

# Absorption of Benzene by Open-Cell Polyurethane Foams

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## Synopsis

The rate of absorption of benzene by open-cell polyurethane foams of varying pore size (30–85 pores per inch) has been shown to be dependent on the size of the foam samples. Mass transport from the bulk vapor to the matrix surface appears to be a significant resistance when compared with the rate of diffusion in the matrix itself. Even though these foams have a large permeability to air at low pressures, pore diffusion appears to be more significant than bulk flow in describing the absorption process, resulting in absorption behavior which is more characteristic of closed-cell foams. A dual resistance model of the absorption process has been used to estimate matrix diffusivities and pore mass transfer coefficients. Although the model was inadequate in some regards to describe completely the absorption process, the significance of the unexpected pore diffusion resistance to mass transfer was quantified. The dependence of pore diffusion on foam size reflected the qualitative interpretation that was apparent from the absorption curves. While the reason for this anomalous behavior remains unknown, open-cell foams cannot be considered simply as a high-surface-area thin-walled form of the matrix material in describing the absorption process; the effect of foam size must also be considered.

## INTRODUCTION

The diffusion of gases and water vapor in closed-cell foams<sup>1–6</sup> and the transport of water and air across certain open-cell materials have been subject to detailed study.<sup>7–10</sup> While the former is important to the blowing process in certain foam systems<sup>1–4</sup> and the insulation properties of the foam,<sup>5,6</sup> the latter is the basis of some commercial membrane filters.<sup>7–10</sup> The diffusion of organic vapors in open-cell foams, particularly the absorption process in open-cell polyurethane foams, however, has not been investigated. It was the purpose of this study to confirm the suggestion that an open-cell foam represents a high-surface-area thin-walled form of the matrix material and the effects of pore size and bulk dimensions should be negligible on the absorption rate. As it turned out, the situation was more complex, necessitating a more detailed investigation of the effect of foam structure on absorption.

## THEORETICAL

### Model of Foam Absorption

The open-cell foams under study were assumed to consist of cylindrical struts of approximately constant diameter in almost hexagonal array [(Fig. 1(a)]. (In fact, the struts were more cone-shaped.) The length of the strut was related to the pore size, and the number of struts was determined by the porosity of the foam.

In order to interpret the results of the absorption experiments, it was assumed that the foam matrix could be modeled as a single cylindrical strut, of diameter equal to the average measured strut diameter of the foam (and total surface area equivalent to the matrix surface area). The resistance to mass transfer offered by the pores was incorporated into a single vapor-phase mass transfer coefficient  $h$ , defined by

$$N = h(P_{f,b} - P_{f,s}) \quad (1)$$

where  $N$  is the molar flux of organic vapor to the polymer surface and  $P_{f,s}$  is the vapor pressure at the surface, which, in general, is not equal to the bulk vapor pressure  $P_{f,b}$ . The assumed concentration profile is illustrated in Figure 1(b).

With the assumption of instantaneous equilibrium at the strut surface, instantaneous establishment of the vapor-phase concentration profile and a constant matrix diffusivity  $D_m$ , the absorption process in the model strut is described by<sup>11</sup>

$$\frac{M_t}{M_\infty} = \frac{2LD_m t}{a^2} - \frac{8L^2}{3\pi^{1/2}} \left(\frac{D_m t}{a^2}\right)^{3/2} - L^2 \left(\frac{D_m t}{a^2}\right)^2 (1/2 - L) \quad (2)$$

where  $L = ah/KD_m$ ,  $M_t$  = mass uptake at time  $t$ ,  $M_\infty$  = equilibrium mass uptake at  $t = \infty$ ,  $K$  = distribution constant between vapor and solid, and  $a$  = radius of strut.

