THE MEASUREMENT AND ANALYSIS OF THE DIFFUSION OF TOLUENE IN POLYMERIC FILMS

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by

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Abstract

The Measurement and Analysis of the Diffusion of Toluene In Polymeric Films

by

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The measurement and analysis of the diffusion of organic vapors in polymeric films is complex and the interpretation of the results is not very well understood. A quasi- isostatic system for measuring the permeation of organic vapors has been developed and a detailed description of the apparatus and analysis is given. The system is used to study the vapor concentration dependent diffusion and permeation of organic vapors in oriented polypropylene and Saran (polyvinylidene chloride) polymeric films. The results from the quasi-isostatic permeation measurements are compared to results obtained from gravimetric electrobalance sorption studies. It was found that the permeation, diffusion and sorption processes for toluene vapors in these films are highly dependent on the concentration of vapor in contact with the film. This is partly due to the increased segmental mobility of the polymer chains due to the sorption of the toluene permeant by the polymer. The diffusion coefficients were evaluated using the half time and lag time methods from the sorption and permeation studies respectively. The lag time and half time diffusion coefficients are transient state diffusion coefficients and significantly differed from the calculated steady state diffusion coefficient. The steady state diffusion coefficients were evaluated from the steady state permeability coefficient from permeability experiments and by the solubility coefficient from equilibrium sorption experiments. The difference between the transient diffusion coefficients and the steady state diffusion coefficients is explained in terms of the free volume theory for diffusion.

Dedicated to my grandfather, Albert Lawrence Baner.

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Nomenclature

Symbol	
a	vapor activity - vapor pressure of permeant/saturated vapor pressure of permeant (p/p_o)
a_1	vapor activity on the high concnetration side of permeation test film
A	area of film sample (cm^2)
A	Frequency factor free volume theory Eqn.(32).
b	characteristic parameter of Langmuir equation, Eqn. (27)
B	measure pf minimum hole size for jump process in free volume theory Eqn. (35).
c_i or c_1	concentration of permeant in the face of the polymer in contact with the permeant (gm/cm^3)
c_2	concentration of permeant in the face of the film in contact with the zero or low permeant vapor concentration
Cs	Equilibrium solubility of a contacting vapor concentration in a polymer
c_m	sorbed concentration of vapor corresponding to a complete monolayer sorption Eqn. (27)
D	differential diffusion coefficient (cm^2/sec)
D	integral diffusion coefficient (cm^2/sec)
D_o	preexponential diffusion coefficient or limiting diffusion coefficient Eqn. (29) (cm^2/sec)

D_1

Dss

D_s

D_d

$D_{t1,}$

D(c)

E_p

E_d

f

f_o

H_s

ierfc

k

K c

c

kg k

L t

mg m

mmHg m

M_t an

M Eq

mil 0.

n,m in

D_{lag}	integral diffusion coefficient from lag time data Eqn. (17) (cm^2/sec)
Dss	Steady state diffusion coefficient (cm^2/sec)
D_s	Diffusion coefficient from sorption curve Eqn. (23) (cm^2/sec)
D_d	Diffision coefficient from desorption curve Eqn (23)
$D_{t1/2}$	Half time diffusion coefficient Eqn. (22)
D(c)	diffusion coefficient as a function of concentration
E_p	activation energy of permeation Eqn. (38) (kcal/mol)
E_d	activation energy of diffusion Eqn. (29) (kcal/mol)
f	fractional free volume Eqn. (33)
f_o	fractional free volume at zero vapor concentration Eqn. (35)
H_s	heat of sorption Eqn. (25) (kcal/mol)
ierfc	inverse error function
k	limiting slope of plot of $\ln(M_s - M_t)$ versus t, Eqn. (24)
K	constant relating vapor pressure dependence of permeability coefficient Eqn. (41).
kg	killigram
L	thickness of the film sample before swelling (cm or mil)
mg	milligram
mmHg	millimeters mercury
M_t	amount of diffusant taken up by sheet in time t Eqn. (19)
M	Equibrium sorption at infinite Eqn. (19)
mil	0.001 inches
n,m	indices

n	number of monolayers present for sorption Eqn (28)
OPP	orientated polypropylene
OPP/PVDC	OPP coated on one side with PVDC
PVDC	polyvinylidene chloride or saran
ppm	parts per million permeant concentration in nitrogen (Ìg/ml, w/v)
P	Permeability rate at steady state (g/m^2·hour)
P	Permeability Coefficient (g·structure/M^2·day·ppm) or (g·structure/m^2·day·a)
P_o	limiting permeability coefficient, The permeability coefficient at zero permeant partial pressure p_o saturation vapor pressure
p_1	permeant partial pressure at the ingoing side of the film
p_2	permeant partial pressure at outgoing side of film
q	quantity of permeant in low concentration permeation cell chamber
Q_t	amount of permeant which passes through membrane in time t
Q_L	heat of vaporization for pure liquid penetrant Eqn (28)
Q_1	heat of absorption Eqn (28)
r	correlation coefficient
R	ideal gas law constant
RH	Relative humidity
s.d.	standard deviation
S	Solubility coefficient (g/cm^3 ppm)
S	integral solubility coefficient (g/cm^3 ppm)
S_o	prexponential solubility coefficient Eqn (25)

	or the solubility coefficient at zero permeant concentration Eqn (26)
t	time
$t_{1/2}$	time required for sorption to reach 1/2 M_s Eqn (22)
T	absolute temperature (^oK)
T_g	Polymer glass transition temperature
V	volume of permeation cell chamber (cm^3)
X_m	crystalline mass fraction in semicrystalline polymer Eqn (36)
α	proportionality factor for diffusion coefficient vapor activity dependency Eqn (31) or statistical probability of a type I error
β	effectiveness f actor of penetrant molecule for increasing the free volume of polymer Eqn (33) constant in modified BET equation Eqn (28)
Σ	summation operator
ϵ	relaxation effects in diffusion Eqn. (60)
γ	proportionality factor for diffusion coefficient concentration dependency Eqn (30)
γ_m	modified proportionality factor for steady state diffusion coefficient concentration dependency Eqn (49)
μg	microgram
σ	proportionality factor for solubility coefficient vapor concentration dependency Eqn (26)
ϕ	fickian effects in diffusion Eqn (60)

θ	lag time (time) Eqn (17)
π	pi - 3.14159
∞	infinity

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Introduction

The study of the diffusion of organic vapors through polymeric packaging films is needed to characterize the film's ability to exclude deleterious vapors from interacting with the product and to prevent loss of product volatiles which may decrease product quality and shelf life. It is known that the diffusion of organic vapors in polymers is dependent on the concentration of the vapors in the polymer, which is related to the permeant concentration above the polymer (Meares, 1965a). This behavior makes it important to monitor and specify the permeant concentration at which a permeability rate or diffusion coefficient is measured.

Most methods used for measuring organic vapor permeation in polymers have at least one of the following limitations: (1) they utilize complex and difficult to use apparatus, (2) they are not suitable for testing thin films and soft polymers, (3) they can only be applied to a limited permeant concentration and/or (4) they cannot study the effects of copermeants (Talwar, 1974).

The purpose of this study is to develop and evaluate a practical method for comparing the relative diffusion rates of organic vapors in common packaging films. This required the development of a suitable measurement technique as well as a method for data analysis.

To be of maximum value as a test method for determining the permeation and diffusion of organic vapors in packaging films the method must have the following attributes: (1) the apparatus must be inexpensive and easy to use, (2) it must be capable of evaluating films at different thicknesses, barrier properties, and structure, (3) it can test the complete organic vapor pressure range from zero to saturation vapor pressure, (4) the effects and interactions of copermeants and relative humidity can be studied, and (5) tests can be made at different temperatures. A quasi-isostatic test procedure is selected as the method which can be adapted to allow evaluation of the above listed criteria.

In addition to a good vapor permeation measurement technique for vapor permeation through films, the analysis and interpretation of the data is equally important for proper application to packaging problems. One of the difficulties in studying the permeation and diffusion of organic vapors in polymers is the vapor concentration dependency of diffusion. Studies were conducted on the concentration dependent diffusion of toluene in films containing oriented polypropylene and polyvinylidene chloride polymers.

Interpretation of experimental results from permeation and sorption studies for these organic vapor-polymer systems is discussed. Evaluation is made of the applicability of the lag time d

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diffusion coefficient to these systems where the diffusion coefficient is concentration dependent and Henry's law solubility is not obeyed. The permeability coefficient from permeation measurements and the solubility coefficient, which is obtained by sorption measurements, were used to calculate the diffusion coefficient using the relationship, $P = D \cdot S$. Diffusion coefficients derived from this expression were compared to the lag time diffusion coefficient and the results interpreted using the free volume theory.

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Literature Review

The Importance of Studying The Permeation Behaviour Of Organic Vapor Through Polymeric Packaging Materials

The loss or gain of organic vapors by a product in a package occurs by two mechanisms: the mass transfer or permeation of the vapor in or out of the package and sorption or desorption of organic volatiles by the packaging material. In absolute barrier systems like well closed metal or glass containers the loss or gain of organic volatiles from the package system is insignificant. The phenomena of sorption and permeation are especially applicable to the semipermeable package systems constructed from polymeric materials. This study will address one aspect of the phenomenon; the measurement of the mass transfer of organic volatiles through polymeric packaging films by permeation.

When selecting a package system for a product it is important to know the product's characteristics and what effect the gain or loss of organic vapor can be expected to have on product quality. It is desirable to identify which vapors are the most important determinates of product quality and to quantify the level of organic vapor gain or loss which will affect product quality. For example, the loss or gain of a specific volatile component from a product may change its functional properties. In the case of a food products the food's aroma serves as a sensitive and primary indicator of quality (Niebergall, 1978).

The equilibrium vapor pressures and types of organic volatiles in the product and the concentrations and types of vapors in the environment the package will be exposed to need to be identified. This information is important because the permeant vapor pressure and the type and/or mixture of vapors that come in contact with the package will determine the magnitude of sorption and permeation in and out of the polymer package.

