ϵ = minimum value of intermolecular potential energy
(ϵ/k) = molecular force constant
σ = constant in Equation (6) characterizing the concentration dependence of S

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Permeation through Plastic Films

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Data are presented on the solubility in and permeation through polyolefin films of a number of gases and liquids. The permeation rates are found to be dependent on the type of film, the concentration and the temperature. A classical diffusion model explains the permeation mechanism and other relations serve to correlate the data.

Polymer films can function as remarkably selective membranes, separating mixtures of chemically dissimilar and sterically different compounds (*2, 6, 8, 9, 11, 12*). The process is, however, not well understood. In this work and in the previous work (*5, 6*), permeation of hydrocarbon gases at subcritical and supercritical conditions and hydrocarbon liquids through polymeric films has been studied. The results discussed in this paper are mainly on gas permeation at elevated pressures.

THEORETICAL BACKGROUND

The diffusion through plastic films at steady state is described by Fick's first law:

$$J = -D \frac{dC}{dX} \qquad (1)$$

If D, the diffusion constant, is independent of concentration C, then Fick's law can be integrated to give:

$$J = \frac{D}{L} (C_1 - C_2) \qquad (2)$$

In gas permeation, Henry's law is generally assumed to apply (*8, 10*);

$$C = Hp \qquad (3)$$

Equations (2) and (3) can be combined to give:

$$J = \frac{DH}{L} (p_1 - p_2) \qquad (4)$$

or

$$J = \frac{P}{L} (p_1 - p_2) \qquad (5)$$

The permeation constant or permeability, P, is defined as:

$$P = DH \qquad (6)$$

P and D were both found to be pressure dependent for permeation of organic gases at pressures up to 120 lb./sq.in.abs. by Li and Henley (*5*). However, H remained constant over this pressure range for nonglassy polymeric films (*13*). Since D varies with pressure, and thus presumably with solute concentration in the film, the restriction of D being independent of C limiting the integration of Equation (1) becomes unrealistic at elevated pressures. A new equation must be obtained which accounts for the variation of D with C and C with pressure and solute composition for mixtures to permit integration of Equation (1). This paper has been unable to provide this rigorous relationship but does provide some insight into the mechanisms which must be considered. In the present work, the pressure effect on gas permeation was examined at pressures up to 1,500 lb./sq.in.abs., well above the critical pressures of the gases studied.

EXPERIMENTAL

PERMEATION

Material

All chemicals used were of the technical grade. No further purification was done on them. The polymer films did not have additives in them such as anti-oxidants and coatings. The polyethylene and polypropylene films had a crystalline content of 55 and 64% respectively.

Equipment

The equipment for liquid permeation has been described elsewhere (*5*). The equipment for gas permeation consisted of two permeation cells and their associated pressure gauges, valves, etc. A permeation cell is shown in Figure 1. The working pressure limit of all equipment was at least 2,000 lb/sq. in. gauge. The pressure limit of the gas permeation runs was usually the legal shipping pressure limit of the gas cylinder. The permeation cells were modified back pressure regulators. The diaphragms and other mechanisms were removed from the pressure regulators to enable insertion of the polymer films, filter paper, and seals.

Procedure

The experimental procedure for liquid permeation, defined as the permeation of mixtures from the liquid phase on one side of the film to the vapor phase on the other side (*2*), is described elsewhere (*6*) and always used films which had been preannealed for 24 hr. in *n*-heptane at 75°C. for the reasons given in that description. The experimental procedure for gas permeation was simple once the system was without leaks. Before every run the film was saturated with the feed for at least 12 hr. Even with saturation, permeation during the first hour was slightly slower than during subsequent time intervals.

After saturation the downstream pressure was set to the desired pressure by opening the cell bypass valves. With the bypass valves closed the upstream pressure was then set to its desired value. The time was noted and designated $t = 0$. After approximately 1 hr. the first data were taken of the volume of gas permeated, the time, and upstream and downstream pressures. The volume of gas permeated was determined by bleeding the permeating gas on the downstream side beyond the back-pressure regulator into a water manometer until the downstream pressure beyond the back-pressure regulator was reduced to its original value of 1 atm. The volume of gas permeated was measured by the volume of water it displaced in the manometer. This procedure gave the volume of the permeate at room temperature and atmospheric pressure. Permeability was then calculated from Equation (5). Its relationship with pressure was correlated by the use of Equation (7) in the pressure range where Henry's law holds.

The most significant error in measuring the volume in this manner was reducing the downstream pressure to exactly its original value. This error could be reduced by increasing the permeation time or reducing the volume of downstream system.

Annealing the polyethylene and polypropylene film was necessary to produce reproducible results (*6*). The film was immersed in *n*-propyl alcohol for 24 hr. at 75°C. and then dried under vacuum prior to permeation to prevent the amorphous and crystalline contents of the film from changing during permeation. This procedure did give reproducible results within experimental error.

SORPTION

The solubility of gases in polymer films were determined by the quartz spring balance method. This method involves the use of a quartz spring in a high pressure cell with sight glass. The polymer sample is hung onto the tip of the spring. The solubility of the gas in polymer is determined by measuring the extension of the quartz spring with a cathetometer with buoyancy effect taken into account.