The mass transfer coefficient was, in turn, related to foam structure depending on the assumed mechanism of vapor-phase mass transfer. If bulk flow was assumed to be the dominant mode of mass transfer, Darcy's law was used; if diffusion was assumed, Fick's law was used. A correction was made for the relative areas of matrix, pore space, and bulk foam, since  $h$  was defined per unit area of matrix. Thus, for bulk flow,

$$h_B = \frac{K_P \bar{P}_f S_b}{\mu R T (1 - \epsilon) S_m \delta} \quad (3)$$

and for diffusion,

$$h_D = \frac{\mathcal{D} \epsilon S_b}{R T (1 - \epsilon) S_m \delta} \quad (4)$$

where  $S_b$  = the specific surface area of the bulk foam,  $S_m$  = specific surface area of matrix =  $4/d_s$ ,  $d_s$  = strut diameter =  $2a$ ,  $\epsilon$  = porosity,  $T$  = temperature,  $R$  = gas constant,  $P_f$  = average pressure in vapor phase,  $\mathcal{D}$  = self-diffusivity of organic vapor at  $T$ , and  $K_P$  = Darcian permeability of foam;  $\delta$  is the thickness of the fictive layer which offers the same resistance to mass transfer as the real pore vapor phase according to the film theory of mass transfer. The presence of cylindrical geometry (Fig. 1) is incorporated into the film thickness  $\delta$ . The factors  $S_b/(1 - \epsilon)S_m$  in eq. (3) and  $\epsilon S_b/(1 - \epsilon)S_m$  in eq. (4) correct for the bulk/matrix area and the pore/matrix area ratios, respectively.

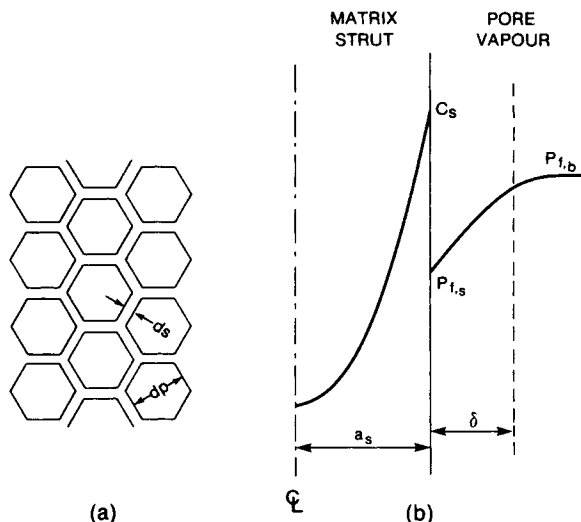


Fig. 1. (a) Model of foam matrix showing cylindrical struts in a hexagonal array. (b) Concentration profiles in model of foam absorption. Equilibrium is assumed at the matrix/pore interface.  $\delta$  defines a hypothetical film which offers the same resistance to mass transfer as the pores.

## MATERIALS AND METHODS

### Foams

Scott industrial polyurethane foam (Foamade Industries Ltd., Toronto) of three pore sizes was investigated. The relevant properties of the foams are listed in Table I. The degree of similarity among matrix chemical structures was unknown. The pore size and strut diameter were checked microscopically. Matrix densities were measured with a pycnometer. The permeability of the foams to air at low pressure gradients was determined by measuring the pressure drop ( $\Delta P$ ) across the foam, squeezed inside a tube, as a function of air flow rate  $Q$ .

TABLE I  
Properties of Polyurethane Foams

	30 ppi <sup>a</sup>	60 ppi	85 ppi
Bulk density, g/cm <sup>3</sup>	0.0226	0.0244	0.0301
Matrix density, g/cm <sup>3</sup>	1.13	1.34	1.24
Porosity $\epsilon$	0.980	0.982	0.976
Pore diameter $d_p$ , cm	0.085	0.042	0.030
Strut diameter $d_s$ , cm	$14 \times 10^{-3}$	$7 \times 10^{-3}$	$5 \times 10^{-3}$
Specific surface area of matrix $S_m$ , cm <sup>-1</sup> <sup>b</sup>	$2.9 \times 10^2$	$6 \times 10^2$	$8 \times 10^2$
Air permeability $K_p$ , cm <sup>2</sup> <sup>c</sup>	$7 \times 10^{-5}$	$2 \times 10^{-5}$	$2 \times 10^{-5}$
Average equilibrium uptake (25°C, 95 mm Hg), g benzene/g matrix	0.423	0.306	0.315
Benzene distribution constant $K$ , mole/cm <sup>3</sup> matrix/mm Hg vapor	$7.6 \times 10^{-5}$	$5.4 \times 10^{-5}$	$5.3 \times 10^{-5}$

<sup>a</sup> ppi = Pores per inch; pore diameter (in.) = 1/ppi.

