm Hg) for 6 days reduces and delays the maximum flux of DCM. One observes also that a small amount of benzene was still present in the PVC membrane after this 6 day treatment (o). On the other hand, immersion of the PVC membrane in DCM for 1 h, followed by applying a vacuum for 6 days, resulted in a delayed appearance of benzene, probably due to structural changes resulting from membrane interaction (dissolution) with concentrated DCM. We also observe a lower initial value of the slope
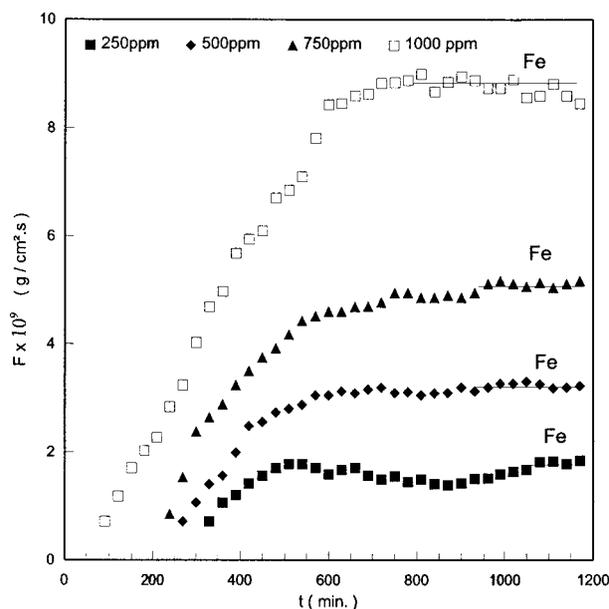
Figure 6 Permeation profiles of aqueous DCM solutions through PVC 240 at 303 K using an ASTM-cell.
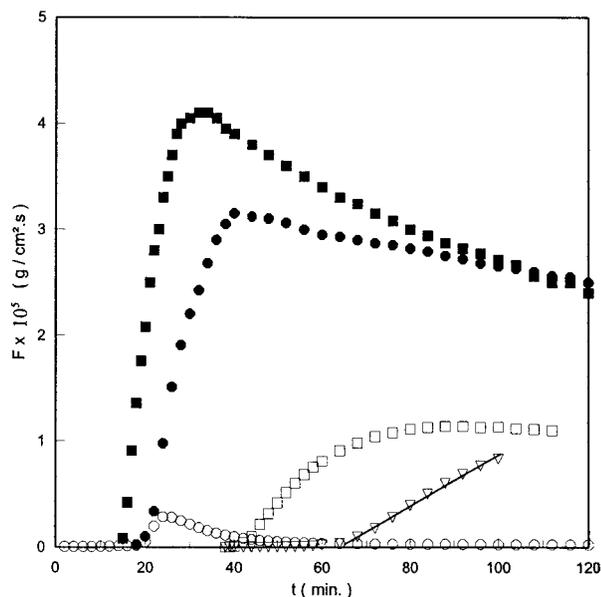
Figure 7 Permeation profiles of DCM (closed symbols) and/or benzene (open symbols) through pretreated PVC 240 at 303 K using an ASTM-cell. (■) DCM/untreated geomembrane (see also Fig. 4); (●) DCM/benzene contaminated membrane (see text); (○) residual benzene/benzene contaminated membrane; (□) benzene/untreated geomembrane; (▽) benzene/DCM contaminated membrane.

of the benzene F versus t curve. In addition, the slope is now constant.