DISCUSSION OF RESULTS

SORPTION

In order to gain better insight into the effect of pressure on permeation, the solubilities of individual gases as well as gas mixtures were studied. The solubilities for nitrogen, methane, and ethylene were determined at pres-

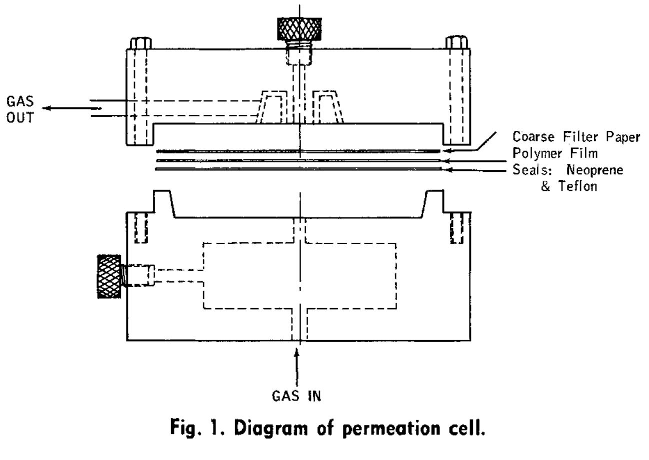

Fig. 1. Diagram of permeation cell.

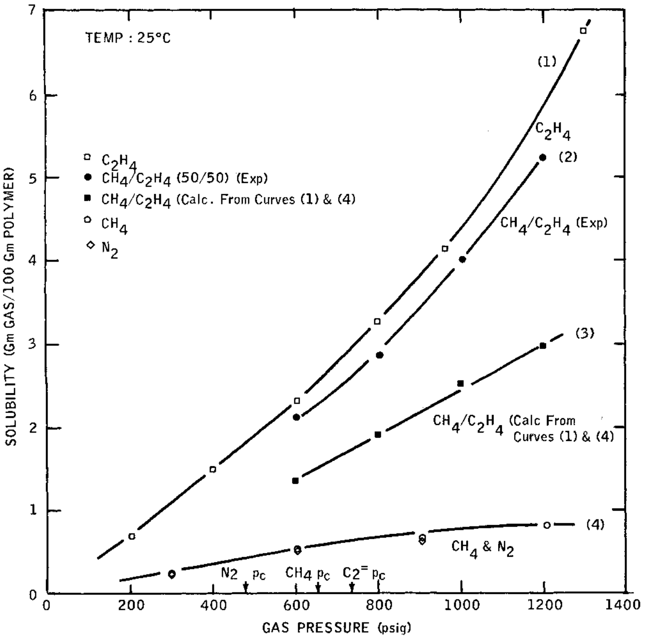

Fig. 2. Solubilities of methane, ethylene, nitrogen, and methane-ethylene mixture in polyethylene.

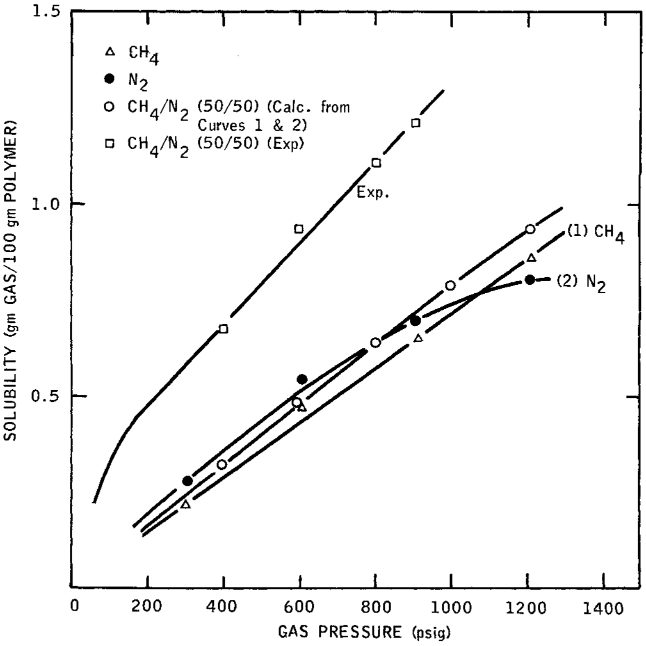

Fig. 4. Solubilities of methane, nitrogen, and methane-nitrogen mixture in polyethylene.

sures up to 1,400 lb./sq.in.gauge by the quartz-spring balance method. The solubility of ethylene was found to increase exponentially with increasing pressure whereas those of methane and nitrogen increase asymptotically toward a saturation value (Figure 2). The solubility of ethylene is expected to level off at pressures beyond the pressure range investigated because ethylene is not likely to dissolve completely the plastic film. These solubility curves show that they can be approximated by a straight line at low pressures, roughly up to the critical pressure of the gases studied. This means that, in general, Henry's law holds only in the subcritical pressure region whereas appreciable deviation occurs at higher pressure.