The Level of Organic Volatiles in The External and Internal Package Envirements

In foods and other products the absence or presence of volatiles in the package or product may create changes in the sensory properties of flavor and smell. Loss of volatiles from the product may reduce the flavor below a threshold concentration of the volatile in the food so that consumers cannot detect the product's characteristic flavor. A product can also be deemed unacceptable when contaminating volatiles entering the headspace of the package from the external environment exceed the threshold levels for detection of those volatiles. Product aroma vapors exhibit readily observable odors at total vapor concentrations in air of 0.1 to 1 ppm (g/ml) (Weurman,

1974). The main components (by weight) of such vapors will be present in amounts from 0.001 to 0.1 ppm while trace components will be found in the 10^{-5} ppm range and lower (Weurman, 1974). Table 1 lists threshold values for some common volatile compounds (Weurman, 1974). From this table it is apparent that trace components are capable of contributing to the overall quality of the product. The quantity of a volatile that can be lost or gained before it is under the threshold level of the volatile is determined by the headspace volume of the package, the content of the package and interaction with these volatiles by the product and package.

Predicting the levels of the volatiles in the internal or external environment of the package is quite difficult. For the external environment volatiles the OSHA maximum exposure concentration limits for humans are indicative of the levels of organic volatiles that may be found in a work environment. The OSHA limits for toluene, methyl ethyl ketone, and ethyl acetate are 0.2 ppm (μg/ml) averaged over 8 hours, 0.59 ppm, and 1.4 ppm respectively (Weast, 1983). Although these levels seem low it is likely that volatile concentrations may exceed these levels in poorly ventilated areas such as storage rooms and in trucks or when the package is stored in close proximity to a strong source of volatiles.

The volatile concentration in the headspace of the package is dependent

Table 1

Odor Threshold Values For Compounds In Air

Taken from Human Response To Environmental Odors, C. Weurman, Academic Press, 1974.

Compound source:	Teranishi	Leithe	Laffort
Acetone		1.1	2.0×10^{-3}
Benzene		0.96	
Butyric Acid	2.4×10^{-4}	2.0×10^{-7}	
Ethanol	0.10	0.00012	0.01
Isopropanol	0.09		0.01
Menthol			0.01
Methyl acetate			6.0×10^{-4}
Methyl butyrate			1.0×10^{-5}
Phenol			2.0×10^{-3}
Vanillin		5.0×10^{-7}	

OSHA Exposure Limits

Taken from table D-132 Handbood of Chemistry and Physics, R.C. Weast ed., CRC Press, (1982).

Ethyl acetate	1.4 ppm
Isopropanol	0.98 ppm
Methyl Ethyl Ketone	0.59 ppm
Toluene	0.2 ppm averaged over 8 hours

Values given in ppm (μg/ml).

on the equilibrium vapor pressure of the volatiles with the product and the rate of loss or gain through the package walls. Vapor pressure of pure aroma volatiles are reported to lie in the range of 10 to 10^{-3} mmHg (Haring, 1974). These volatiles are usually present as minor components of the packaged product. The total content of aromatic materials in food products (with the exception of spices) is usually in the range from 1 to 100 mg. per kg. (Niebergall, 1978). For solutions of materials the ideal case is assumed to hold true so that the partial vapor pressure of an odorant in the headspace above a mixture will be directly proportional to the odorant concentration as predicted by Raoult's law or by Henry's law, $p=kc$ (Haring, 1974). For Raoult's law, k is the saturated vapor pressure of the pure odorant at the test termperature. For Henry's law, k is a constant which is specific for dilute solutions. In some cases positive deviations can occur in Raoult's law if the solute and solvent belong to chemically different types (Haring, 1974). The prediction of volatiles in solid products is much more difficult because the odorants are no longer in one homogeneous liquid phase and sorption/desorption of the vapor by different parts of the product is likely to occur.

The Permeation Mechanism For The Transfer of Organic Vapors Through Polymers

The rate of permeation of a substance through a material is usually described by the permeability coefficient (P), expressed as the quantity of permeant that passes through a material of a unit thickness, per unit time, per unit surface area for a given concentration or pressure gradient of the permeant (e.g. grams-mils/m^2· day · mmHg). The permeability coefficient ($\bar{P}$) can be determined from direct measurement of the rate of transfer of a substance through a material or from the relationship $\bar{P} = D \cdot S$, where D and S are separately determined (Crank and Park, 1968). D is the diffusion coefficient which describes the rate of movement of a diffusing permeant through the polymer, usually expressed as length^2/unit time (e.g.cm^2/sec). S is the solubility coefficient of the permeant in the polymer, expressed as the amount of permeant sorbed in the polymer matrix per gram or volume of polymer per unit pressure gradient (e.g. g/g·mmHg).

Mass transport through polymeric materials occurs by a diffusion process rather than by a flow process such as Knudsen or Poiseuille flow that occurs through porous materials (Lebovitz, 1966). The diffusion processs is influenced by the characteristics of the polymer and

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and diffusant molecule, the temperature, and in the case of organic vapors the concentration of the diffusant in the polymer. Thus, if permeation is to occur, the permeant molecule has to undergo the following processes in succession: (i) dissolution of the penetrant molecule into the surface of the polymer film; (ii) diffusion of the penetrant molecule through the polymer matrix; and (iii) desorption of the permeant molecule from the other surface of the film (Lebovitz, 1966). Meares (1965a) describes the permeation process in the following way :

> "Where the diffusate and polymer are miscible and constitute a single phase, diffusion takes place uniformly throughout the polymer determined by the gradient of the chemical potential of the diffusate. The polymer sheet separates two gases with unequal partial pressures so that more of the diffusing substance dissolves in the polymer at the high pressure side than the low pressure side. This sets up a concentration gradient across the polymer film and diffusion takes place down this gradient. There is a continuous net dissolution of the diffusant into the polymer at the high pressure side and a net evaporation of the diffusant at the low pressure side side maintaining the gradient. Usually after a transient state buildup a steady state of flow is

> attained with a constant transmission rate, provided a constant pressure difference is maintained across the film. It is speculated that some flow may also take place through an interconnecting capillary or crack system as a result of a pressure gradient or nature of the polymer structure. A partially crystalline polymer consists of almost impermeable crystalline regions and relatively amorphous regions. Boundaries between these regions may act like a network of cracks and pores."

The diffusion process is able to take place because polymer molecules have a random kinetic agitation or heat motion. The polymer chain segments have vibrational, rotational and translational motions that continually create temporary "holes" in the polymer matrix. The creation of these "holes" allows penetrant molecules to move through the polymer matrix under the influence of the concentration gradient. The amplitude and motion of the polymer molecules is directly related to the temperature, chemical composition and morphology of the polymer. The glass transition temperature (Tg) marks the transition from a "glassy" polymer state to a "leathery" polymer physical state. This increased flexibility of the polymer is caused by the unfreezing (on heating) of micro brownian motion of polymer chain segments 20-50 carbon atoms in length (Boyer, 1977).

This increase in polymer chain segmental mobility above the glass transition temperature corresponds with an increase in permeability and diffusion.

Small diffusant molecules like the permanent gases: oxygen, nitrogen and carbon dioxide, have almost no effect on the polymer molecules while sorbed into the polymer matrix. Their kinetic agitations are rapid compared to those of the polymer chains. The rate of diffusion of these molecules is therefore controlled by their agitation which is related to the amount of energy present in the system, as measured by the temperature. If a concentration gradient is present across a film the frequency of the jumps of the diffusate past the polymer chains gives a net flux of the diffusate molecules through the film (Meares, 1965a). Organic vapors which are comparable in size or larger than the polymer chain segments diffuse by a more complicated mechanism which is dependent on the motions of both the polymer and diffusant molecule. The molar volumes of organic penetrants are larger than the molar volumes of the permanent gases. Organic molecules may also have greater solubility in the polymer. These effects result in significant swelling of the polymer by sorbed organic molecules. Organic molecules sorbed by the polymer act as a plasticizer, lowering the glass transition temperature and increasing the polymer's segmental motions at all temperatures, which results in further plasticization and swelling

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(Meares,1965b). Diffusion depends on the frequency of penetrant molecular jumping and polymer chain segmental mobility, therefore the diffusion and permeability will increase with the sorbed vapor content. The sorbed vapor content of a polymer is primarily related to the chemical similarities between the polymer and diffusate and the vapor pressure of the diffusate that the polymer is exposed to (Fujita, 1968).

The diffusion of organic vapors in polymers is dependent largely on the segmental mobility of the polymer chains at a given temperature. For a given polymer, in the absence of any plasticizing agents, the cohesive energy density, which is a quantitative measure of the attractive forces holding the polymer chains together in the polymer matrix, determines the polymer's melt and glass transition temperatures. Polymers which are soft and rubbery at room temperature (25° C) are referred to as elastomers. The distribution of their molecular segments and kinetic motions are quite similar at the molecular level to those of molecules in a normal liquid (Meares, 1965a; Rogers, 1965). Because the behavior of normal liquids has been well studied the mechanisms of sorption, diffusion and permeation of organic vapors are best understood for elastomers and polymers well above their glass transition temperatures (e.g. polyethylene, polypropylene). Diffusion and permeation in polymers at temperatures below the polymer's Tg has anomalous and mo

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and more complex behavior that is not well understood at this time (Hernandez, 1984). The remaining discussion will be limited to the permeation, diffusion and sorption characteristics of organic vapors in polymers at temperatures well above the polymer's glass transition temperature.

