

# NOTES

## Sorption and Permeation of Organic Contaminants Through High-Density Polyethylene Geomembranes

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### INTRODUCTION

Geomembranes are used as liners to protect the environment from hazardous toxic contaminants. High-density polyethylene (HDPE) represents 40 to 45% of the raw material used in the manufacture of geomembranes.<sup>1</sup>

Although geomembranes are rarely exposed to pure contaminants, surprisingly little research has been conducted using multicomponent systems in contact with geomembranes. Nelson and colleagues<sup>2</sup> and Mickelsen and associates<sup>3</sup> investigated breakthrough times and the associated fluxes as a result of membrane–mixture contact. In recent work, Xiao and coworkers<sup>4</sup> reported on the substantial effect of mixture transport through PVC membranes.

In this note, we report further on an experimental study involving the transport of a mixture of penetrants through HDPE geomembranes.

### EXPERIMENTAL

**Materials and Chemicals** An HDPE geomembrane HD40, provided by Texcel (Beauce-Nord, Quebec, Canada) was used in this study. The monomer molecular weight, the density, and the membrane thickness are 28.0 g/mol, 0.94 g/cm<sup>3</sup>, and 1.12 ± 0.10 mm, respectively. The crystallinity is reported to be about 35%. The organic

penetrants considered were dichloromethane (DCM) and glass distilled-grade benzene purchased from OmniSolv (Toronto, Canada). In addition, A.C.S. Spectro grade trichloroethylene (TCE) was obtained from Anachemia (Montreal, Canada). The physical properties of the penetrants can be founded in Gallant and Yaws<sup>5</sup> and in Barton.<sup>6</sup>

**Methods** At the outset, a gravimetric method as well as the ASTM method were used to study the permeation of organic liquids through HDPE geomembranes. The experimental setup as well as the experimental protocols are summarized by Xiao and associates.<sup>4</sup> The liquid sorption experiments were performed as described by Unnikrishnan and Thomas.<sup>7</sup> The vapor sorption was carried out using a Cahn balance as described by Xiao and associates.<sup>4</sup>

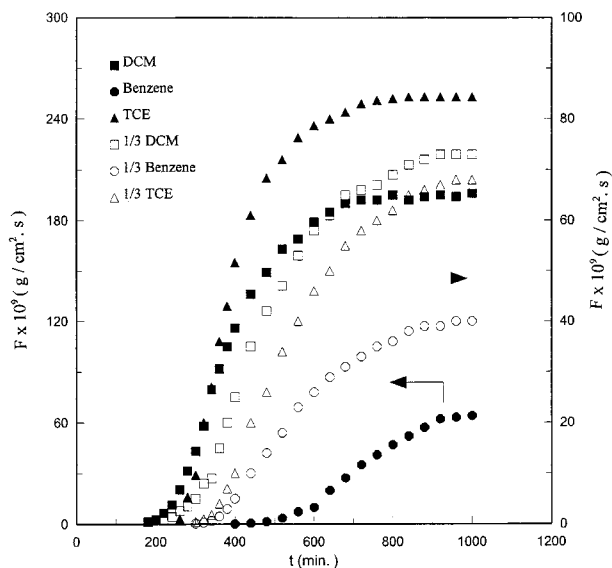
### RESULTS AND DISCUSSION

**Permeation Tests** The gravimetric cell (G-cell) was found to be inappropriate due to the low permeation flux and the sensitivity limitations of the method.

Breakthrough times can be obtained from flux-versus-time plots obtained via the ASTM technique involving a more sensitive GC system. Figure 1 reveals that DCM has the shortest breakthrough time, followed by TCE and benzene. This figure also illustrates the permeation behavior of equal weight mixtures of DCM, benzene, and TCE.

The diffusion coefficient has been calculated using the equation proposed by Rogers<sup>8</sup>:

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**Figure 1** Flux versus time of pure DCM; pure benzene and pure TCE; and mixture of DCM, benzene, and TCE through HD40 geomembranes at 303 K measured using an ASTM cell.

$$\ln(t^{1/2}F) = \ln \left[ 2c_1 \left( \frac{D_0}{\pi} \right)^{1/2} \right] - \frac{l^2}{4D_0t} \quad (1)$$

where  $l$  is the thickness of the membrane;  $c_1$  is the penetrant concentration at  $x = 0$ , i.e., at the upstream side of the membrane; and  $D_0$  is a constant limiting diffusion coefficient (zero concentration diffusion coefficient) as  $t \rightarrow 0$ . Equation (1) describes the initial part of the permeation profile.