<sup>b</sup>  $S_m = 4/d_s$ .

<sup>c</sup> Foam diameter = 0.63 cm; tube diameter = 0.48 cm; pressure gradient range = 100–1000 dyn/cm<sup>3</sup>.

Darcy's law ( $Q/A = -K_P \Delta P/\mu L$ ;  $L$  = length,  $A$  = area,  $\mu$  = air viscosity) was assumed to calculate the Darcian permeability  $K_P$ . The foams were subject to lateral compression during these measurements (strain = 0.24). The benzene distribution constant was calculated from the average equilibrium uptake determined below, according to eq. (3).

Cylindrical rods of the foams were cut from slabs, frozen with liquid nitrogen, with cork borers mounted in a drill press. Rectangular blocks of the 60-ppi (pores per inch) foam for sorption experiments were cut using scissors. Different sizes of foam slabs necessitated the use of different shapes of foam samples.

Two other predominantly open-cell foams were also investigated. An SBR rubber foam and a 20% nitrile rubber foam (Polysar Ltd. Sarnia, Ontario) were used as cylindrical rods for absorption measurements. Although no detailed characterizations were undertaken, the pore structure of both foams was very irregular and the average pore diameter was much less than that of the 85-ppi polyurethane.

### Sorption Measurements

The rates of absorption and desorption of benzene in these foams were measured at 25°C as a function of the foam sample dimensions. A saturated benzene atmosphere ( $P_{f,b} = 95$  mm Hg) was used for all experiments. The initial condition for the absorption experiments was a vacuum ( $P_f = 0$  mm Hg) which was maintained for at least 2 hr before each experiment. A Cahn RG automatic electrobalance placed inside a sealed chamber and connected to a benzene reservoir was used to monitor continuously weight gain or loss by the sample. The benzene atmosphere was established within 1 to 1.5 sec. The balance, benzene reservoir, manometer, and valves were all enclosed in a temperature-controlled cabinet.

## RESULTS

Typical absorption curves ( $M_t/M_\infty$  vs.  $t^{1/2}$ ) for benzene in polyurethane foam are shown in Figure 2 for the 85-ppi foam. Foam size is represented by the inverse of the specific surface area of the bulk foam,  $(S_b)^{-1}$ , e.g., for a cylindrical rod of length  $L$  and diameter  $d$ ,  $S_b = 4/d + 2/L$ . After an initial slow absorption,  $M_t/M_\infty$  increased almost linearly with  $t^{1/2}$  until  $M_t/M_\infty \sim 0.5$ . (The time to establish the benzene atmosphere is only a small fraction of the initial lag period.) It is clear that since the curves do not coincide, there is an effect of foam size on the rate of absorption of benzene.

This effect of bulk foam dimensions on absorption is demonstrated further by using the slope of the linear region to calculate the apparent diffusivity in the matrix (Fig. 3) and the apparent bulk diffusivity (Fig. 4). The specific surface area of the matrix  $S_m$  (Table I) (a constant for all foams of the same pore size) and the bulk specific surface areas  $S_b$  were used, respectively, to convert the slope to a "diffusivity." For the two largest samples of the 85-ppi foam, the absence of any recognizable linear region required the use of a three-term equation for absorption in cylindrical samples.<sup>12</sup> The linear region slope avoids the effect of the initial slow absorption on the calculation of the apparent diffusivity.

