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The Permeability of Saranex Film to Flame-Retardant Vapors

INTRODUCTION

The permeabilities of the flame-retardant vapors, BrCHClF and $BrCF_3$, and of the atmospheric gases, N_2 and O_2, diffusing through Saranex film have been measured for a number of temperatures in the range 25° to 100°C. The data are used to estimate the rate of loss of the flame-retardant vapors from rigid Saranex containers.

The construction of gas containers from low-permeability plastic films offers the possibility of long-term storage coupled with the capability of rapid release of the gas upon rupture of the film by mechanical or thermal means. In this investigation the permeability of Saranex film to the flame-retardants BrCHClF and $BrCF_3$ is measured; and the long-term storage performance of rigid thin-film containers constructed from this material and operating under ideal conditions is evaluated. The containers are considered to have some form of mechanical backing so that they may withstand differences between internal and external pressures and are treated as rigid.

EXPERIMENTAL

Saranex film (Dow Chemical Co., U.K.) is a laminate of the type polyethylene: poly(vinylidene chloride–co-vinyl chloride): polyethylene, with layer thicknesses in the ratio 1:2:1 and of average thickness 5.1×10^{-3} cm. The central layer, which is protected by the outer layers of polyethylene, is equivalent to Saran film and provides the high-barrier properties. The occurrence of pinholes is also reduced by the laminated structure of the film.

The gases, O_2 and N_2 (British Oxygen Co., U.K.), were supplied spectrally pure and were used directly. The flame-retardants BrCHClF and $BrCF_3$ were supplied by I.S.C. Chemicals Co. and were subjected to freeze–thaw procedures to remove permanent gases. Traces of water vapor were removed by passing the retardants through a bed of activated S10 zeolite (Bayer AG) at room temperature.

Permeabilities were measured by using conventional techniques in which the pressure on the upstream face of the membrane was held constant, while that on the downstream face was recorded as a function of time by means of a McLeod gauge.[1] The boiling points of BrCHClF and $BrCF_3$ are, respectively, 36° and −58°C. McLeod gauge pressures in compression were less than 15 cmHg, and condensation of the vapor was not a problem; also, departures from the ideal gas laws in this region were not sufficiently large to warrant corrections.

The permeability of Saranex film to gases is low, and it was necessary to use films of large cross-sectional area to obtain reasonably accurate flow rates. The diffusion cell was constructed from two large glass flanges, in one of which was placed the support for the membrane. This consisted of a perforated zinc disk, 0.05 cm thick and 10.2 cm in diameter, with 14 holes per cm^2, each 0.2 cm in diameter. The disk was supported in the glass cell by a set of ¼-in. aluminum rods. A filter paper was placed between the film and the zinc disk, and the glass flanges were sealed together with Araldite epoxy resin. The temperature of the diffusion cell was controlled to within ±0.2°C with an air thermostat.

RESULTS

Permeabilities

The permeability $\bar{P}$[cc S.T.P. cm/cm^2 sec (cmHg)] was independent of pressure for all of the penetrants in the range 0–30 cmHg. The results are given in Figure 1 and for all gases are well represented by the relation

$$\bar{P} = \bar{P}_0 \exp\{-E_p/RT\}.$$

The permeability of polyethelene to gases is several orders of magnitude greater than that for Saran,[2] so that the permeability of the laminate is largely controlled by that of the latter. Since the Saran layer accounts for half the thickness of the Saranex film, it follows that $\bar{P}$ for Saranex is twice that for Saran. By use of the Saranex results of Figure 1, values of $\bar{P}$ for O_2 and N_2 diffusing in Saran are estimated at 30°C and are 6.2×10^{-13} and 13×10^{-14}, respectively; this is in satisfactory agreement with the values of 5.3×10^{-13} and 9.4×10^{-14} previously reported for Saran.[2,3] The temperature coefficient E_p for BrCHClF, $BrCF_3$, O_2, and N_2 has the values 90, 65, 70, and 76 kJ/mole^{-1}, respectively. The value for oxygen compares favorably with a value of 66.5 kJ/mole^{-1} previously reported for O_2 diffusing in Saran.[3]