Table I summarizes diffusion coefficients ( $D_0$ ) obtained using eq. (1) for different penetrants and penetrant mixtures. Breakthrough times are also indicated. In most cases, DCM exhibits the highest limiting diffusion coefficient, followed by TCE and benzene. This is consistent with the results obtained for the break-

through times; that is to say, the shorter the breakthrough time, the greater the diffusion coefficient. The data obtained for mixture transport differ from those obtained for pure component transport. For example, we note that at 303 K the breakthrough time of benzene is 405 min, whereas it becomes 310 min for mixture transport. Also, its diffusion coefficient  $D_0$  increases from  $0.98 \times 10^{-8} \text{ cm}^2/\text{s}$  to  $1.2 \times 10^{-8} \text{ cm}^2/\text{s}$ , as expected. The situation with respect to TCE is less straightforward and would require a more detailed thermodynamic analysis.<sup>3,9,10</sup> The diffusion coefficients reported here agree well with those found in the literature. For example: for benzene to diffuse in HDPE geomembranes, we obtained a value of  $0.46 \times 10^{-8} \text{ cm}^2/\text{s}$  from a permeation test at 298 K, compared with a value of  $0.49 \times 10^{-8} \text{ cm}^2/\text{s}$  obtained by Ramsey<sup>1</sup> via a sorption test at room temperature.

The zero-concentration diffusion coefficient,  $D_0$ , as listed in Table I, increases with increasing temperature, which results in a shorter breakthrough time. Both the breakthrough time,  $t_b$ , and  $D_0$  obey Arrhenius-type relations:

$$D_0 = A_D e^{(-E_D/RT)} \quad (2a)$$

$$t_b = A_b e^{(E_b/RT)} \quad (2b)$$

$A_D$  and  $A_b$  are pre-exponential factors for diffusion and breakthrough, and  $E_D$  and  $E_b$  are the activation energies for diffusion and breakthrough, respectively.

For pure penetrant transport, the activation energy obtained via  $D_0$  differs from that obtained via  $t_b$  and we observed  $E_D$  to be larger than  $E_b$ . For example: for benzene we obtained  $E_D = 77.3 \text{ kJ/mol}$  and  $E_b = 66.2 \text{ kJ/mol}$ . As expected, both energies are of the same order of magnitude.  $E_D$  represents the energy required to open a hole (in the Eyring sense) in the polymer matrix in order to accommodate diffusing molecules.