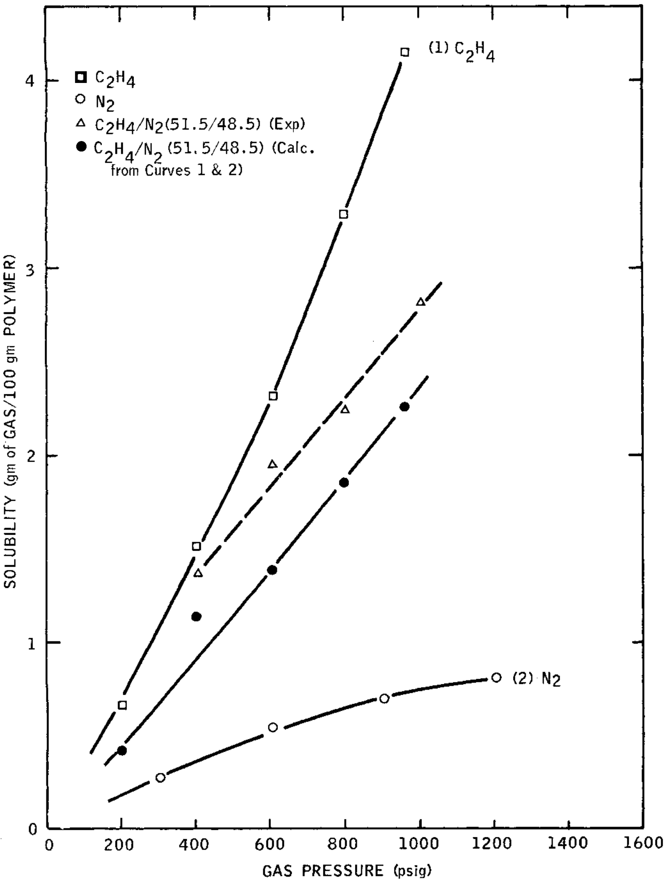

Fig. 3. Solubilities of ethylene, nitrogen, and ethylene-nitrogen mixture in polyethylene.

The overall solubilities of methane-ethylene, methane-nitrogen, and ethylene-nitrogen mixtures in polyethylene are also determined. The data show a very high plasticizing effect of the preferentially permeating compound. The plasticizing effect means that the sorption of the more soluble compound in polymer increases the solubility of the less soluble compound and therefore raises the total solubility of the mixture, that is, the solubility curve determined experimentally is much higher than the curve calculated from the solubilities of the individual gases at their partial pressures in the mixture (Figures 2, 3 and 4). This plasticizing effect further complicates the derivation of a reliable gas permeation equation for high pressures.

PERMEATION

Gases

The literature data and our results (Figure 5) all show that gas permeability is a function of pressure. Li and Henley (5) correlated permeability with pressure up to 120 lb./sq.in.gauge successfully by the following

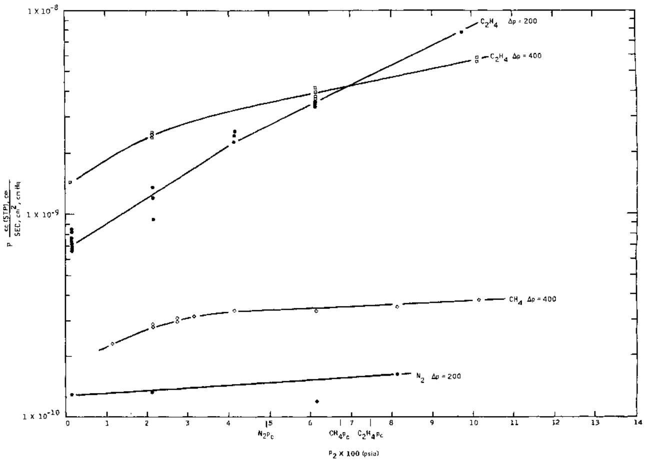

Fig. 5. Permeabilities of methane, ethylene, and nitrogen.

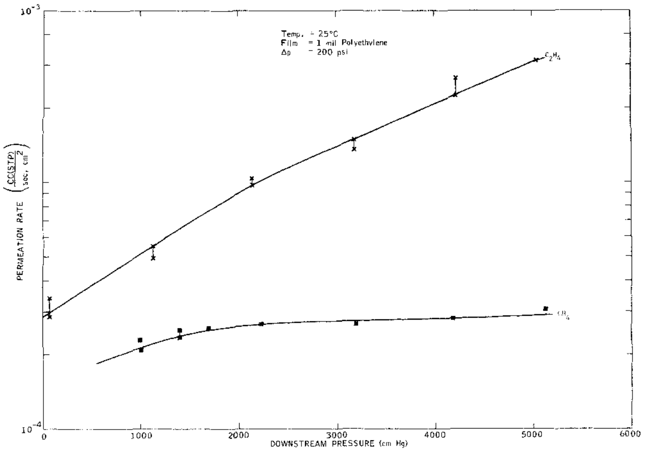

Fig. 6. Permeation of methane and ethylene through polyethylene film.

$$P = P_o' e^{Ap} \tag{7}$$

This equation is a simplified version of Equation (8) at low pressures where Henry's law holds. Equation (8) is obtained by combining the well established Equation (9) with Equation (10):

$$P = \left(\frac{H}{H_o}\right) P_o e^{aHp} \tag{8}$$

$$D = D_o e^{aC} \tag{9}$$

$$P_o = D_o H_o \tag{10}$$

As already shown by the solubility data, the solubility coefficient is independent of pressure at low pressures (approximately up to the critical pressure of the permeating gas). Hence,

$$\frac{H}{H_o} P_o = \text{constant} = P_o' \tag{11}$$

$$aH = \text{constant} = A \tag{12}$$

Equation (7) can, therefore, be used to describe the pressure dependence of permeability with P_o' and A as constants as long as the solubility coefficient remains pressure-independent. As data on solubility and solute interaction with polymers and other solutes become available in the future, it will be desirable to return to an integration of Fick's first law with the proper pressure and concentration dependence of D applied.