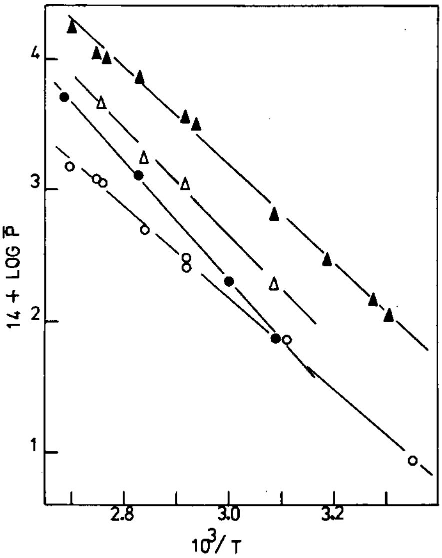

Fig. 1. Temperature–dependence of the permeability $\bar{P}$ [cc S.T.P. cm/cm^2 sec (cmHg)] for $BrCF_3$ (○); BrCHClF (●); N_2 (△); and O_2 (▲) in Saranex.

Time–Dependence of Penetrant Pressure in Saranex Containers

Consider a slab of thickness l, of area A, and with a finite volume V on the face $x = l$, and a constant pressure of penetrant on the face $x = 0$. Let p denote the penetrant pressure in V; p_0 its initial value which may be zero; and p_c the constant pressure which may be zero, on the face at $x = 0$. It is assumed that the solubility of the penetrant in the slab obeys Henry's Law and that the diffusion coefficient D of penetrant in the slab is constant. The initial concentration of penetrant in the slab is considered to be uniform. Solutions to this problem are available which give p as a function of time.[4,5,6] When Al/V is small, other geometries such as the hollow sphere reduce to the result for the slab.[6] When $p_0 > p_c$, and with zero initial concentration in the membrane, one obtains for the special case $p_c = 0$:

$$p/p_0 = \sum_{n=1}^{\infty} A_n \exp\{-DQ_n{}^2t/l^2\} \tag{1}$$

which describes the decay of pressure in the volume V. Also:

$$A_n = \frac{2\cos Q_n \sin Q_n}{Q_n + \cos Q_n \sin Q_n} = \frac{2H}{H + H^2 + Q_n{}^2} \tag{2}$$

and the Q_n are nonzero positive roots of

$$Q \tan Q = H \tag{3}$$

where

$H = KAl/V$. The partition coefficient K is the ratio of the penetrant concentration in the slab to that in the gas phase. When $p_0 < p_c$ and with an initial uniform concentration in the slab of σp_c where σ is the Henry's Law solubility constant, one obtains for $p_0 = 0$:

$$p/p_c = 1 - \sum_{n=1}^{\infty} A_n \exp\{-DQ_n{}^2t/l^2\} \tag{4}$$

which describes the increase in pressure in the volume V.

Equations (1) and (4) may be represented by the single equation

$$f(p) = \sum_{n=1}^{\infty} A_n \exp\{-DQ_n{}^2t/l^2\} \tag{5}$$

where $f(p) = p/p_0$ for pressure decay and $f(p) = 1 - p/p_c$ for a pressure increase in the volume V.

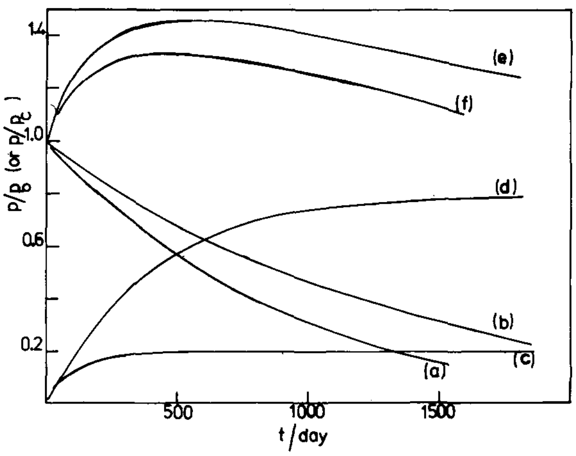

Fig. 2. The pressure ratios p/p_0 for $BrCF_3$ (a) and BrCHClF (b); and p/p_c for O_2 (c) and N_2 (d); and $\Sigma(p/p_0)$ with $p_0 = p_c$ for $O_2 + N_2 +$ BrCHClF (e) and $O_2 + N_2 + BrCF_3$ (f) as a function of time at 30°C for a rigid cubic Saranex container with $V = 1$ cm^3 and $l = 0.0051$ cm.