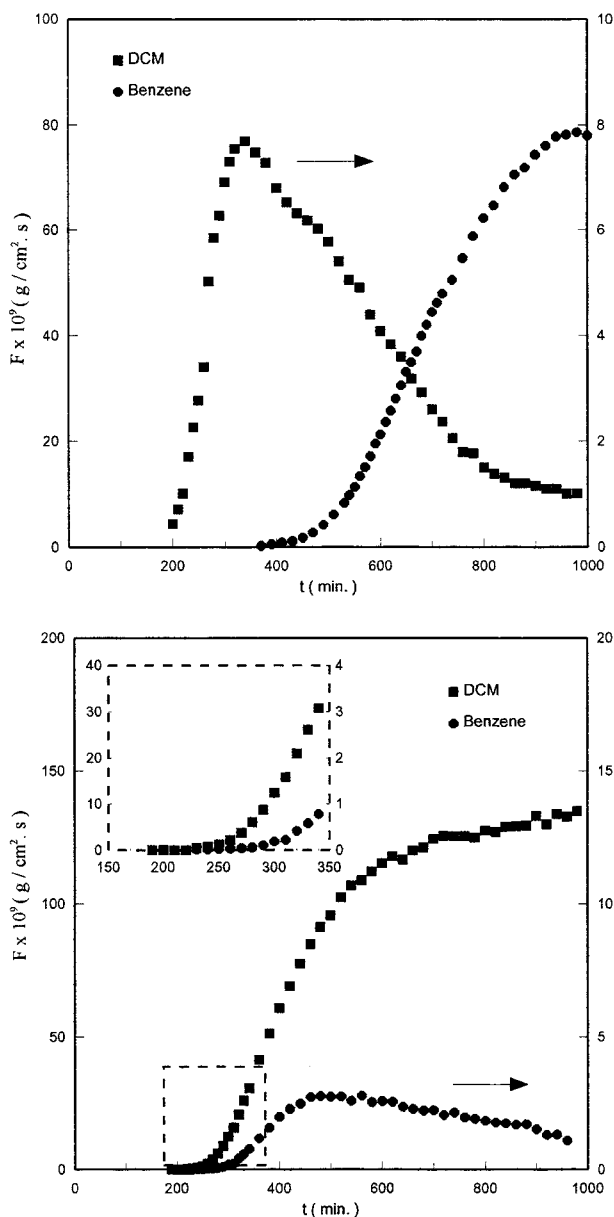
Equation (2a) can be considered a simplified version of the more general eq. (4) in Duda and coworkers.<sup>11</sup> This latter equation involves the interaction parameter  $\chi$ , in such a way that larger values of  $\chi$  are associated with low values of  $D_0$ . The value of  $\chi$  at 298 K for

**Table I** Diffusion Coefficients and Breakthrough Times of Organic Liquids in HD40 Geomembranes

Temperature (K)	Diffusion Coefficient $D_0 \times 10^8 \text{ (cm}^2/\text{s)}$ and Breakthrough Time <sup>a</sup> $t_b \text{ (min)}$					
	Pure Penetrant			Mixture of Penetrants <sup>b</sup>		
	DCM	TCE	Benzene	DCM	TCE	Benzene
293	0.73 (610)	0.51 (485)	0.32 (910)	1.2 (580)	0.53 (790)	0.53 (770)
298	1.6 (330)	0.81 (350)	0.46 (580)	1.7 (340)	0.88 (460)	0.89 (450)
303	2.7 (200)	1.2 (260)	0.98 (405)	3.0 (210)	1.6 (300)	1.2 (310)
308	4.2 (160)	1.5 (175)	1.6 (220)	4.1 (160)	1.8 (215)	1.7 (200)
313	6.5 (120)	2.5 (120)	2.1 (165)	6.0 (110)	3.2 (145)	3.0 (125)

<sup>a</sup> Numbers in parentheses refer to the breakthrough times.

<sup>b</sup> Permeation of a penetrant mixture ( $\frac{1}{3}$  DCM,  $\frac{1}{3}$  benzene and  $\frac{1}{3}$  TCE by weight).



**Figure 2** (A) Benzene permeation through a DCM-contaminated HD40 geomembrane at 303 K measured using an ASTM cell. The contamination time was 120 min; that is to say: the breakthrough time for benzene is 270 min. (B) DCM permeation through a benzene-contaminated HD40 geomembrane at 303 K measured using an ASTM cell. The contamination time was 120 min; that is to say: the breakthrough time for DCM is 110 min.

benzene is 0.8; this is the largest  $\chi$  value pertaining to this study and it is associated with the lower value for  $D_0$  (see Table I).

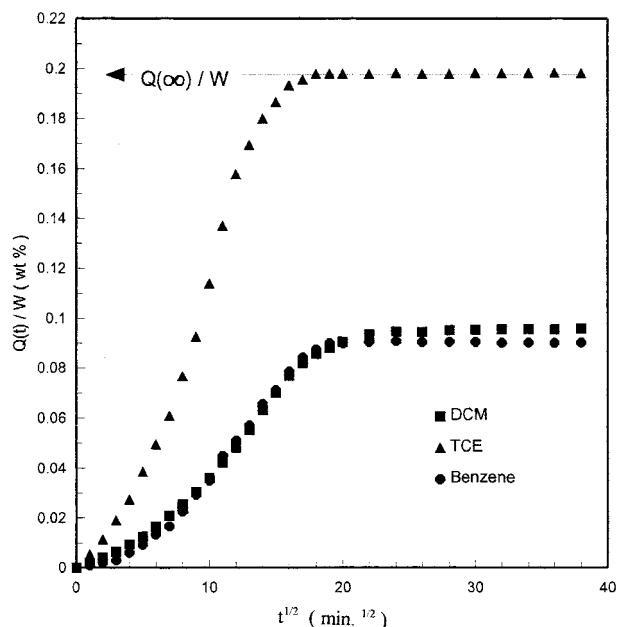
**Contamination** Figure 2 represents the permeation profiles for benzene through a DCM-contaminated HDPE membrane (A) and for DCM through a benzene-con-