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Permeability Theory For Organic Vapor Permeation In A Sheet

The general theory of permation can be expressed by a series of mathematical expressions which are summarized here from Rogers (1964). A more complete treatment of the mathematical expressions can be found in Crank (1973). The rate of permeation or the transmission rate (P) (or flux, J) is defined as the amount of penetrant passing, during unit time, through a surface of unit area normal to the direction of flow:

$$P = Q / A t \qquad (1)$$

Where Q is the total amount of permeant which has passed through area (A) during time (t). Given a unit area of film L (cm) thick exposed to a penetrant at pressure p_1 on one side and a lower pressure p_2 on the other side the concentration of the penetrant in the first layer of film ($x = 0$) is c_1 and in the last layer ($x = L$) is c_2. When the rate of permeation through a plane at a distance x from the high pressure surface is P, the rate through a plane at a distance x + dx will be $P + (\partial P/\partial x)dx$. Therefore the amount retained per unit volume of polymer is equal to the rate of change of concentration with time:

$$- \partial P/\partial x = \partial c/\partial t \qquad (2)$$

In the steady state of flow $\partial c/\partial t$ is zero, P is constant and the rate of permeation is directly proportional to the concentration gradient as expressed by Fick's first law of diffusion:

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$$P = -D \, \partial c / \partial x \qquad (3)$$

Where D is the differential diffusion coefficient. Assuming D to be constant, this can be integrated between the two concentrations c_1 and c_2:

$$P \int_{x=0}^{x=L} dx = - D \int_{c2}^{c1} dc$$

to give:

$$P = D \, (c_1 - c_2) \; / \; L \qquad (4)$$

The equilibrium concentration c_1 and c_2 of penetrant in the surface layer of the polymer can be related to the partial pressures p_1 and p_2 in the gaseous phase by Henry's law, $c = S \cdot p$. Here S is the solubility coefficient of the penetrant in the polymer and c is the concentration of vapor (g/g) in the polymer. When Henry's law is obeyed there is a linear relationship between concentration and pressure and S is constant so that:

$$P = D \cdot S \cdot (p_1 - p_2) \; / \; L$$

or

$$\bar{P} = D \cdot S = P \cdot L \; / \; (p_1 - p_2) \qquad (5)$$

Where $\bar{P}$ is the permeability coefficient which is the quantity of permeant permeated through a film of thickness L per unit membrane area, per unit permeant driving force. Unlike permeant-polymer systems involving permanent gases such as oxygen, D and S are not constant for all permeant pressures for organic permeant-polymer systems. When D varies as a function of the concentration of permeant for organic permeant-polymer systems, $D = f(c)$. From Equations (3) and (4) the

expression of Fick's second law takes into account the change in the diffusion coefficient with concentration at different locations within the polymer:

$$\partial c/\partial t = \partial/\partial x \, (D(c) \, \partial c/\partial x) \qquad (6)$$

A mean value of D can be calculated for a range of permeant concentrations (c), to give the mean or integral value of the diffusion coefficient ,$\bar{D}$, over the concentration range c_1 to c_2 Rogers (1964):

$$\bar{D} = \int_{c2}^{c_1} D(c) \, dc \Big/ \int_{c2}^{c_1} dc = \int_{c2}^{c_1} D(c) \, / \, (c_1 - c_2) \qquad (7)$$

Determination of $\bar{D}$ over several consecutive ranges of concentration enables one to estimate the dependence of D on concentration. Equation (7) simplifies to Equation (8) when $c_2 = 0$ (ie most permeation experiments) and $\bar{D}$ is determined for a number of values:

$$\bar{D} = 1 \, / \, c_1 \int_{o}^{c_1} D(c) \, dc \qquad (8)$$

When experimental conditions are such that c_2 is always zero and $\bar{D}$ is determined for a number of values of c_1, D can be expressed as some explicit function of c. Then D as a function of c can be found by simple differentiation. In any case $\bar{D}$ can be plotted versus c and the slope as a function of c leads to an estimate of the desired concentration dependence of D(c) (Rogers, 1965a).

In the steady state of flow through a planar membrane the permeability

rate P is constant by definition:

$$P = - D\ (dc/dx) = \text{a constant} \qquad (9)$$

Therefore regardless of the fact that D(c) may be a function of concentration and dc/dx is therefore nonlinear, the product of these two quantities is a constant in the steady state of flow. By integration between c_1 and c_2, the two surface concentrations of the membrane of thickness (L) one obtains:

$$P = (1\ /\ L)\int_{c2}^{c_1} D(c)\ dc = \bar{D}\ (c_1 - c_2)\ /\ L \qquad (10)$$

Where D is the integral diffusion coefficient defined by equation (7). When $c_1 >> c_2 \approx 0$ equation (10) reduces to:

$$P\ L = \int_{o}^{c} D(c)\ dc \quad \text{or} \quad D(c) = d(L\ P)/dc \qquad (11)$$

and an estimate of the dependence of D(c) on c can be obtained either analytically or graphically from the dependence of (L P) on c (Rogers, 1964).

Another estimate of $\bar{D}$ follows from the definition of the permeability coefficient as the product of the diffusion and solubility coefficients. When the diffusion process is concentration dependent:

$$P = \bar{P}\ (p_1 - p_2)\ /\ L \qquad (12)$$

where $\bar{P}$ is the value of the permeability coefficient for the pressure gradient $(p_1 - p_2)$, corresponding to the equilibrium surface concentrations c_1 and c_2 which define the integral diffusion coeffient. Thus from Rogers (1964):

$$P = [1/(c_1-c_2)\int_{c2}^{c_1} D\ dc]\cdot[(c_1-c_2)/(p_1-p_2)]\cdot[(p_1-p_2)/L]$$

$$\bar{P} = \bar{D}\ \bar{S} \qquad (13)$$

so that $$\bar{D} = \bar{P}\ /\ \bar{S} \qquad (14).$$

For the usual experimental conditions where c_2 and p_2 are approximently equal to zero, the quantity $\bar{S} = (c_1-c_2)/(p_1-p_2)$reduces to the solubility coefficient, $S = c_1/p_1$.

The above permeability theory derivation only considers the case where D and $\bar{P}$ are functions of concentration and S is constant. However in many organic permeant-polymer systems the solubility coefficient (S) is a function of the concentration of permeant in the polymer and does not always follow Henry's law, partricularly at high permeant concentrations.

When a permeant diffuses through a membrane in which it is soluble there is an interval of time from when the permeant first enters the membrane until the steady state of permeation is established. During this time both the rate of flow and the concentration at any point in the membrane vary with time. If the diffusion coefficient is constant, the membrane is initially free of permeant and the permeant is continually removed from one side of the membrane ($c_2 = 0$), the amount of permeant (Q_t)which passes through the membrane in time (t) is given by (Crank, 1975):

$$Q_t/LC_1 = Dt/L^2 - 1/6 - 2/\pi^2 \sum_{n=0}^{\infty} (-1)^n/n^2 \exp(-Dn^2\pi^2 t/L^2) \qquad (15)$$

As t goes to ∞ the steady state of permeation is approached and the exponential terms become negligibly small so that the transmission profile curve of Q_t versus t tends to the line

$$Q_t = Dc_1/L\ (t - L^2/6D) \qquad (16)$$

This line has the intercept, θ , on the t-axis given by:

$$\theta = L^2/6D \qquad (17)$$

From the lag time the diffusion coefficient can be deduced from Equation 17 and finally the solubility can be obtained from Equation 14 (Daynes, 1920 and Barrer, 1941).

Frisch (1957,1958,1959) and Pollack and Frisch (1959) have developed expressions which allows the calculation of the diffusion coefficient from time lag data for systems in which the functional dependence of D on any or all of the variables: concentration, spatial coordinates and time, are known or can be assumed. Frisch (1957) gives expressions for the time lag in linear diffusion through a membrane with a concentration dependent diffusion coefficient. Frisch's method yields numerical values for parameters of the diffusion coefficient concentration dependence expression (i.e. $D = D_o\exp(\gamma c)$). This method can be quite complex as the concentration (c) as a function of x is necessary and can be very complicated (Crank and Park, 1968).

Pollack and Frisch (1959) have shown for a large class of functional diffusion concentration dependencies (D(c) on c the following inequality holds:

$$1/6 \leq \theta D/L^2 \leq 1/2 \qquad (18)$$

Thus an estimate of the integral diffusion coefficient can be made using the time-lag expression derived for a constant D, Equation 17 is at worst too small by a factor of three (Rogers, 1964).

Sorption And Desorption Theory of Organic Vapors In A Sheet

Constant Diffusion Coefficient:

When the concentration of permeant within the surfaces of a membrane of thickness (L) is maintained constant over time, the amount of diffusant, M_t, taken up by the sheet in a time t is given by (Crank and Park, 1968):

$$M_t/M_\infty = 4(Dt/L^2)^{1/2}[1/\pi^{1/2} + 2\sum_{n=0}^{\infty}(-1)^n \mathrm{ierfc}(nL/2(Dt)^{1/2}] \qquad (19)$$

The uptake of permeant by the membrane is considered to be a process controlled by a constant diffusion coefficient D, and M_∞ is the equilibrium sorption at infinite time. The value of D can be deduced from a graph of M_t/M_∞ versus $(t/L^2)^{1/2}$ when the slope of the initial approximately linear portion of the graph up to 50% of the M_∞ is a staight line (Crank and Park, 1968). If D is a function of concentration and increases as the concentration of the permeant increases, the graph is linear over a larger increase in M_t.

Another form of the sorption-desorption equation is (Crank and Park, 1968):

$$M_t/M_\infty = [1-8/\ {}^2]\sum_{m=0}^{\infty}[1/(2m+1)]\cdot\exp[(-D(2m+1)^2\pi^2 t)/L^2] \qquad (20)$$

From Equation 20 the value of t/L^2 for which $M_t/M_\infty = 1/2$ which is written as $(t/L^2)_{1/2}$ is approximated by (Crank and Park, 1968):

$$(t/L^2)_{1/2} = (-1/\pi^2 D)\ \ln[\pi^2/16 - 1/9\ (\pi^2/16)^9] \qquad (21)$$

The diffusion cofficient, assumed to be constant, determined from Equation 21 is sometimes referred to as the half-time diffusion coefficient is given by

$$D_{t1/2} = (0.04919\ L^2)/t_{1/2} \qquad (22)$$

Concentration Dependent Diffusion Coefficient:

For systems where there is a concentration dependent diffusion coefficient (e.g. polymer-organic vapor systems) the initial gradient from each sorption curve yields a mean of integral diffusion coefficient values (D) using Equation 22 (Crank and Park, 1968). Calculations have shown that this integral diffusion coefficient obtained from one experiment is a reasonable approximation to Equation 8 (Crank and Park, 1968). The limits of integration here become the concentration c_1 at the surface of the sheet and c_2 in the center of the sheet. By measuring the integral diffusion coefficient at several permeant concentrations a graph of Dc_1 versus c_1 can be drawn and numerical or graphical differentiation with respect to c_1 gives a first approximation to the relationship between D and c.