The dual transport resistance model expressed by eq. (2) was used to describe

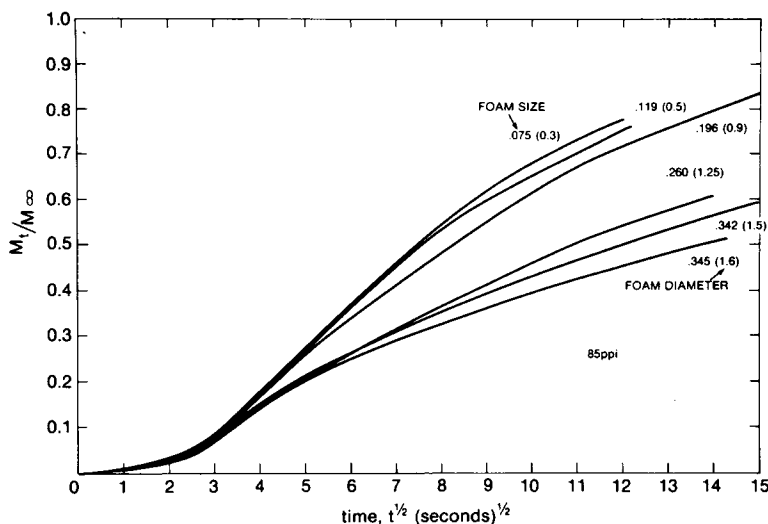


Fig. 2. Typical absorption curves for benzene in a polyurethane foam (85 ppi, 25°C, 95 mm Hg). Foam size (and foam diameter) in centimeters listed beside each curve.

the absorption process in these foams in more detail. Direct search-with-search-region contraction permitted determination of the best values of  $D_m$  and  $L$  that fit the experimental data by minimizing the sum of the squares of the deviations. Although the optimum value of the product of  $D_m$  and  $L$  (directly proportional to  $h$ , the pore phase mass transfer coefficient) could be determined readily, the best value of  $D_m$  was more difficult to isolate. The performance index minimum was not very sensitive to the value of  $D_m$ , introducing some concern about the significance of the optimum  $D_m$ .

The matrix diffusivity and the pore mass transfer coefficient, as calculated from the optimum product of  $D_m$  and  $L$ , eq. (2), are plotted in Figures 5 and 6 as functions of foam size ( $S_b$ )<sup>-1</sup>.

## DISCUSSION

### Apparent Diffusivity

Figure 2 clearly shows that the suggestion that an open-cell foam represents merely a high-surface-area thin-walled form of the matrix is unsuitable to completely describe the absorption process. If the complete matrix surface had been exposed to a uniform benzene pressure, regardless of the particular location of the cell, all the sorption curves should have been coincident.

The presence of a second transport process is apparent in Figures 3 and 4. This second transport process is significant, even for the largest pore-size foam (30 ppi), causing a sevenfold change in apparent diffusivity over the range of sample size investigated. The effect of sample size appears similar for both 30- and 85-ppi foams; the different curve shapes for the 60-ppi foam may reflect the fact that these samples were rectangular blocks and eq. (1), with the inherent assumption of unidirectional diffusion, may be invalid.

The most logical source of this second transport process is the network of pores through which the benzene vapor must be transported to reach the matrix sur-

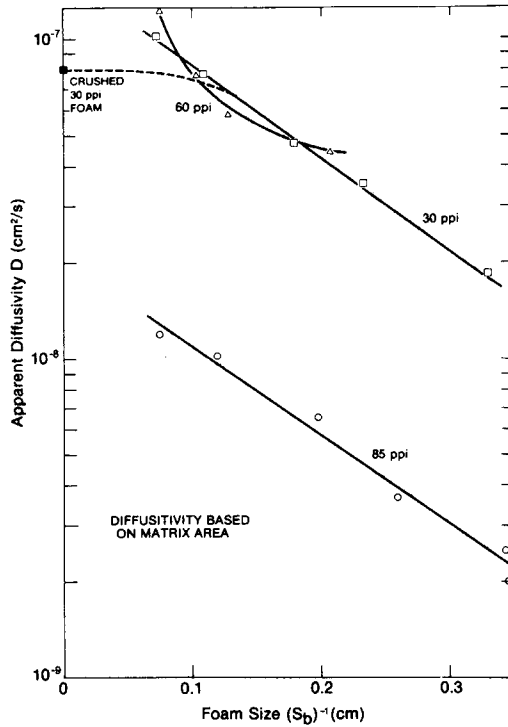


Fig. 3. Effect of foam size on the apparent diffusivity of benzene based on the matrix specific surface area  $S_m$ . Foam size is taken to be the inverse of the specific surface area of the bulk foam  $(S_b)^{-1}$  or the foam volume/area ratio. The diffusivity of benzene in a crushed sample of the 30-ppi foam is shown for comparison.

face. On this basis it is easy to understand that the apparent matrix diffusivity (Fig. 3) should increase as the bulk dimensions of the foam are reduced (reducing the transport resistance associated with the porous network) and should approach the matrix diffusivity as the sample dimensions are reduced to zero. The matrix diffusivity of the 30-ppi foam was estimated by determining the rate of absorption of a ground sample of the foam and assuming the specific surface area of the 30-ppi matrix. This value has also been plotted on Figure 3, suggesting the curve of apparent matrix diffusivity against sample dimensions should level off at a sufficiently low-bulk specific surface area at which pore transport resistance has become negligible.