In the current work, Equation (7) was used to correlate permeability with pressure in the subcritical pressure region for methane, ethylene, and nitrogen gases at 25°C. To evaluate the characteristic constants P_o' and A in Equation (7) we substitute Equations (3), (6), and (7) into Equation (1) and carry out the integration:

$$J = \frac{P_o'}{AL}\left(e^{Ap_1} - e^{Ap_2}\right) \tag{13}$$

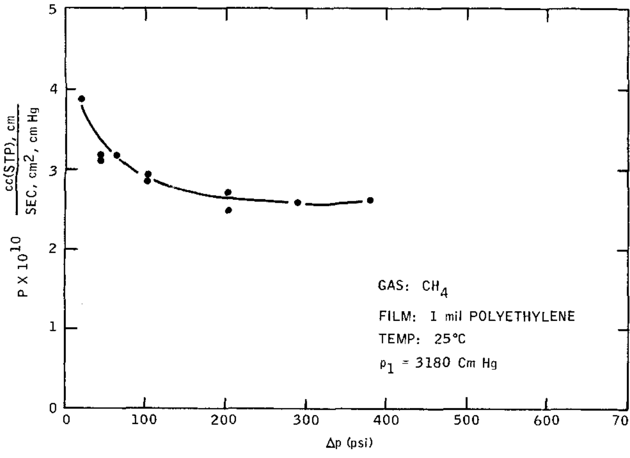

Fig. 7. Permeability is a function of Δ_p.

Substituting $p_1 = p_2 + \Delta p$ into Equation (13)

$$J = \frac{P_o'}{AL}\left[e^{A(p_2+\Delta p)} - e^{Ap_2}\right] = \frac{P_o'}{AL}\left(e^{\Delta p} - 1\right)e^{Ap_2} \tag{14}$$

Let $K = e^{\Delta p} - 1$, then:

$$J = \frac{P_o'}{AL} K e^{Ap_2} \tag{15}$$

Taking logarithm on both sides:

$$\ln J = \ln \frac{P_o' K}{AL} + Ap_2 \tag{16}$$

If Δp is kept constant, a plot of $\ln J$ vs. p_2 should give a straight line. P_o' and A can then be evaluated from the slope and the intercept. The variation of permeation rates of methane and ethylene with the downstream pressure, from which P_o' and A are calculated, are shown in Figure 6. The constants P_o' and A evaluated are summarized in Table 1. They show that the pressure dependence of the permeability of organic compounds is much greater than

TABLE 1. CORRELATION OF PERMEABILITY WITH PRESSURE AT SUBCRITICAL PRESSURES

Gas	$P = P_o' e^{Ap}$ $P_o' \times 10^{10}$	$A \times 10^4$
N_2	1.28	0.58
CH_4	1.90	3.21
C_2H_4	6.63	5.90

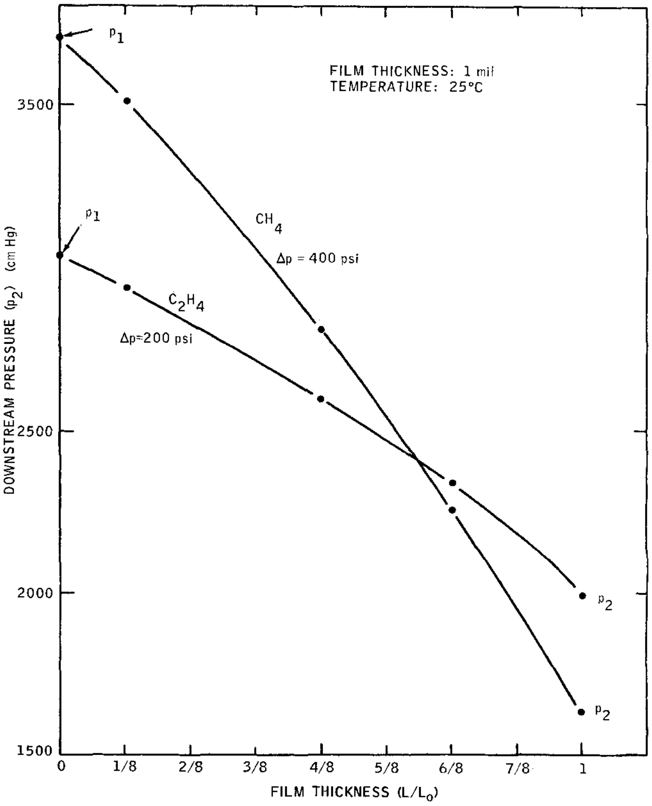

Fig. 8. Hypothetical pressure gradient of methane and ethylene in polyethylene films.

that of inorganic compounds.

Although it was reported previously (5) that the permeation constant is independent of the pressure differential across the membrane, this is true only for small Δp, such as 15 lb./sq.in. For large Δp, our present results indicate that permeability is definitely a function of Δp, as shown in Figure 7.

The hypothetical pressure profiles inside the membrane were calculated for methane and ethylene (Figure 8). The easiest way to calculate such profiles is as follows: For a given set of data, namely, J, p_1, and p_2, one can obtain P_o' and A as described before. Then substitute X for L and p_{2X} for p_2 in Equation (13):

$$J = \frac{P_o'}{AX}\left(e^{Ap_1} - e^{Ap_{2X}}\right) \qquad (17)$$

Dividing Equation (17) by Equation (13) and rearranging terms, one gets

$$\frac{X}{L} = \frac{e^{Ap_1} - e^{Ap_{2X}}}{e^{Ap_1} - e^{Ap_2}} \qquad (18)$$

The hypothetical pressure, p_{2X}, was calculated from the above equation for each value of X/L. It should be noted that

$$p_{2X} = p_1 \qquad \text{when } \frac{X}{L} = 0$$

and

$$p_{2X} = p_2 \qquad \text{when } \frac{X}{L} = 1$$

The hypothetical pressure profiles calculated have quite small curvature. This is in contrast to the concentration profiles computed for liquid permeation using the classical diffusion model with the exponential concentration dependence of diffusivity. The profiles in liquid permeation show a very slow decrease of concentration with distance in the film until over ¾ of the way toward downstream side of the film. From there on, the concentration drops very rapidly to a value depending on the downstream pressure (6). This means that in liquid permeation, practically all the resistance to diffusion is at the downstream edge of the film whereas in gas permeation, the resistance is quite uniform throughout the entire film. The difference between liquid permeation and gas permeation is not in kind but rather in degree. The large difference between the concentration profiles calculated for liquid permeation and for gas permeation is merely due to the fact that the upstream and downstream concentrations in liquid permeation can be very different, resulting in concentration profiles of large curvature; whereas the two end concentrations in gas permeation are quite small, resulting in almost flat concentration profiles.