The average of the values of the integral diffusion coefficients calculated from sorption and desorption data is

$$D_{ave} = 1/2\ (D_s + D_d) \qquad (23)$$

a better approximation to D than either D_s or D_d separately (Rogers, 1964). In many polymer systems the diffusion coefficient depends approximately either linearly or exponentially on concentration. For these cases Crank (1956) has produced correction curves showing the difference between $(1/c_1)\int_o^{c_1} D(c)\,dc$ and D/D_o. When M_t/M_∞ is greater than 0.4 or so the solution of Equation 20 then becomes (Rogers, 1964):

$$\ln(1- M_t/M_\infty) = \ln(k/\pi^2) - D\pi^2 t/L^2 \qquad (24)$$

The value of D can then be calculated from the limiting slope (k) at large values of t of a plot of $\ln(M_\infty - M_t)$ versus t or t/L^2 (Rogers, 1964).

Characteristics of Organic Vapor Mass Transport Through Polymers Above Their Glass Transition Temperature

Permeation Measurements:

Most investigations involving the diffusion of organic vapors in polymers above their Tg have been theoretical sorption-desorption types of studies, where the effects of the type of polymer, penetrant, temperature and penetrant concentration on the diffusion coefficient have been measured (Fujita, 1968). The published permeation data for organic vapors in polymers is very limited and is divided between results from studies with glassy polymers and studies with polymers above their glass transition temperatures. The glass transition temperature, (Tg), of a polymer marks the change in polymer properties from glassy type structure properties to an amorphous type structure properties as the temperature increases marking the onset of polymer chain segmental mobility for a polymer (Rodriguez, 1970). Recently there has been a number of papers published involving studies on the organic vapor permeation characteristics of various commercial homopolymer and laminate structures and applying the results to packaging problems with foods (Hilton and Nee, 1978, Becker et. al., 1983, Gilbert et. al., 1983, Murray, 1984, DeLassus, 1986).

The conditions of a typical permeation measurement utilizes: (i)

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constant surface concentration of permeant at the film surfaces where one surface of the film is maintained at a penetrant concentration of approximently zero and the other is at the equilibrium concentration corresponding to a permeant pressure P_1; (ii) constant temperature; and (iii) the diffusion coefficient is assumed to be a function of concentration only. Traditionally the literature on studies involving the diffusion of gases and vapors through polymer membranes utilized a manometric technique for quantitation under the above mentioned test conditions (Stannett et.al., 1972). Recently both isostatic and quasi-isostatic test methods have been described for studying the diffusion of organic vapors through barrier films using gas chromatographic analysis for quantitation (Stannett et al., 1972, Zobel, 1982, Baner et. al., 1986, Hernandez et. al. 1986). In the quasi-isostatic method, the accumulation of diffusate in the low partial pressure (low concentration) side of the film is measured as a function of time. The amount of vapor, q, which has passed through a unit area of film during time, t, is plotted as a function of time giving a characteristic permeation curve or transmission profile (see Figure 16). Typically, vapors permeating through a polymer at a temperature above its Tg, gives a the plot of (q) versus (t) that is convex towards the time axis and asymptotically approaches a straight line as the time increases (Fujita, 1968). When the asymptotic portion of the curve gives a rate of permeation dq/dt, which is independent of time, the permeation is said to be in steady state. The slope of this straight line gives the

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permeation rate (P) for the given experimental conditions. The concentration of diffusate in the film no longer changes with time when the steady state is reached.

Sorption Measurement:

The surface concentration of a diffusant in contact with its vapor or solution can be interpreted in terms of the diffusion coefficient (Crank and Park, 1968). The surface concentration is usually obtained from the equilibrium determination of the uptake of vapor by the solid polymer. Sorption kinetic measurement can also be used to calculate the diffusion coefficient. Determination of the diffusion coefficient by the sorption technigue has many advantages over the permeation lag time method because such problems as leakage, membrane distortion, and problems from holes in the membrane are eliminated (Crank and Park, 1968). However interpretation of the diffusion coefficient when time effects are present is still a problem for the sorption method as well.

In a sorption experiment a uniform film of a given polymer initially equilibrated with vapor of a given diffusate substance at a certain pressure or concentration is suddenly exposed to a different pressure or concentration of the same vapor. The gain or loss in weight of the film is measured as a function of time (t), while a constant pressure or concentration is maintained. In most experiments the initial pressure or concentration in contact with the film is zero (Fujita, 1968).

Data from a sorption experiment is generally reported in the form of a sorption curve. The sorption curve is produced by plotting the amount of vapor M(t) (in grams) absorbed in or desorbed from a unit gram or cubic centimeter of dry polymer against the square root of time (t) (Fujita, 1968). For theoretical analysis a plot $M(t)/M_{\infty}$ against the ratio $(t)^{1/2}L$ is made, where L is the thickness of the dry film and M_{∞} is the equilibrium sorbed concentration of vapor in the polymer. This plot is referredto as the reduced sorption curve (Fujita, 1968).

The distribution of diffusant and its change with time in a given film during absorption and desorption are governed by the one-dimensional differential equation due to Fick with the space coordinate in the direction of film thickness (Fujita, 1968). Solutions of Fick's equation applied to sorption experiments where at $t=0$ the concentration of diffusate is uniform in the film is subject to the following assumptions: 1) D is a function of c only; 2) when the ambient pressure of the permeant is changed from an initial value to a final pressure the concentrations in the film instantaneously increase to an equilibrium value with the contacting pressure (Fujita, 1968). Sorption curves having characteristics expected from the above assumptions are called Fickian or normal type. Studies of the diffusion of small molecules in polymers at temperatures well above the polymer's glass transition

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temperature have shown that the kinetics of sorption of organic vapor are invariably Fickian (Fujita, 1968). Deviations from Fickian sorption behavior have been observed when the temperature of the sorption measurements are at or below the polymer's glass transition temperature (Fujita, 1968).

The following is a summary of important Fickian sorption features from Fujita (1968):

(a) Both absorption and desorption curves are linear in the initial stage. For absorption, the linear region extends over 60% or more of M_∞. For D(c) increasing with c the absorption curve is linear almost up to the final sorption equilibrium.

(b) Above the linear portions both absorption and desorption curves are concave to the abscissa axis.

(c) For the same initial and final concentrations a series of absorption curves or desorption curves for films of different thicknesses are superposable to a single curve if each curve is replotted in the form of a reduced curve.

(d) The reduced absorption curve always lies above the corresponding reduced desorption curve if D is an increasing function of c . Both reduced curves coincide over the entire range of t when D is constant. The divergence of the two curves increases the more concentration dependent D is on c.

(e) For absorptions the initial slope of the rec

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reduced curve becomes larger as the concentration increment increases provided that D increases with c in the concentration range studied. Fujita (1968) further notes that criteria (a), (b) and (c) are independent of the form of D as a function of c thus when these criteria are satisfied the system is said to exhibit Fickian sorption.

At the molecular level the essential conditions for Fickian sorption is the high mobility of polymer segmental units. This explains why the sorption kinetics of organic vapors by polymers become Fickian when the measurement is carried out at temperatures well above the glass transition temperature (Fujita, 1968).

Permeability is related to diffusion and solubility by the relationship $\bar{P} = D \cdot S$. The complex permeability process is best understood by considering the effects of various factors on solubility and diffusion. This portion of the text on the characteristics of the permeation and diffusion of organic vapors through polymer membranes follows from the excellent review in the chapter on Permeability and Chemical Resistance by C.E. Rogers from the book Engineering Design for Plastics edited by E.Baer (1964).

Solubility Characteristics

The solubility of a mobile component in a solid can be described as the distribution of the component between two or more phases. The uptake of penetrant by a solid is called sorption and can be considered to have adsorption or absorption as the basic mechanism (Rogers, 1964). There is no way of distinguishing between either physical adsorption and chemisorption or between absorption and adsorption, so that the overall process is best considered a composite of these various modes (Rogers, 1964).

The dependence of the solubility coefficient on temperature generally follows an Arrhenius type relationship:

$$S = S_o \exp(- Hs/RT) \qquad (25)$$

Where Hs is the apparent heat of solution (Rogers,1964). The process of sorption by a polymer may be considered to involve two stages: first condensation of vapor onto the polymer surface followed by solution of the condensed vapor (Rogers, 1964). The heat of solution can be expressed as the sum of the molar heat of condensation (H_c) and the partial molar heat of mixing (H_1). The heat of mixing is always positive and the heat of condensation can be positive or negative depending on whether the molecule is a gas or vapor. For permanent gases, Hs is slightly positive so that S increases slightly with temperature. However for the more condensable vapors (like organic compounds) Hs is negative due to the relatively large heat of condensation, thus the solubility decreases with increasing temperature (Rogers, 1964).

A sorption isotherm is a curve that relates the equilibrium concentration of the penetrant in the polymer (c), to the concentration of penetrant (p) surrounding the solid, at any constant temperature. There are four basic types of isotherms observed in polymer systems. These isotherms depend on the degree of penetrant-polymer interaction (Rogers, 1964). Type I follows Henry's law where the concentration is linearly dependent upon pressure. Type II is characteristic in systems where only a unimolecular layer of sorbed substance forms on the substrate showing a concave curve towards the pressure axis. Type III sorption is characteristic of multilayer adsorption where the attractive forces between penetrant and solid are greater than those of the penetrant molecules themselves, giving a sigmoid shaped curve. Type IV sorption forms a convex curve towards the pressure axis. Type IV sorption results when forces between the penetrant and substrate are relatively small so that the sorption process occurs essentially randomly. The solubility coefficient at a given permeant partial pressure can be calculated from these sorption isotherms by dividing the sorbed concentration (c) by the corresponding ingoing pressure (p). An empirical equation describing the type IV isotherm for the sorption of

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of nonpolar organic molecules in polyethylene and other nonpolar polymers is:

$$S = S_o \exp(\sigma c) \qquad (26)$$

Where S_o is the extrapolated value of S at $c=0$ and σ is a characteristic parameter for the penetrant-polymer system at a given temperature (Rogers et.al., 1960).