It appears that for both the 30-ppi and 85-ppi foams the bulk diffusivity (Fig. 4) increased with increasing sample size and then leveled off with sufficiently large samples. Similar behavior was observed for the latex foams, which on this scale and for the particular size range studied had a small dependence of apparent diffusivity on sample size. This is akin to the behavior that is expected of closed-cell foams where bulk flow is negligible compared to pore diffusion.<sup>1</sup> The closed-cell foam may be considered to be homogeneous for diffusion calculations, and a transport parameter, based on the bulk surface area  $D_b$ , may be defined to characterize the diffusion process. Similarly, large samples of open-cell foams may also be considered homogeneous in this context. However, it is in the intermediate size range (volume/area ratios of 0.1 to 0.3) where the combined effect

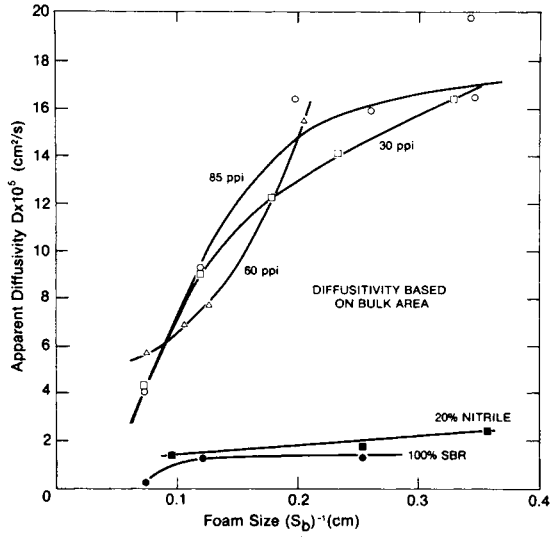


Fig. 4. Effect of foam size on the apparent diffusivity of benzene based on the bulk specific surface area  $S_b$ . The diffusivity of benzene in two latex foams is shown for comparison.

of the two transport processes—matrix diffusion and pore transport—must be considered.

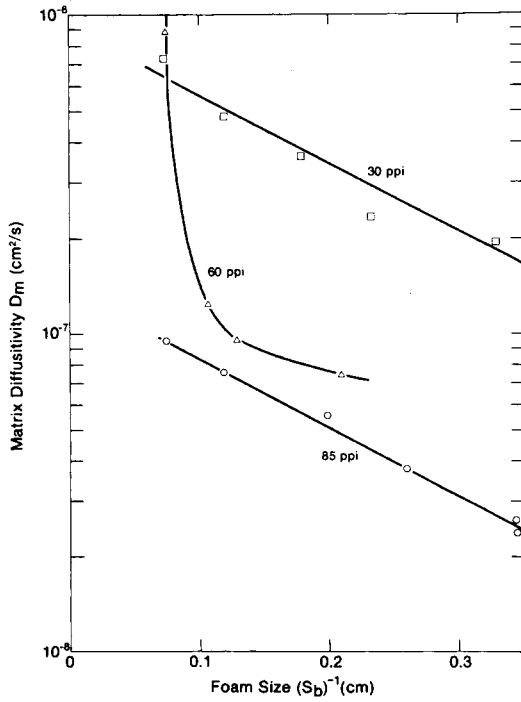


Fig. 5. The matrix diffusivity as function of pore diameter and foam size. The matrix diffusivity was estimated from eq. (2).