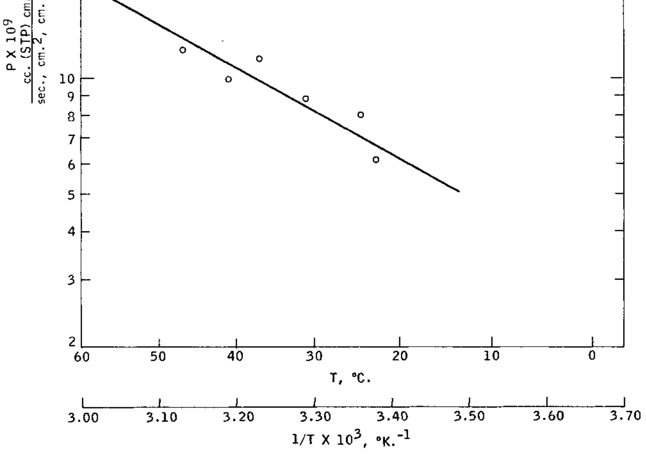

Fig. 9. Permeation constant of polyethylene vs. temperature.

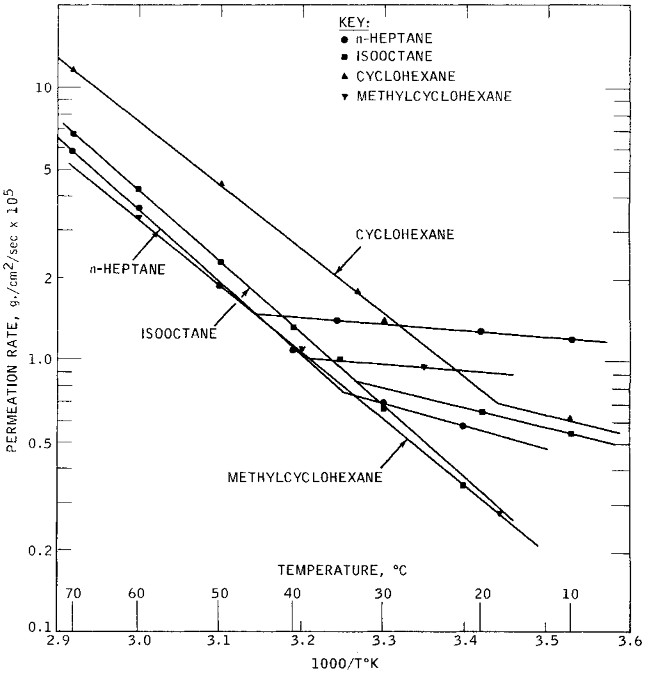

Fig. 10. Permeation rates for paraffins and naphthenes through 1 mil annealed polypropylene film.

Our work with Saran membrane shows that it is practically impermeable to ethylene. The very low permeation rate of paraffins through Saran is also true in liquid permeation as discussed in the next section.

The temperature effect on the permeation of ethylene through polyethylene at supercritical pressures can be expressed in an Arrhenius functional form (Figure 9), and analysis of the results give the following values for the constants at $p_1 = 870$ lb./sq. in. gauge and $p_2 = 760$ lb./sq. in. gauge.

$$P = P_o'' e^{-E_P/RT} \qquad (19)$$

$$E_P = 5{,}070 \text{ cal./g. mol.}$$

$$P_o'' = 3.84 \times 10^{-5} \frac{\text{CC(STP), cm.}}{\text{sec., sq.cm., cm.Hg.}}$$

or

$$P = 3.84 \times 10^{-5} e^{-5070/RT} \qquad (20)$$

The E_P value is in the same order of magnitude as those at the subcritical pressures (5). Both E_P and P_o'' should be pressure dependent.

Liquid

As mentioned above, in liquid permeation there is also an exponential concentration dependence of diffusivity (7). The liquid permeation, similar to gas permeation, is apparently a special case of ordinary diffusion and can be explained by a classical diffusion model (6). The results shown here in Figures 10 and 11 are additional to those already published by Long (6). They indicate that paraffins, naphthenes, and benzene permeate through poly-

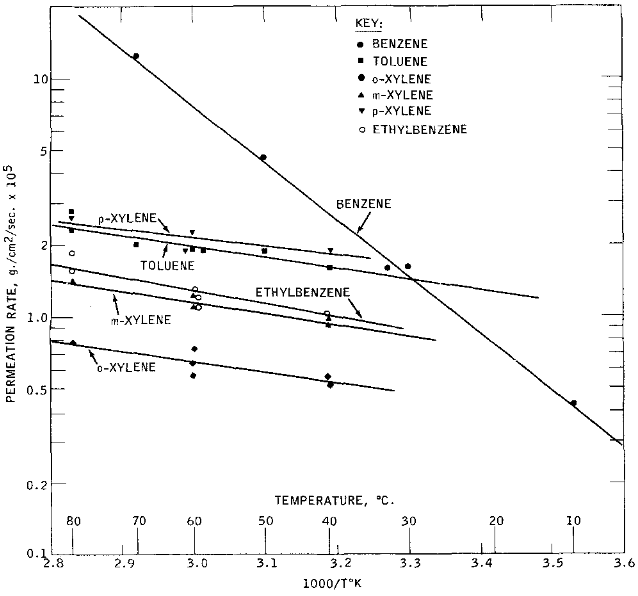

Fig. 11. Permeation rate for aromatics through 1 mil annealed polypropylene film.

propylene films at a rate which is quite temperature sensitive while the other aromatics have relatively flat permeation rate-temperature curves. Furthermore, nitrogen, sulfur, and oxygen atoms in a molecule greatly reduce permeation rate through polypropylene. In contrast, the more polar molecules permeate through Mylar faster than the hydrocarbons. Teflon and Saran also show large differences in permeation rate for different molecular types.