The Langmuir equation for sorption leads to a type II isotherm. The solubility coefficient can be written as:

$$S = c/p = b\, c_m / (1 + bp) \qquad (27)$$

where c_m is the maximum possible sorption and b is a parameter characteristic of the system (Rogers, 1964). The modified BET equation can be used to describe type II, III, and IV isotherms (Rogers,1964).

$$S = c/p = \frac{\beta c_m [1 - (n + 1)(p/p_o)^n + n(p/p_o)^{n+1}]}{(p_o - p)\cdot[1 + (\ -1)(p/p_o) - \beta (p/p_o)^{n+1}]} \qquad (28)$$

where: p^o is the permeant saturated vapor pressure

c_m is the sorbed concentration of vapor corresponding to a complete monolayer sorption

$\beta = \exp(Q_1 - Q_L / R\,T)$ where Q_1 is the heat of adsorption for the first layer, Q_L is the heat of vaporization for the pure liquid penetrant.

n = number of layers on which sorption can take place

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The magnitude of the solubility for a penetrant in a polymer increases with : (i) the chemical similarity of the penetrant-polymer; (ii) the more condensable or lower the boiling point of the vapor; (iii) the larger the molar volume of the condensed penetrant; and (iv) the lower the percent crosslinking and the crystallinity of the polymer (Rogers, 1964). The sorption of penetrant by the polymer has a profound effect on the solid's properties. In addition to the plasticizing action of the sorbed penetrant there may be changes in the polymer structure due to swelling and distortion incurred during sorption as well as actual chemical attack on the polymer (Rogers, 1964).

Diffusion Characteristics

The temperature dependence of diffusion coefficients over small temperature ranges at a constant vapor concentration can be represented by an Arrhenious type relationship:

$$D = D_o \exp\left(-E_d / R\,T\right) \qquad (29)$$

Where E_d is the apparent activation energy for the diffusion process (Rogers, 1964). The activation energy of diffusion is associated with the energy required for 'hole' formation in the polymer matrix plus the energy required to move the molecule through the polymer structure. The pre-exponential factor, (D_o), can be thought of as being related to the frequency and magnitude of the holes or 'looseness' within the polymer microenvironment in the absence of penetrant. The activation energy of the polymer increases at temperatures above the polymer's glass transition temperature (Rogers, 1964).

The magnitude of the concentration dependence of diffusion in any given polymer is dependent on the temperature, molecular size, chemical similarity between penetrant and polymer and the penetrant concentration in the polymer. The solubility coefficient is often essentially constant at low vapor activities for the more volatile vapors while the diffusion coefficient exhibits significant concentration dependence. The concentration dependence of the diffusion coefficient can be represented by the equation:

$$D = D_o \exp(\gamma c) \qquad (30)$$

Where γ is a characteristic constant, D_o is a pre-exponential factor representing the diffusion coefficient at zero concentration or the limiting diffusion coefficient and c is the concentration of permeant in the polymer (Rogers, 1964).

The diffusion coefficient may deviate significantly from a linear or exponential dependence on c when the measurements are made over wide temperature ranges and vapor concentration, or activity, especially with more easily condensable vapors (Rogers, 1964). Such behavior has been observed for allyl chloride in polyvinylacetate; for n-alkyl acetates in polymethylacrylate; and for hydrocarbons in polyethylene (Meares, 1958a b; Fujita, 1960; Rogers, 1960). The concentration dependence in these systems can be represented by a simple exponential function of vapor activity:

$$D = D_o \exp (\alpha a_1) \qquad (31)$$

Where α is a constant and a_1 is the vapor activity on the high concentration side of the film (Rogers, 1960). Equation 31 may be a more general equation which includes as special cases Equation 30.

The magnitude of D_o depends primarily on the chemical nature, size, and shape of the penetrant and the morphology of the polymer. The constants γ and α can be interpreted as characterizing the effectiveness of various penetrants to plasticize a polymer and to facilitate its segmental mobility (Rogers, 1964). For the diffusion of homologous hydrocarbon vapors in various elastomers at a given temperature, γ and α increase as the size and shape of the diffusing molecules decrease and as the chemical similarity of the penetrant polymer system increases (Rogers, 1964).

A penetrant molecule with a branched structure decreases the diffusion coefficient more than the effect on D caused by an increase in its carbon chain length. This indicates that diffusion occurs preferentially along the direction of greatest length of the permeant molecule (Rogers, 1964). The molecular weight of a polymer has little effect on the diffusion rate whereas chemical modification and mophology of the

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polymer have a much greater effect (Rogers, 1964). The diffusion coefficient decreases with an increased degree of crosslinking and crystallization and with the amount of impermeable filler. Orientation by stretching the elastomers does not appreciably affect either solubility of diffusivity until elongation results in an increase in crystallization (Rogers, 1964).

Free Volume Theory:

The effect of the polymer structure on diffusion can usually be described in terms of the Free Volume Theory. The Free Volume Theory has been shown to provide a fairly reasonable explanation of the princpal features of the concentration and temperature dependence of the diffusion of organic vapors in amorphous polymers above their Tg (Fujita, 1968). The theory states that the mobilities of both the polymer chain segment and the diffusant molecule in a polymer-penetrant mixture are primarily determined by the amount of 'free volume' present in the system. The reason why the diffusion coefficients of polymer-organic penetrant systems are so markedly concentration dependent is because the mobilities of diffusant molecules and polymer chain segments are extremely sensitive to slight changes in the average free volume of the system (Fujita, 1968).

Fujita, (1961) considered that the mobility of the diffusant component

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is related to its diffusion coefficient relative to the plane of reference moving with the polymer component. The mobility of the diffusant depends on the average fractional free volume f of the system.

These are related through an expression generally referred to as the Doolittle type, originally introduced by Doolittle (1951, 1952) to describe the temperature-dependence of the viscosity of simple liquids (Fujita, 1968). The Doolittle type equation was then taken by Williams et. al. (1955) to derive their noted WLF equation. The WLF equation has proved extremely useful for representing the temperature dependence of steady flow viscosities and relaxation times of amorphous polymers in solid and in concentrated solution (Fujita, 1968).

The relationship between the diffusion coefficient D and the fractional free volume f is given by Peterlin (1977):

$$D = A \exp(-B/f) \qquad (32)$$

Here A is a frequency factor and B is a measure of the minimum hole size for the jump process. Fujita (1961) had assumed that

$$f = f_o + \beta c \qquad (33)$$

where c is the mass fraction of the penetrant f_o is the fractional free volume at zero vapor concentration and β denotes the the effectiveness of the penetrant molecule for increasing the free volume of the polymer. Substituting Equation 33 into Equation 32 and assuming $\beta c << f_o$ Kwei and Wang (1972) got the expression:

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$$D = D_o \exp (\gamma c) \qquad (34)$$

where

$$\gamma = B \beta / f_o^2 \qquad (35)$$

Equation 35 shows that the concentration coefficient γ depends on f_o and β. That is, γ is a function of not only the fractional free volume but also of the interaction between the penetrant and the polymer (Choy et. al., 1984). Ng et. al. (1985) modified the γ term of Equation 34 to take into consideration the effect of crystallinity on the free volume of the polymer:

$$\gamma = B \beta / [f_o^2(1-X_m)] \qquad (36)$$

Where the quantity $(1-X_m)$ is the amorphous mass fraction of the the semicrystalline polymer. Crystallites in the polymer serve to decrease the segmental mobility of polymer chains in the amorphous phase of the polymer (Ng et. al., 1985).

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Permeability Characteristics

The temperature dependence of the permeability coefficient over small ranges of temperature can be described by an Arrhenius type relation:

$$\bar{P} = \bar{P}_o \exp\left(-E_p / R\,T\right) \qquad (37)$$

Where E_p is the apparant activation energy for the overall permeation process and the prexponential factor $\bar{P}_o$, is the permeability coefficient at zero degrees Kelvin (Rogers, 1964). The apparent activation energy E_p follows from the definition $\bar{P} = D\,S$ where:

$$E_p = E_d + H_s \qquad (38)$$

and

$$\bar{P}_o = D_o \cdot S_o \qquad (39)$$

The concentration dependence of the permeability coefficient for systems that follow the solubility behaviour in Equation (26) and diffusion behaviour described by Equation (31) can be written as a combination of the two equations:

$$P = P_o \exp\left(\alpha a_1 + \gamma c\right) \qquad (40)$$

When the sorbed vapor concentration increases rapidly with increasing vapor pressure, a plot of log $\bar{P}$ versus vapor activity becomes nonlinear (Rogers et al, 1960). When the solubility of the vapor approximates Henry's law, log $\bar{P}$ varies linearly with vapor pressure or activity (Rogers, 1964). At sufficiently low vapor activities Equation (40) reduces to a linear dependence of $\bar{P}$ on vapor pressure:

$$\bar{P} = \bar{P}_o + K \cdot p \qquad (41)$$

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where K is a constant and p is the vapor pressure (Cutler et. al, 1951).

In most polymer-penetrant systems the permeability generally increases with the chemical similarity between components. The permeation rate through the nonpolar polymer membrane polyethylene, is lowest for strongly polar penetrant molecules and greatest with hydrocarbons in the following order: alcohols, acids, nitro-derivatives, aldehydes and ketones, esters, ethers, hydrocarbons and halogenated hydrocarbons (Rogers, 1964). The molecular weight of the polymer has been found to have little effect on the rate of permeation (Rogers, 1964). The limiting diffusion coefficient (D_o) decreases and the limiting solubility coefficient (S_o) increases exponentially with an increase in the overall molecular volume and cross sectional area of the penetrant. As a consequence of this compensating behavior, $\bar{P}_o$ is much less dependent on the penetrant size and shape than either S_o or D_o is individually (Rogers, 1964).