taminated HDPE membrane (B). After DCM contamination, the breakthrough time for benzene was reduced by approximately 120 min. In the case of benzene contamination, benzene elutes with DCM, and the breakthrough time for both chemicals is reduced and is now 260 min for benzene and 110 min for DCM.

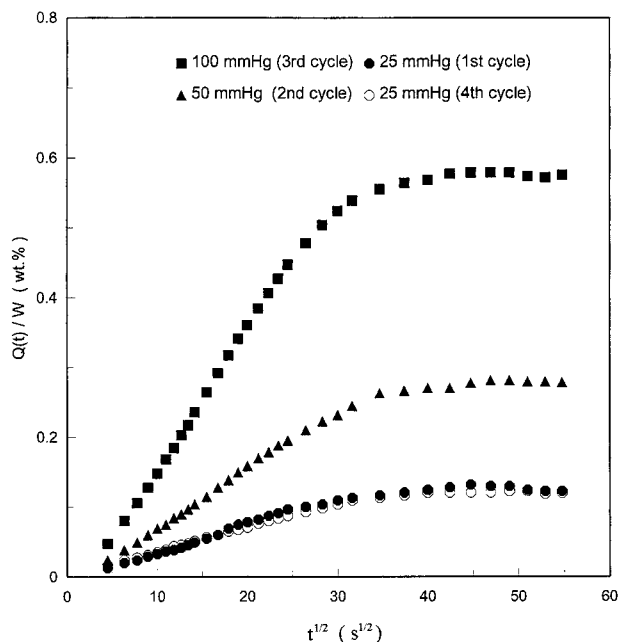
As expected, the obtained values for  $D_0$  are superior to those obtained via tests which did not involve membrane pretreatment (contamination). For example: the values for  $D_0$  are now  $1.6 \times 10^{-8} \text{ cm}^2/\text{s}$  for benzene and  $4.8 \times 10^{-8} \text{ cm}^2/\text{s}$  for DCM in the benzene-contaminated test.

**Sorption Mechanism** In contrast to PVC geomembranes, HDPE geomembranes do not experience significant swelling (less than 2%) during either liquid or vapor sorption. The results of the sorption experiments are presented as the wt % uptake ( $Q(t)/W$ ) of the penetrant by 100 g of the membrane as a function of the square root of time, where  $W$  is the weight of the dry membrane. Figures 3 and 4 illustrate the sorption of different liquids and the vapor sorption of DCM at different pressures, respectively, onto HDPE geomembranes at 303 K.

In the vapor sorption tests, a single membrane sample was used for all sorption and desorption cycles shown in Figure 4, eliminating errors which may be due to membrane non-uniformity; that is to say, the degassed specimen was first exposed to 25 mmHg DCM vapor for a sorption test. Once the weight change was less than  $10^{-6}$  g in a 50-min interval, desorption was initiated to eventually complete the cycle. A second cycle, this time at 50 mmHg, was then initiated. A total



**Figure 3** Liquid sorption of DCM, TCE, and benzene in HDPE at 303 K.



**Figure 4** Vapor sorption of DCM in HDPE at 303 K, measured using a Cahn balance.

of four cycles are illustrated in Figure 4. The tests revealed the sorption/desorption process to be reversible. Also, DCM does not seem to introduce any structural modification in the HDPE membrane. This is different from the case of a PVC membrane.<sup>4</sup>