Steady state permeation rates for ten different hydrocarbons through polypropylene film were obtained through a temperature range from 10 to 80°C. The results (Figures 10 and 11) how that paraffins and napthenes behave as one class while aromatics except benzene behave as a different class. That is, the slopes of the Arrhenius plots for permeation are equivalent to about 5 k.cal./mole for saturates and 2 k.cal./mole for aromatics. Furthermore, the saturates show a break in the permeation rate curve near the glass transition temperature while the aromatics do not. Below this break temperature the saturates also have an apparent permeation activation energy of about 2 k.cal./mole, much like the aromatics.

The lack of reproducibility of the break-point is believed due to the immediately previous history of the polymer film. Although the film was annealed in *n*-heptane before use, it gets a variety of thermal treatments in obtaining data at various temperatures and a systematic cooling technique was not used in this work. Therefore, in getting data at low temperatures, that is, below 40°C., sometimes the temperature was approached in slow steps over a period of days and sometimes directly from a 70°C. run. Since solvent diffuses out of the polymer relatively slowly at low temperatures and the glass transition temperature is sensitive to the concentration of solvent in the film (*1*), it is not too surprising that the break-points vary. While there is no question that, with saturates, the transport properties and presumably the structure of the polymer shows definite differences in the low temperature region of our studies, our major interest is in the higher temperature region where rapid permeation occurs. Therefore, we leave the study of the low temperature structure changes to the polymer morphologists. The higher Arrhenius slopes for saturates at higher temperatures indicate that the increase in permeation rate with temperature must involve something more than simply diffusion. Some polymer-solvent interaction must also be involved, such as increasing amorphous polymer content.

Benzene appears to be unique among the aromatics in that it behaves more like the saturates and in fact essentially duplicates the permeation rates of cyclohexane. The reason for the differences in permeation character of the various solvents is not yet known in detail and is probably a combination of factors. For example, aromatics have a higher dry film diffusivity than saturates, naphthenes have the greatest solubility in polypropylene, and paraffins have a greater plasticizing effect per unit weight of dissolved hydrocarbon (*6*). Probably all these effects are involved in steady state permeation.

Highly polar molecules such as water, methanol, and acetic acid permeate through polypropylene from 10 to 100 times slower than hydrocarbons (Figure 12). Since these are small molecules which are very likely not associated clusters in the plastic, the low diffusion rate is probably due to low solubility in the polymer and the consequent low driving force for diffusion.

Solvent	Permeation Rate at 60°C., g./sq.cm./sec. × 10^5
n-heptane	3.6
methylcyclohexane	3.3
toluene	2.0
water	0.009
methanol	0.022
acetic acid	0.076

As the ratio of hydrocarbon to hetero-atom in a nonhydrocarbon molecule increases, the permeation rate also increases. This is shown in Figures 12 and 13. These figures also indicate that a nitrogen atom reduces permeation rate more than a sulfur atom, which in turn reduces rate more than oxygen atom, which finally reduces rate more than a chlorine atom. Thus polypropylene may also find use in rejecting *N*, *S*, and *O* compounds from hydrocarbons.

While polyolefin films generally behave pretty much alike in their permeation characteristics, Teflon, Saran, and Mylar behave quite differently from polypropylene. Teflon (Figure 14) shows the same large difference be-

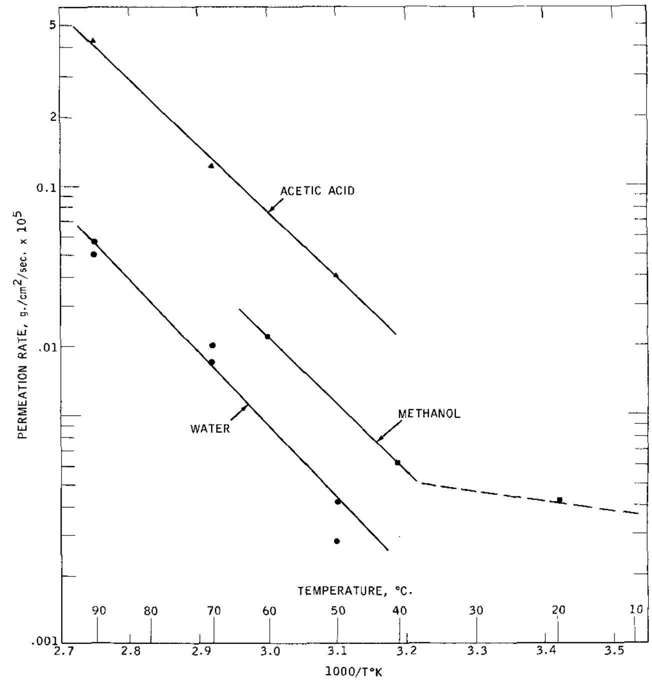

Fig. 12. Permeation rates for water, methanol, and acetic acid through 1 mil annealed polypropylene film.