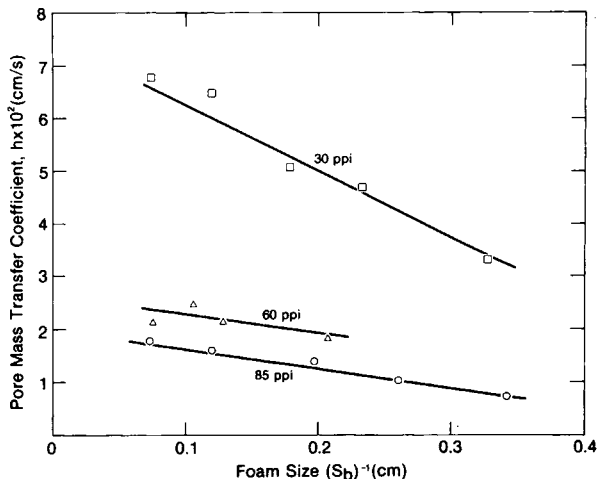


Fig. 6. Pore phase mass transfer coefficient from eq. (2) as a function of pore diameter and foam size.

### Estimation of Mass Transfer Coefficients

It is clear from Figure 5 that the implied model is inadequate to describe the absorption process. Instead of being independent of foam size, the matrix diffusivity decreased exponentially with increasing foam size, exhibiting the same behavior as in Figure 3. (Despite the insensitivity of the performance index minimum to  $D_m$ , the semilogarithmic relationship between  $D_m$  and foam size clearly indicates the statistical significance of the calculated  $D_m$ .) Again the 60-ppi foam is different from the others; however, in Figure 5 it appears that much of this difference could be eliminated if the results for the smallest sample are ignored.

While the mass transfer coefficients (Fig. 6) decrease with increasing foam size as expected, the actual inverse dependence with increasing foam size predicted by eq. (3) or (4) is not apparent. This is further confirmation of the inadequacy of the proposed model.

The experimentally determined values of pore-mass transfer coefficients agree reasonably well with the order of magnitudes of the steady-state resistances for pore diffusion listed in Table II, suggesting that pore diffusion rather than bulk flow is important in the absorption process.

According to these steady-state resistances, the effect of pore transport should be negligible and there should be no effect of bulk foam dimensions on the apparent diffusivity. Inspection of Table II shows that bulk flow should be much more rapid than pore diffusion (parallel resistances), while matrix diffusion is much slower than bulk flow (series resistances). Hence, matrix diffusion should be the limiting transport resistance. However, on the basis of the experimental results, it is suggested that pore diffusion is more important than bulk flow in foams, giving rise to absorption behavior which is more characteristic of closed-cell foams than of highly permeable open-cell materials.

Assuming that diffusion is the dominant pore transport process, eq. (4) can be used to estimate the fictive vapor film thickness  $\delta$  over which the pore pressure difference is assumed to exist according to the film theory of mass transfer (Fig. 7). The fictive film thickness is comparable to the size  $(S_b)^{-1}$  of the foam sample.



TABLE II  
Steady-State Resistances for Transport in Foams (25°C, 95 mm Hg)<sup>a</sup>

Pore size	Matrix diffusion <sup>b</sup>	Pore diffusion <sup>c</sup>	Pore bulk flow <sup>d</sup>
30 ppi	$2 \times 10^9$	$5 \times 10^8$	$9 \times 10^2$
60 ppi	$1 \times 10^9$	$9 \times 10^8$	$6 \times 10^3$
85 ppi	$8 \times 10^8$	$2 \times 10^9$	$1 \times 10^4$

<sup>a</sup> Order of magnitude analysis (mole benzene/cm<sup>2</sup> matrix area sec mm Hg vapor phase pressure difference)<sup>-1</sup>. Resistance =  $\Delta P/N = (\text{mass transfer coefficient})^{-1}$ . Resistances based on steady-state transport across a plane film of thickness equal to strut diameter  $d_s$  or bulk foam thickness  $l = 1$  cm. Correction is made for bulk/matrix area and pore/matrix area ratios and for the benzene distribution constant between vapor and matrix. Benzene viscosity =  $73 \mu\text{p}^{13}$ ; benzene self-diffusivity =  $0.240 \text{ cm}^2/\text{sec}^{14}$ ; average pressure =  $1.263 \times 10^5 \text{ dyn/cm}^2$ ; matrix diffusivity, assumed to be  $10^{-7} \text{ cm}^2/\text{sec}^{15-19}$

<sup>b</sup> From Fick's law.

<sup>c</sup> From eq. (4).

<sup>d</sup> From eq. (3).