We note that in general, a flux F is related to a generalized thermodynamic force X as follows:

$$F = \sum_i L_{ik}X_k \qquad (7)$$

where the coefficients L_{ik} are the Onsager kinetic coefficients. Of particular interest are the diagonal coefficients L_{ii}, which are the proper coefficients, representing pure effects such as conductivity, diffusion, etc. The off diagonal coefficients L_{ik} ($i \neq k$) are mutual coefficients describing cross effects, that is to say: interference between irreversible processes i and k.[10]

In particular, the mass flux F is related to the concentration gradient and the time evolution of the concentration can be expressed in the following form[15]:

$$\frac{Dc}{Dt} = \frac{L_{11}}{\rho T}\frac{\partial(\mu_B - \mu_{DCM})}{\partial c}\frac{\partial^2 c}{\partial x^2} \qquad (8)$$

Here, D/Dt is the substantial time derivative, L_{11} is the Onsager transport coefficient of diffusion, μ is the chemical potential, and the subscripts B

and *DCM* refer to benzene and dichloromethane, respectively. That is to say: we do not consider interactions between the benzene and the dichloromethane molecules traveling through the membranes. We consider only L_{11} and $L_{ik} = 0$ ($i \neq k$).

In the case of benzene, the linear relation between the flux and the time observed in Figure 7 suggests that the coefficient of $\partial^2 c/\partial x^2$ in eq. (8) should not be constant, but should be a function of concentration.

Figure 8 also shows the permeation of DCM and benzene through a PVC 240 geomembrane. Here the experimental conditions are as follows. In one test, the membrane has been in contact with benzene for 20 min prior to measuring the DCM permeation (■). Compared to the situation illustrated in Figure 4, we note, as expected, a shorter breakthrough time for DCM. In the case where the membrane was continuously challenged with a mixture of 0.1 mol fraction benzene and 0.9 mol fraction DCM (□), we observe a delayed and reduced DCM flux, confirming observations made in the context of Figure 7. That is to say: as a result of the contamination, residual benzene leaves the membrane, simultaneously with the DCM removal, as was the case for the test involving the mixture supply.
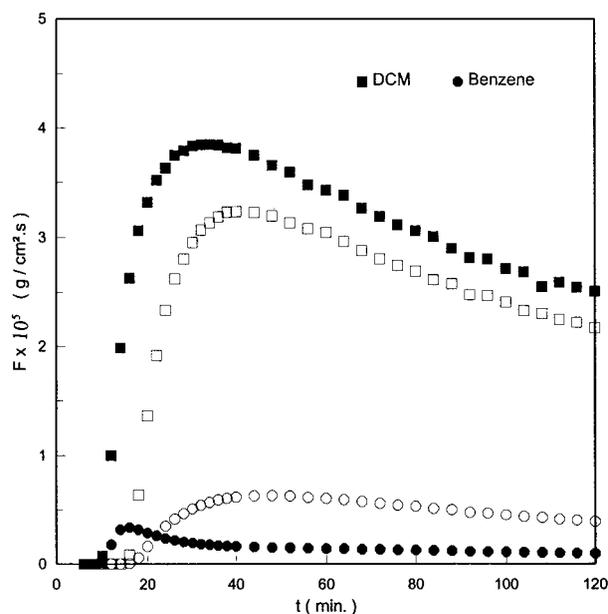
Figure 8 Permeation profiles of DCM and benzene through PVC 240 at 303 K using an ASTM-cell. (■) DCM/benzene contaminated membrane (see text); (●) benzene/benzene contaminated membrane (see text); (□) DCM/untreated membrane (see text); (○) benzene/untreated membrane (see text).

NOMENCLATURE

c_1	penetrant concentration on the challenged surface of a membrane (mmol/cm^3)
D	diffusion coefficient (cm^2/s)
D_0	limiting diffusion coefficient at zero concentration (cm^2/s)
F	permeation flux (g cm^{-2} s^{-1})
Fe	permeation flux at equilibrium (g cm^{-2} s^{-1}) or (mg m^{-2} s^{-1}) or (g m^{-2} s$^{-1)}$
$l(o)$	membrane thickness at $t = 0$ (cm)
$l(t)$	membrane thickness at t (cm)
$Q(t)$	$Q(t) = W(t) - W(o)$ (g)
$Q(\infty)$	weight change of a membrane at $t = \infty$ (g)
t	time (s)
t^*	transition time (s) [see Fig. 3(b)]
t_b	breakthrough time (s)
T	absolute temperature (K)
$W(o)$	membrane weight at $t = 0$ (g)
$W(t)$	membrane weight at t (g)

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