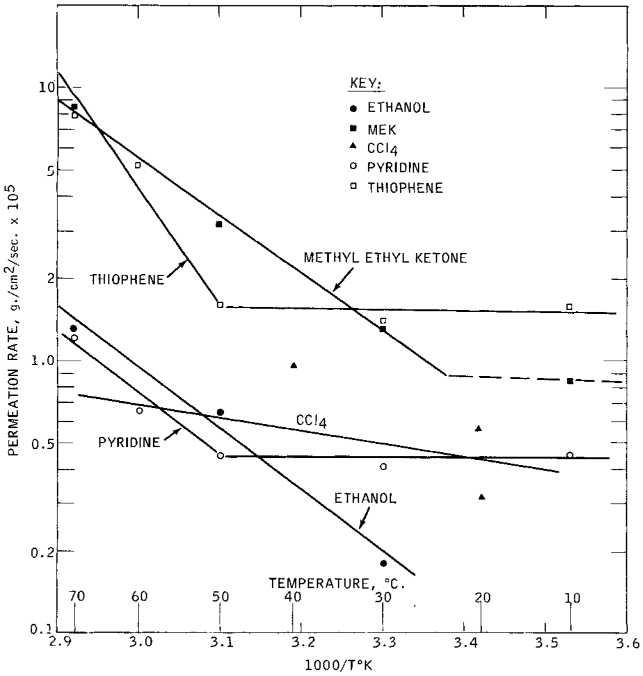

Fig. 13. Permeation rate for ethanol, MEK, carbon tetrachloride, pyridine, and thiophene through 1 mil annealed polypropylene film.

tween hydrocarbon (high rate) and oxy-compound (low rate) permeation rates as polypropylene. However, it reverses the relative permeation rates of water and ethanol and of *n*-heptane and toluene. On the other hand, Saran (Figure 15) shows large differences between toluene and *n*-heptane but passes water and ethanol at about the same low rate as *n*-heptane. Apparently the aromatic ring has a strong effect with Saran.

In contrast to polyolefin films, Mylar (Figure 16) essentially reverses the relative permeation rates of various compounds. It is most permeable to water, gradually decreases in permeability through the heteroatomic molecules, and shows its lowest permeability with *n*-heptane. Thus, by proper choice of the membrane, we can start at either end of the polarity scale for the material we want to selectively permeate through the film. This is important because we usually want to permeate the component present in the feed at the lowest concentration.

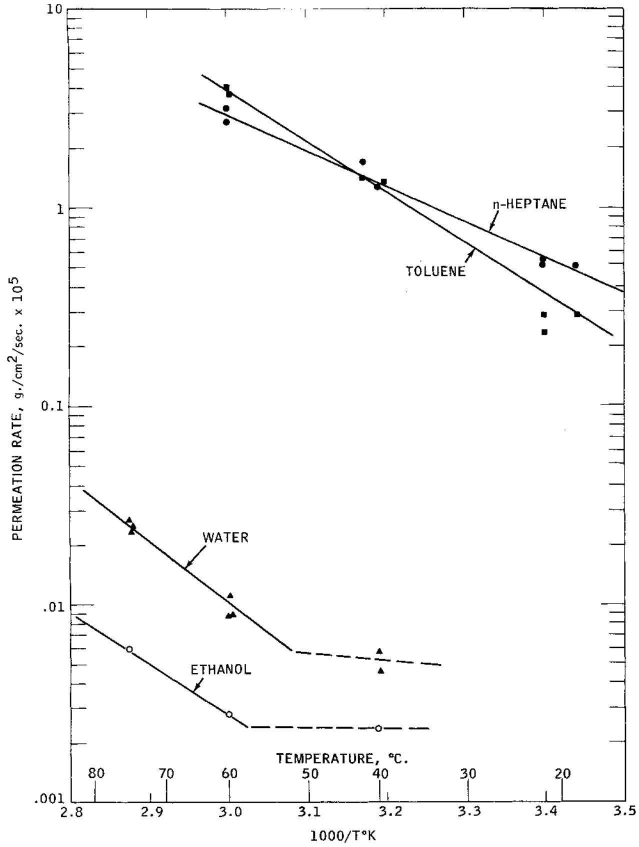

Fig. 14. Permeation rates of solvents through annealed 1 mil Teflon film.

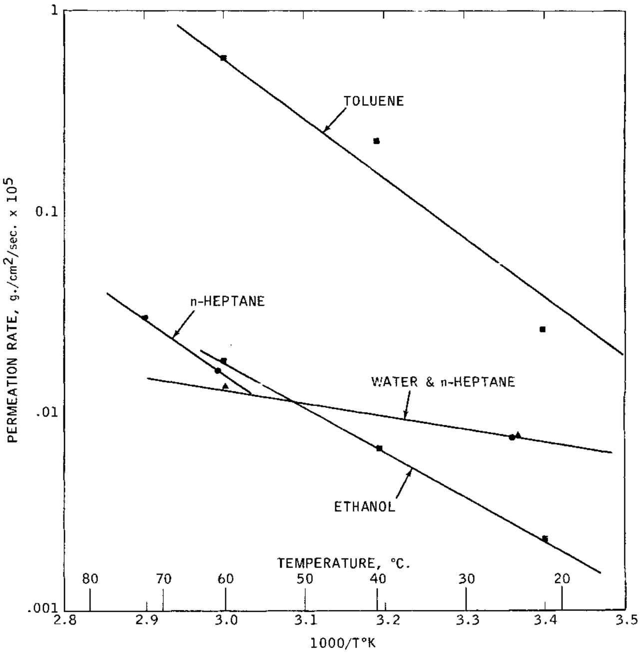

Fig. 15. Permeation rate of solvents through annealed 1 mil Saran film.