Furthermore, for small samples it increases linearly with increasing  $(S_b)^{-1}$ , with a slope approximately unity. For the cylindrical samples, therefore,  $\delta$  is comparable to half the radius of the foam. For the larger samples [ $(S_b)^{-1} > 0.2$ ], however,  $\delta$  levels off, becoming independent of foam dimensions. This is the same behavior that was exhibited by the apparent bulk diffusivity in Figure 4. Pore transport is dominating the absorption process, and the absorption process

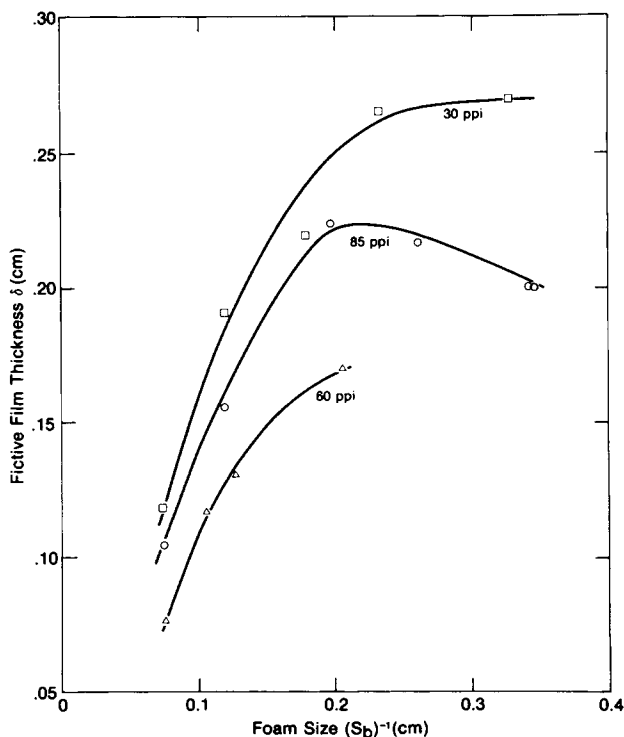


Fig. 7. Fictive film thickness  $\delta$ , as defined by eq. (4), as function of pore diameter and foam size. Diffusion was assumed to be the dominant mode of mass transfer in the pores.

can be characterized by a single transport parameter reflecting the foam size independence of both matrix diffusion and pore diffusion.

The model of diffusion in an open-cell foam that has been used here to estimate both the matrix diffusivity and the pore mass transfer coefficient is strictly valid only in the limit where the matrix diffusion process is the rate-controlling step ( $L \gg 1$ ). The model assumed a constant mass transfer coefficient throughout the absorption process, i.e., over the complete matrix surface. No account was taken of the distribution of the matrix surface through the foam, with some surface a further distance away from the bulk vapor than the matrix surface near the periphery of the foam. As a result, the matrix that is near the periphery would be exposed to a relatively higher pressure of benzene than that in the interior, with a consequently higher bulk-to-surface rate of mass transfer than in the interior. In the model, the rate of mass transfer is assumed equal for all the matrix surface, averaging out the effect of nonuniform matrix surface distribution. That this averaging process is inadequate is clear from the inconsistencies in Figures 5, 6, and 7.

### CONCLUSIONS

The absorption of benzene by open-cell polyurethane foams is not as simple as expected. Transport of benzene through the pores and to the matrix surface offers significant resistance to mass transfer even in the most porous (30 ppi) foam. In fact, despite the open-cell network, the absorption process is similar to that in closed cell foams, with both pore diffusion (rather than bulk flow) and matrix diffusion important in determining the rate of absorption.

Absorption of benzene by a foam, initially at equilibrium in a vacuum and containing no benzene, appears controlled by two transport processes. The benzene diffuses to the matrix surface through the open-cell network, causing the pressure in the pores to rise to the bulk vapor pressure. In series with this pore diffusion, the organic vapor is absorbed by the foam matrix, diffusing into the interior of the matrix strut until equilibrium is attained. The higher internal surface area of the matrix and the relatively large distribution constant render the resistances to pore diffusion and matrix diffusion comparable. However, the reason for diffusion rather than bulk flow being more significant in pore transport is unclear. Further experimentation will be required for the elucidation of this anomaly.

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