An empirical relationship has been developed for the permeability factor of polyethylene (PE) to a number of organic liquids that can be useful in prediction of the permeability of PE to different organic vapors (Salame, 1961, 1981). This relationship is based on the number of carbon atoms in the penetrant molecule as well as on the other functional groups or atoms present in the molecule and the molecular structure of the penetrant.

The permeation rate can be expected to decrease as the symmetry and cohesive energy density of the polymer increases (Rogers, 1964). This occurs mainly due to a decrease in the diffusion coefficient. Furthermore, the permeability decreases with an increased degree of cross linking and crystallinity in the polymer (Rogers, 1964). The diffusion coefficient is also largely responsible for this decrease in permeability. The solubility is affected relatively little, except at high degrees of crosslinking and crystallinity. There does not appear to be any simple relationship between the initial polymer density (as related to crystallinity content and morphology) and the value of $\bar{P}$ and D for vapors that markedly swell a polymer (Rogers, 1964). Variations in polymer density and morphology in the absence of vapor, are due to structural differences such as chain branching and to the thermo-mechanical history of the sample (i.e. orientation and crystallization conditions) (Rogers, 1964). The presence of solvent undoubtedly disrupts the initial local configuration of crystalline and amorphous regions so that the effective density and local molecular configurations vary in a nonlinear fashion both with time and as a function of distance in the sample (Rogers, 1964).

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Organic Vapor Permeation Measurement Techniques

There are three common techniques which have been used by researchers to measure the permeation of organic vapors through polymer films. A gravimetric technique, an absolute pressure type method and an isostatic or quasi-isostatic type method.

The gravimetric technique measures the weight gain or loss of an organic permeant permeating through a known surface area of a film sample. One of the more common approaches, the cup test, uses a shallow cylindrical dish containing liquid penetrant with the membrane sealed over the top. The assembled cup is placed in a controlled temperature and atmosphere environment and the weight loss of permeant through the membrane is measured (Lebovits, 1966; Martinovich and Boeke, 1957). A variation of this method involves filling a polymer pouch with silica gel absorbant, exposing it to an organic vapor atmosphere and measuring the uptake of vapor by the increase in weight over time (Laine and Osburn, 1977). The steady state permeation rate in these methods is reached when there is a constant weight gain or loss by the pouch or dish. The problems associated with these gravimetric methods include the limited vapor pressure range that can be used which prevents characterizing the concentration dependence of the permeability and diffusion coefficients and the lack of sensitivity of the method, particularly with the low permeation rates found with high barrier

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films. Other problems associated with the gravimetric method include the inability to evaluate the effects of co-permeants and sealing problems with the dish or when forming a pouch (Talwar, 1974).

The two remaining methods can be described as partition cell methods, where the permeant being tested is isolated on one side of the film and then detected on the other side as a function of time.

The absolute pressure method uses volumetric or manometric measuring techniques to directly measure the permeating gas or vapor. For pressure measurements this is done using a pressure gauge such a a MacLeod gauge or a calibrated capillary tube containing mercury for volumetric measurements. The sample is clamped into a permeation cell so that the only path for the vapor to move from one chamber to the other is through the film sample. The steady state permeation rate is determined from the conditions when there is a constant increase in pressure or volume with time in the low pressure side of the cell. Most organic vapor permeation measurements made before 1970 are variations of a high vacuum/time-lag see Hilton 1978 technique that was developed by Barrer and Skirrow (1948), and Rouse (1947) for measuring the permeation of gases such as O_2 and CO_2 (Stannet et. aL, 1972). Rogers et al (1956), Meyers et al (1957) and Meares (1958a) have made modifications and refined this method for measuring the permeation and diffusion of organic vapors through polymer films. A pressure-volume

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method was developed for measuring vapor permeabilities that correlates well with results obtained from the manometric measuring technique (Van Amerongen, 1946).

The American Society for Test Methods, ASTM, has developed a standard procedure D-1434-82 (Gas Transmission Rate of Plastic Film and Sheeting) which uses the pressure differential method and the so called 'Dow Gas Transmission Cell' for determining gas transmission rates of polymer films. This method is not considered suitable for measuring organic vapor permeation without some modifications to the test cell (Rogers, 1964).

The manometric/volumetric high vacuum methods have found widespread applicability and usage and are accepted techniques for measuring the permeation of gases and vapors through polymer membranes. Most theoretical studies of permeation and diffusion of specific organic vapor-polymer systems have used this method (Rogers, 1964). There are some problems with this method however, that detract from its overall usefulness. The high vacuum/lag time apparatuses used are quite complex and must have perfect seals in order to maintain a vacuum over long periods of time (particularly when testing high barrier films). Furthermore because there is an absolute pressure differential across the film, thin or easily deformable pressure sensitive films cannot be used without some kind of film support, especially at high pressure

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differentials. A more fundamental problem with the method also exists because the detection system cannot differentiate between co-permeating vapors. The method is therefore restricted to measuring the permeation of pure vapor only and the effects of copermeants, in particular water vapor, cannot be evaluated.

Most of the problems associated with the gravimetric and pressure differential methods can be avoided by the use of an isostatic and quasi-isostatic permeation method. With the isostatic and quasi-isostatic methods there is no absolute pressure differential between the two sides of the film. The partial pressure differential of the test vapor, provides the driving force with the total pressure on both sides of the film being equal to one atmosphere. This system allows films of any type and thickness to be evaluated over a range of permeant partial pressure values.

In an isostatic system the film sample is clamped in a permeation cell and the desired permeant concentration, in a carrier gas, is flowed continually over one side of the film. An inert carrier gas stream (the same as the permeant carrier gas) is flowed simultaneously over the low concentration side of the film carrying the permeant vapor to a detector. The steady state permeation rate is equal to the steady state concentration of permeant in the sweep gas times the sweep gas flow rate.

An early isostatic test method was developed that used chemical sorption of the permeating gases for quantification (Davis, 1946). Chemical sorption methods suffer from lack of sensitivity and better permeant detection methods are now available. Thermal conductivity detectors have been used to measure the increase of permeant in the sweep gas (Ziegel et al,1969; Pastenak et al, 1970). Small thermistors were also used to detect the presence of permeant in the sweep gas (Yasuda and Rosengren, 1970; Giacin and Gyeszly, 1981). One of the major problems with these uses of thermal conductivity detectors and thermistors is their inability to distinguish between contaminating vapor or co-permeants in the sweep gas. To a lesser degree, there are problems of calibrating these detectors for the specific permeant vapor and concentrations found and the effect of sweep gas flow rate on calibration. The use of a flame ionization detector (FID) has the advantage that the detector is relatively unaffected by the presence of the carrier gas and water vapor (Zobel, 1982). However the FID alone cannot distinguish between co-permeating organic vapors. A gas chromatograph sampling system coupled with an FID was used to separate and detect a complex mixture of organic permeants (Caskey, 1967, Pye el. al., 1976, Hernandez,1984).

One of the problems with the isostatic method is that the detectors exhibit a limit of sensitivity which must be exceeded to allow the detection of the minute amounts of vapor that may pass through a high barrier film sample. An FID can only detect about 10^{-4} to 10^{-2} μg of a compound. This may cause problems when testing high barrier film samples where permeation rates are exceedingly low. This problem may be overcome by using a cold trap in the sweep gas stream to condense out and accumulate the organic vapors over a given time interval (Niebergall et al, 1978). The accumulated sample is then injected into a gas chromatograph with an FID for separation and detection.

The quasi-isostatic measurement technique is a variation of the isostatic method, where instead of having a sweep gas flowing through the low concentration side of the permeation cell the low concentration chamber is initially filled with the inert sweep gas and then sealed. The accumulation of permeant in the low concentration chamber is then measured as a function of time. The Lyssy quasi-isostatic permeability apparatus model L63 uses thermistors in the static cell chamber (Lockhart, 1969). Problems with using the thermistors as detectors include the calibration of the thermistor and the lack of specificity of the thermistor to co-permeants and contaminating vapors. A technique was developed whereby gas samples from the static cell chamber were removed periodically and injected directly into a gas chromatograph with an FID for quantitation (Gilbert and Pegaz, 1969, Baner et. al., 1986). This method overcomes the problem of mixed vapors and the effect of relative humidity on the detector.

A third variation of the isostatic type of vapor permeability is the static type system. Here a volatile liquid permeant is placed in a reservoir below a film sample to provide the concentration gradient driving force through the film. The permeating vapor then accumulates above the film in the upper chamber of the permation cell . This chamber is sampled using a gas tight syringe and injected into a gas chromatograph with FID for quantition (Gilbert and Pegaz, 1969; Hilton and Nee, 1978; Murray and Dorschner, 1983). One of the problems with using this method is that it is limited to testing only at the saturation vapor pressure of the permeant, so that the concentration dependence of the permeation and diffusion process cannot be studied. Other problems cited include the establishment of a concentration gradient in the vapor phase next to the membrane surface, as in the case of rapidly permeating film-permeant systems, which may lead to anomalous results (Meyers et al, 1957).

Other methods for determining the permeability rates of organic vapors in polymer films have been developed but have not seen widespread use and acceptance. Stannett et al, (1972) discusses several of these other measurement systems.

The measurement systems of Niebergall et al, (1978), Gilbert and Pegaz, (1969); and Caskey, (1967) all contain the necessary elements for an accurate and versatile method for determining the permeability of organic vapors through polymer packaging films. A successful system to use for routine and theoretical evaluation of polymer film barrier properties for packaging applications and research needs to be able to evaluate the permeability of the test film as a function of the following parameters:

(1) thickness
(2) type of film
(3) barrier properties
(4) permeant concentration
(5) co-permeants including relative humidity
(6) simple and inexpensive design
(7) reproducibility

With these requirements in mind a quasi-isostatic system based the Gilbert and Pegaz (1969) design was developed.