For large enough t the first term in the summation dominates, irrespective of the value of H. However, systems with small H approach the large t-limit more quickly than systems with large H. Equation (5) now becomes

$$f(p) = A_1 \exp\{-DQ_1{}^2t/l^2\}. \tag{6}$$

Further, from eq. (3), when H is sufficiently small, $\tan Q_1 \simeq Q_1$ and $Q_1{}^2 \simeq H$; so that from eq. (2):

$$A_1 \simeq 2/(2 + H).$$

When $H \ll 2$, then A_1 tends to unity and

$$f(p) = \exp\{-DHt/l^2\}. \tag{7}$$

Introducing the Henry's Law solubility constant σ in place of the partition coefficient K, one obtains

$$H = \sigma ATlp_s/VT_s$$

where T_s and P_s are the standard temperature and pressure, respectively. With $\bar{P} = D\sigma$, eq. (7) can be written as

$$f(p) = \exp\{-\bar{P}ATp_st/VT_sl\}. \tag{8}$$

Provided H is sufficiently small, the long-term behavior of the function $f(p)$ may be estimated from a knowledge of $\bar{P}$ only. For larger H values, eq. (6) may be used, but requires a knowledge of both D and σ. Finally, for small times, additional terms in the summation of eq. (5) are required.

We have used eq. (8) to estimate the long-term behavior of the flame-retardant vapors BrCHClF and $BrCF_3$ in rigid box-type containers constructed from Saranex film by means of the permeability data of Figure 1. The effect of edges and corners is considered to be negligible; and with the approximations inherent in eq. (8), the pressure of vapor in a unit cube relative to the initial pressure p_0 has been evaluated as a function of time. The results are shown in Figure 2 and represent ideal behavior in that all practical problems associated with seals in such containers are neglected and, further, a constant D as implied in eq. (1) is assumed throughout. It is anticipated that plasticization effects will become more significant the closer p_0 approaches to the saturation vapor pressure of the flame-retardant liquid and that, for a given temperature and p_0, they will be more pronounced for the higher-boiling-point liquid, BrCHClF.

TABLE I
Half-life, $t_{1/2}$ (day), for Penetrants in Rigid Cubic Saranex Containers (l = 0.0051 cm)

Penetrant	V, cm^3		
	1.0	10^3	10^6
CHBrClF	914	9140	91,400
$CBrF_3$	598	5980	59,800
O_2	65	650	6,500
N_2	271	2710	27,100

The back-diffusion of a 1:4 mixture of oxygen and nitrogen gases in contact with the outside of the box has also been estimated on the assumption that no interaction occurs between the separate gas flows and the results shown in Figure 2. The combined p/p_0 values for O_2, N_2, and flame-retardant vapor are also shown as a function of time for the special case where the initial pressure of vapor inside the box equals the constant pressure of the gas mixture on the outside: i.e., $p_0 = p_c$. The faster back-diffusion of the atmospheric gases results in the pressure in the box passing through a maximum; this effect will be less pronounced the greater p_0 is relative to p_c.

One may also define a half-life $t_{1/2}$ as the time required for $f(p)$ to become ½, so that

$$t_{1/2} = \frac{lVT_s ln2}{\bar{P}ATp_s}. \tag{9}$$

In Table I the half-lives of the penetrants at 30°C are given for cubic containers of volumes 1, 10^3, and 10^6 cm^3.

The storage-life of the containers may be extended significantly by increasing the film thickness l and by decreasing A/V. On the basis of these calculations and bearing in mind the approximations made, the relatively long-term storage performance of rigid Saranex containers would appear to be good.

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