In general, the mechanism of sorption in polymeric membranes can be assessed according to the following equation<sup>12</sup>:

$$\ln \frac{Q(t)}{Q(\infty)} = \ln k + n \ln t \quad (3)$$

where  $Q(t)$  and  $Q(\infty)$  are the sorbed amounts at time  $t$  and at  $t \rightarrow \infty$ . The constant  $k$  is associated with the interaction between the membrane and the penetrant. The value of  $n$  indicates the transport mechanism. In case I (Fickian) transport, the penetrant front advances at a rate proportional to  $t^{1/2}$  ( $n = 1/2$ ). All other cases are non-Fickian. In particular, case II transport is defined as a transport mechanism for which the front is advancing at a rate proportional to  $t$ . Membrane swelling can be observed and the stress field in the sample is significantly altered.

The estimated values of  $n$  and  $k$  from eq. (3) for the DCM systems shown in Figures 3 and 4 are  $n \approx 0.6$  and  $k \approx 12 \times 10^{-4}$  for vapor contact and  $n = 0.76$  and  $k = 5.13 \times 10^{-4}$  for liquid contact.

For DCM vapor sorption at different pressures, the wt % uptake of DCM at  $t \rightarrow \infty$  increases linearly with

increasing pressure and  $0.5 < n < 1$ . The value of  $n$  approaches 0.5 with decreasing vapor pressure. Hopfenberg<sup>13</sup> also noted that there was a change in mechanism from Case II toward Fickian transport with decreasing vapor pressure. One would also expect liquid sorption to be associated with non-Fickian behavior. The  $Q(t)$ -versus-time behavior will be a function of the geometry and the molecular weight of the molecules. In fact, Figure 3 illustrates the expected behavior for the higher-molecular-weight TCE. Note that DCM and benzene have similar molecular weights.

As observed in the case of PVC geomembranes,<sup>4</sup> the desorption curves follow a similar pattern independent of the contaminant sorption history, suggesting a unique desorption mechanism. As for the case of Figure 3b in Xiao and colleagues,<sup>4</sup> the desorption curve contains three different regions and can be analyzed following Stastna and associates<sup>14</sup> in terms of a continuous random walk diffusion model, resulting in a master curve (as in Figure 3c of Xiao and coworkers<sup>4</sup>).

## REFERENCES

1. D. R. Ramsey, *Proceedings of Geosynthetics '93*, Vancouver, 645 (1993).
2. G. O. Nelson, B. Y. Lum, G. J. Carlson, C. M. Wong, and J. S. Johnson, *Am. Ind. Hyg. Assoc. J.*, **42**, 217 (1981).
3. R. L. Mickelsen, M. M. Roder, and S. P. Berardinelli, *Am. Ind. Hyg. Assoc. J.*, **47**, 236 (1986).
4. S. Xiao, C. Moresoli, J. Bovenkamp, and D. De Kee, *J. Appl. Polym. Sci.*, to appear.
5. R. W. Gallant and C. L. Yaws, *Physical Properties of Hydrocarbons*, 2nd ed., Gulf Publishing Co., Houston, TX, 1992.
6. A. F. M. Barton, *CRC Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters*, CRC Press, Inc., Boca Raton, FL, 1990.
7. G. Unnikrishnan and S. Thomas, *J. Appl. Polym. Sci.*, **60**, 963 (1996).
8. C. E. Rogers, in *Engineering Design for Plastics*, E. Baer and E. Robert, Eds., Krieger Publishing Co. Inc., New York, 1975, p. 609.
9. D. G. Miller, V. Vitagliano, and R. Sartorio, *J. Phys. Chem.*, **90**, 1509 (1986).
10. X. Feng and R. Y. M. Huang, *Separation Science and Technology*, **27**, 2109 (1992).
11. J. C. Duda, J. S. Vrentas, S. T. Ju, and H. T. Liu, *AIChE J.*, **28**, 279 (1982).
12. J. S. Chiou and D. R. Paul, *Polym. Eng. Sci.*, **26**, 1218 (1986).
13. H. B. Hopfenberg, in *Membrane Science and Technology*, J. E. Flinn, Ed., Plenum Press, New York, 1970, p. 16.
14. J. Stastna, D. De Kee, and B. Harrison, *Chem. Eng. Comm.*, **105**, 43 (1991).