Organic Vapor Sorption Measurement Techniques

The most common and simplest methods of sorption measurement are gravimetric techniques that measure the weight gain of the polymer, when the polymer sheet is exposed to a constant vapor pressure or concentration (Crank, 1968). Early techniques involved placing a speciman in an organic vapor atmosphere and than removing it at intervals to measure its weight gain (Park, 1950). This method produced errors due to the interuption of the sorption process and errors due to the presence of an air barrier surrounding the polymer through which the permeant must diffuse to reach the polymer (Crank and Park, 1968). One of the more common gravimetric techniques suspends the polymer sample from a calibrated quartz spring and the weight gain is measured by observing the deflection of the spring over time. Examples of this method have been demonstrated by Prager and Long (1951), Kishimoto and Enda (1964), and Jacques and Hopfenberg (1974). More recently what is described by Crank and Park (1968) as a magnetic-weighing method or by others as an electrobalance method (Cahn Instrument Co., Paramount CA.) has been used to measure the sorption of organic vapors by polymers by Berens (1977, 1979), Berens and Hopfenberg (1978, 1981), Choy et. al. (1984) and Ng et al. (1985). The quartz spring and elctrobalance avoid the error of interupting the sorption process for measurement and the error due to 'air barrier' can be overcome by applying a vacuum to the systems (Crank and Park, 1968). Crank and Park (1968) describe several other methods for making sorption measurements. Other methods include a "vibroscope" method where the resonant frequency of a filament varies as the square root of the mass per unit length. Volumetric absorption and pressure decrease measuring apparatuses have also been developed to measure the uptake of permeant by the polymer as well as a light absorption measurement technique (Crank and Park, 1968).

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Interpretation of Data From Quasi-Isostatic Permeation Measurements

The data obtained from the quasi-isostatic permeation method gives the quantity of vapor permeated through a film of surface area (A) of thickness (L) as a function of time. The quantity of vapor which had permeated through the test film in a given time, Q(t), is plotted versus the time elapsed from the introduction of vapor into the high concentration chamber of the permeation cell, to give the characteristic transmission profile or permeation curve (see Figure 12). The permeability coefficient $\bar{P}$, the integral diffusion coefficient $\bar{D}$, and the solubility coefficient S can be determined from the 'time lag' method developed by Daynes (1920) and Barrer (1939), using appropriate solutions of the diffusion equation. The permeability constant is determined by multiplying the slope of the linear portion of the permeation curve, which is the steady state permeation rate, by the membrane thickness and dividing by the area of the membrane and the permeant pressure differential. As a rule, the determination of the thickness of the membrane is the least accurate part of the permeation test, particularly in the case of organic vapor where the effect of film swelling by the vapors is ignored. Typical units for the permeability constant of vapors are grams-cm/m^2-day-mmHg or in the U.S. cc-mil/100in^2-day-atm. When a penetrant diffuses through a membrane in which it is soluble there is an interval from the time the pe

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penetrant first enters the membrane until the steady state of flow is established. The intercept on the time axis of the extrapolated linear steady state portion of the permeation curve is called the time lag, θ. Under ordinary conditions the steady state of flow is reached after a period of two to three times the time lag (Amerongen, 1946).

It has been shown that the time lag is directly related to the constant integral diffusion coefficient $\bar{D}$ by the relationship $\theta - L^2/6\bar{D}$ (Barrer 1939). Expressions have been developed which allow the calculation of diffusion coefficients from the time lag data for systems in which the functional dependence of D on any or all of the variables: concentration, spatial coordinate and time is known or can be assumed (Frisch, 1957, 1958). Even if the exact functional dependence of D on c is not known an estimate of the integral diffusion coefficient $\bar{D}$ can be made using time lag data. With some minor restrictions the following inequality holds for a very large class of functional dependencies of D on c (Pollak and Frisch, 1959):

$$1/6 \leq D/L^2\theta \leq 1/2 \qquad (28)$$

Thus an estimate of the integral diffusion coefficient made using the time lag expression for a constant D, $D \approx L^2/6\theta$, is at worst too small by a factor of three (Frisch, 1957). For most purposes this order of accuracy is quite sufficient since the experimental error in obtaining raw data may be of greater significance than this theoretical variance (Frisch, 1959). The integral diffusion coefficient calculated by the

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time lag method has been shown to agree within experimental error with the steady state of flow D calculated from sorption-desorption type experiments for organic vapors within polyethylene (Rogers et al, 1960).

From equations (12) and (13) the concentration dependency of the solubility coefficient can be determined from calculation of the integral solubility coefficient at different vapors concentrations where $P = D\ S\ (p_1 - p_2)/L$, so that $S = \bar{P} / D$ using $\bar{P}$ and D data obtained from the time lag method.

Thus a single permeation experiment allows calculation of the $\bar{P}$, D and S for a given temperature, vapor concentration and film-permeant combination. In order to determine the concentration dependence of $\bar{P}$, D and S for a given system it is necessary to make permeation measurements at several ingoing vapor concentrations and then plot the integral $\bar{P}$, $\bar{D}$ and $\bar{S}$ versus the concentration of vapor in the polymer. An estimate of the average permeant concentration in the polymer (c) can be obtained from the relationship $\bar{S} = (c_1 - c_2)/(p_1 - p_2)$. Here c_1 is the concentration of vapor in the film at the high pressure side of the film, p_1, and c_2 (which is ≈ 0) is the concentration of vapor in the film at low vapor pressure side of the film, p_2 (where $p_2 \approx 0$). Then using S and the known partial pressure of permeant (p_1) the average permeant concentration in the polymer c, can be calculated

(Rogers, 1964).

Determination of c is however usually made by equilibrium sorption studies. It has been shown that instead of plotting log D versus c, log D can be plotted versus the activity $a_1 = p_1/p_o$ to predict the vapor activity dependence of the diffusion coefficient (Rogers, 1964). The behavior of $\bar{P}$ or S as a function of the vapor activity on the high concentration side of the film has not been described in the literature.

The extrapolation of the graph of log D or log D versus concentration or vapor activity to zero concentration or activity gives the limiting diffusion coefficient, D_o. A method was developed by Meares (1965b) which analyzes the transient permeation state from the transmission profile curve to determine the limiting coefficient D_o for an organic vapor penetrant-polymer system. This method is often referred to as the small times approximation of D.

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Materials

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(1) Orientated Polypropylene (OPP)

Mobil Chemical Co. Films Division, Macedon, N.Y. 14502 Mobil Bicor 306 IG 1.0 mil homopolymer orientated 5.5 times machine direction, 8 times in the cross machine direction. This is representative of a nonpolar polyolefin type film commonly used for its intermediate barrier properties and structural characteristics.

(2) Polyvinylidene chloride (SARAN)

Dow Chemical U.S.A., Midland, MI 48640 . Dow #7323662, Film # XO 1621 10. 1.1 mil uniform material Crystallinity 41% made by a blown bubble process. Saran is a polar type material used for its superior barrier properties. This Saran is considered a high barrier type PVDC copolymer.

(3) Saran coated orientated polypropylene (OPP/PVDC)

Mobil Chemical Co. Films Division, Macedon, N.Y. 14502 Mobil 250 ASW acrylic coating/homopolymer/white opaque polypropylene/ homopoymer skin/saran coating 1.7 - 2.0 mil total thickness, saran coating 0.2-0.3 mil. Titanium dioxide filler in opaque layer. This is an example of a commonly used laminate of the polypropylene and PVDC films.

Permeants .

Toluene. Analytical Reagent 99.98% pure

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Analytical Method

Treatment of Film Samples

All film samples were tested at a room temperature range of 21 to 27°C with a total pressure of one atmosphere on each side of the film sample. The films were tested as they were received from the manufacturer with the exception of damaged samples with nicks and scratches which were discarded. All films were tested at 0% relative humidity (RH) and were stored in a desiccator over $CaSO_4$ desiccant for 2 weeks at 27°C prior to testing.

Permation Studies:

Permeation Cell Design:

Prior to each new test with the permeation cell, the cell parts, fittings, and o-rings were baked out in a laboratory oven at 70°C overnight to remove any residual sorbed permeant from the previous test. After removal from the oven the hot cells were allowed to cool to ambient temperature before beginning a new test. The septa were replaced and fresh vacuum grease applied to the o-rings. The new film samples were placed in the cell and the bolts tightened to a 0.010" gap between the sections while the valves were left open to release any trapped air. The upper and lower cell chambers were flushed with pure nitrogen at a rate of 500 cc/min for 5 minutes and then the valves closed. Before introducing the permeant into the center ring,

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headspace samples were taken to check for residual vapor. The permeant concentration was also monitored at the sample port after the mixing chamber to be sure it maintained a constant concentration level. An exhaust line was connected to one side of the center ring and a test run begun by connecting a permeant line from the dispensing manifold to the center cell chamber. The moment the permeant is first introduced is recorded as time zero. The initial permeant flow rate is set at 70 ml/min. With this flow rate the permeant concentration reaches 95% of its ingoing concentration in 3-5 minutes depending on the permeant concentration used from Equation 42 (Hernandez, 1984):

$$\text{time} = (\text{center ring volume/gas flow rate})\cdot \ln[(c_o-c_i)/(c_t-c_i)] \quad (42)$$

This high of a permeant flow rate ensures that a constant permeant concentration is rapidly attained and is maintained in the high concentration cell chamber of the permeation cell throughout the duration of the experiment including the early stages when the sample is rapidly absorbing permeant. Where c_i is the incoming vapor concentration; c_o is the initial vapor concentration in the center ring; and c_t is the vapor concentration at some time t. When the desired ingoing permeant concentration is reached in the high concentration cell chamber, the permeant flow rate is reduced to 30 ml/min and is maintained. The permeant flow rate is measured downstream from the permeation cell with a soap bubble flow meter. The permeant concentration is monitored at the center ring and mixing chamber sampling port throughout the run.

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Vapor Permeant Quantitation

The flux or permeability rate through the film samples was determined by periodically removing samples (0.5 cc) from the cell's headspace with a gas tight syringe and immediately injecting the sample into a Hewlett Packard 5830A gas chromatograph (GC) equipped with dual flame ionization detectors. The GC was interfaced to a Hewlett Packard 18850A automatic integrator. The column was a 1/8" o.d. X 6′ stainless steel column packed with 5% SP2100 on 100/120 mesh supelcoport (Supelco Inc., Bellefonte, Pa.). The chromatographic analysis conditions were: injection port temperature 200°C, column temperature 175°C, flame ionization detector temperature 350°C, and a Helium carrier gas flow rate of 30 cc/min. This analysis gave a retention time of 1.33 toluene. The automatic integrator parameters used were slope sensitivity of 0.01 and an area unit reject of 100.