SEPARATION OF GASES

The solubility and permeability data suggest that a method for getting high separation factor is to select the upstream and downstream pressures as low as permissible by a given Δp. The pressure drop across a membrane controls the permeation rate whereas the absolute values of the upstream and downstream pressures govern the plasti-

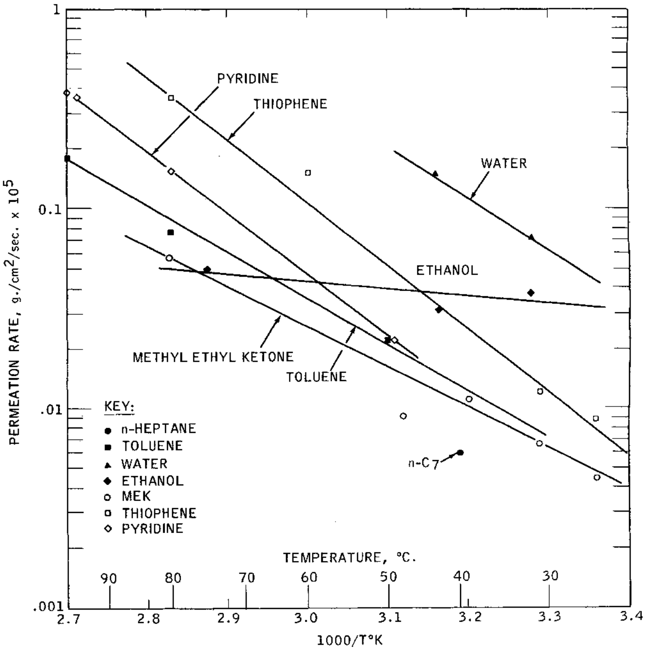

Fig. 16. Permeation rate of solvents through untreated 1.5 mil Mylar.

cizing effect of the permeates and, therefore, the membrane selectivity.

This method for getting high separation factor is proved to be true by the results of ethylene-methane separation which show that separation factor decreases with increasing upstream and/or downstream pressure while keeping Δp constant. Obviously an economic balance must then be made among permeation rate, separation factor, number of stages, and compression costs.

The maximum separation factor obtained thus far for ethylene-methane separation is 3.0 (Table 2). The maximum separation factor usually was reached after continually running the experiment for two days, which shows the relatively slow equilibration of the film. The separation factor in this work is defined for convenience as the concentration ratio of the more permeable compound to the less permeable compound in the product to the ratio in the feed. Because the conventional separation factor is defined as the concentration ratio in the product to the ratio in the raffinate, the conventional separation factor is slightly higher than the separation factor reported here.

The use of thick films with a thickness of 10 mil or higher was for the purpose of applying a high pressure differential across the membrane. The film thickness was found not to affect permeation constant.

TABLE 2. SEPARATION OF METHANE-ETHYLENE MIXTURE

Temperature: 25°C.
Film Thickness: 10 mil. Polyethylene
17 mil. Polypropylene
Feed Composition: C_2H_4/CH_4 50/50 by weight

Upstream pressure Downstream pressure	Polyethylene film	Polypropylene film
	C_2H_4 conc. (wt. %) in permeate	
800/300	63	58
700/200	63	61
600/100	65	63
500/0	71	64
100/0	75	66

CONCLUSION

The permeabilities of liquids and gases through polymeric membranes is concentration dependent. The exponential expression previously proposed by Li and Henley (5) for describing the pressure dependence of permeability is applicable when Henry's law constant is pressure independent, that is, up to about the critical pressure of the gas. At higher pressures the Henry's law constant varies with pressure.

For the liquids and gases studied, the permeation rate of organic gases through polyolefin films is higher than that of the inorganic gases of the same molecular weight. In liquid permeation, nitrogen, sulfur, and oxygen atoms in an organic molecule greatly reduce the permeation rate through polyolefin films. In general, the more polar molecules permeate through the polar films faster than the hydrocarbons. The temperature dependence of the permeation constant for ethylene through polyolefins obeys an Arrhenius type relationship at both subcritical and supercritical conditions. The permeation rate of liquid paraffins, naphthenes, and benzene through polyolefin films is much more temperature sensitive than other aromatics.

The optimum way of separating hydrocarbon gases uses the maximum pressure differential across the film which can be obtained without appreciable plasticizing of the film with dissolved gas. The selectivity is best at low pressures and permeation rate is better at high pressures, where plasticizing occurs. The plasticizing effect can be characterized by the solubility differences of the permeates between their pure state and the state where they are mixed with other compounds. The solubilities of methane, ethylene, nitrogen and their binary combinations have been determined.

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NOTATION

a = parameter characterizing the pressure dependence of C
A = parameter characterizing the pressure dependence of P
C = concentration
d = density
D_o = constant defined by Equation (9)
E_p = permeation energy of activation, cal./g. mol.
H = Henry's law constant [CC(STP)/CC polymer X cm.Hg.]
H_o = constant defined by Equation (10)
J = mass transfer rate defined in Equation (1) [CC(STP)/time, area]
L = film thickness
p_1 = upstream side gas pressure
p_2 = downstream side gas pressure
p_{2X} = hypothetical downstream pressure at X
P = permeation constant or permeability defined in Equation (6)
P_o = constant defined by Equation (10)
$P_{o'}$ = constant defined by Equation (11)
P_o'' = constant defined by Equation (19)
Δp = $p_1 - p_2$
S = solubility of gas in polymer (wt.%)
T = temperature (°K.)
V = volume of permeate
W = weight of absorbed gas in polymer (mg.)
X = distance between film surface and any point inside the film

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