One half milliliter gas samples were taken with a 0.5 cc Hamilton #1750RN gas tight syringe (Hamilton Co., Reno, Nev.) for all sampling. For each headspace sample, a .5 cc volume of nitrogen gas was introduced into the low concentration cell chamber, the syringe pumped several times to facilitate mixing and then a 0.5 cc sample removed for analysis. This procedure replaced the sample volume removed by each sample and avoided excessive puncturing of the septa . Each sample from the headspace removes approximentely 1% of the total quantity of permeated vapor in the cell's headspace and replaces it with nitrogen.

Permeation Data Analysis

The total quantity of permeant in the cell headspace is calculated for each sample by dividing the response in area units (au) obtained from the GC's integrator by the sample volume (0.5 ml) and multiplying it by the detector calibration factor (grams permeant/ GC area unit response) and the volume of the permeation cell's headspace (50 ml).

$$Q = (\text{GC au} / 0.5\ \text{ml}) \cdot (\text{calibration factor g/au}) \cdot 50\ \text{ml}$$

This gives the total number of grams of permeant in the headspace at a given time, t. The procedure for calibrating the gas chromatograph can be found in Appendix C.

As the data is collected it is plotted on a graph with total permeant accumulated in the headspace versus the elapsed time. The curve produced is the transmission profile curve. The steady state permeation region is the portion of the curve where there is a steady increase in permeant concentration with time resulting in a straight line on the transmission profile curve. Several measurements must be made in the steady state region to confirm its linearity. Headspace measurements are discontinued when adequate data has been collected. It is proposed that the run be carried out to a minimum of two to three times the lag time (Siegel and Coughlin, 1970). Eventually with this type of system, the permeation rate decreases as the permeant partial pressure driving force across the film decreases due to accumulation of permeant in the cell's headspace. To impose a constant driving force, the permeability run is usually terminated when the permeant concentration in the lower concentration cell chamber is equal to 2 to 3% of the high cell concentration. However, it was found that measurments in the lower concentration cell chamber could be taken up to concentrations of 10% of the driving force in the high concentration cell chamber before there was a measurable decrease in the permeation rate. For some film-permeant concentration systems tested, particularly those with large diffusion and permeation coefficients, no measurable change in the permeation rate was observed up to 50% of the vapor pressure differential accumulated in the headspace.

According to theory, the slope of the steady state region of the transmission rate profiles gives the permeation rate of the film for the specific conditions of the test. The most accurate method for determining the permeation rate from a series of data points is to plot the transmission profile curve and determine graphically where the curve appears linear and apply linear regression analysis for these data points. The linear regression line gives the best straight line fit for a given set of data points. The slope of the linear regression line is the flux or permeation rate (e.g. grams/hour).

The permeability coefficient ($\bar{P}$) for a specific film-permeant test

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combination is calculated by multiplying the permeation rate (grams/hour) by 24 hours/day and dividing it by the film surface area (50 cm^2) and the permeant concentration (ppm, w/v). For homopolymer films the permeability coefficent can also include units for the films thickness in the numerator by multiplying ($g/day \cdot cm^2 \cdot ppm$) by the thickness of the film (mils or cm). The permeability coefficient for laminate films is expressed as $grams \cdot structure/day \cdot cm^2 \cdot ppm(w/v)$. Laminate structures have different layer thicknesses and combinations of layers which exhibit different behavior towards the test permeant and have potential variation with permeant concentration dependency. All layers of a laminate contribute to the permeability coefficient, making it a unique measurement specific for that film structure. The permeability coefficent is sometimes referred to as the integral permeability coefficient, due to its theoretical derivation from Equations (12), (13) and (14).

The lag time (Θ) can be determined from the x axis intercept of the linear regression line calculated for the steady state permeation region of the transmission profile curve. The integral diffusion coefficient ($\bar{D}$) can be calculated from the equation $\bar{D} = L^2/6\Theta$. This diffusion coefficient is referred to as D_{lag}, the lag time diffusion coefficient. Each reported lag time diffusion coefficient is defined for a specific film-penetrant combination and set of test conditions. D_{lag} is well defined theoretically for a homopolymer film which has a

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uniform structure throughout the film. Homopolymer films are considered to have the same D_o throughout the film due to a relatively uniform structure. In the case of laminate films each film layer has its own characteristic D_o and permeant concentration dependent diffusion coefficient. Estimating the diffusion coefficient for a laminate is further complicated because there is a permeant concentration gradient present in the film. The D_{lag} determined is a composite of these respective diffusion rates and is specific for that combination of film layers and thicknesses under specific test conditions. The D_{lag} for laminate film structures is referred to as an effective lag time diffusion coefficient, specific to that particular structure.

An integral or average solubility coefficient ($\bar{S}$) can be determined from the permeability coefficient ($\bar{P}$) and the lag time diffusion coefficient (D_{lag}) using equation (13). To get the solubility coefficient in the units (gram/cm^3• ppm) the units of the permeability must be converted to (grams•cm/ sec•cm^2 ppm). Like the $\bar{P}$ and D_{lag}, the solubility coefficient for organic vapors is not well defined because the permeant concentration gradient in the polymer matrix is not exactly known. This is particularly true for laminate structures. Therefore the solubility coefficient should be considered an effective solubility coefficient. The solubility coefficient calculated this way assumes that the solubility of the vapor in the polymer follows a

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Henry's law relationship and that the diffusion coefficient calculated using the time lag method (D_{lag}) represents the true steady state diffusion coefficient. Determination of the solubility coefficient is best determined directly by sorption measurements.

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Permeation Test Method

The test method used was based on the quasi-isostatic permeation measurement technique. The principles of this method have been described in the literature review.

Figure 1 shows a schematic of the test apparatus, while an expanded view of the permeability cell is presented in Figure 2. The permeability cells used were constructed from aluminum or stainless steel by the Michigan State University Engineering Department machine shop. The cell was based on the design of Gilbert and Pegaz (1969). The cell consists of three main components; a top and a bottom section each containing a 50ml cavity, and a center ring with a hole the same diameter as the cavities. The cavities in the top and bottom section of the cell form the headspace volumes into which the permeating vapors accumulate. This cell design allows two film samples to be evaluated simultaneously. The top and bottom sections of the cell are equipped with inlet and outlet valves that allow flushing of the cell with nitrogen prior to a test run. This gives an initial headspace composition of 100% nitrogen in the cell chamber. The center ring section of the cell has two Swagelok quick connects (Crawford Fitting Co., Solon, Ohio) which allow the cell to be easily connected and

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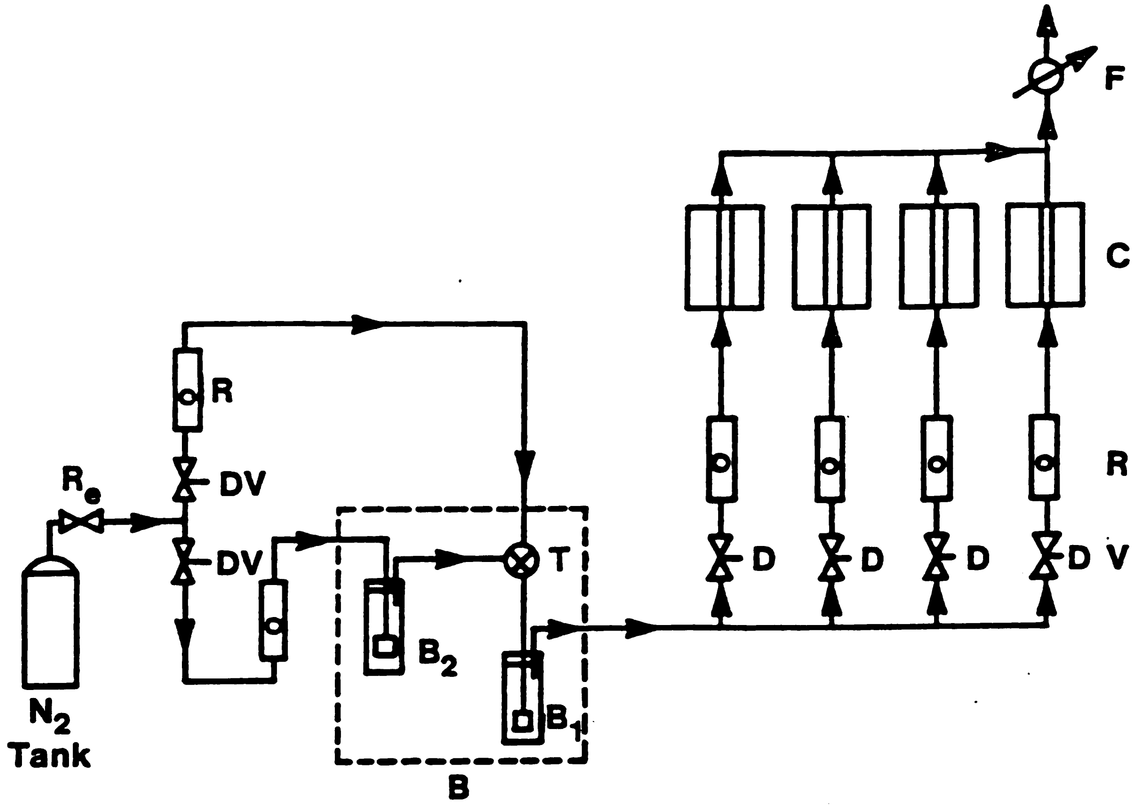

B = Water Bath
B_1 = Glass Mixing Device
B_2 = Glass Vapor Generator
R_e = Regulator
V = Needle Valve
R = Rotameter
C = Cells (Double Chamber)
F = To Waste and Gas Flow Bubble Meter
T = Three Way Valve

Figure 1. Schematic of Permeation Test Apparatus

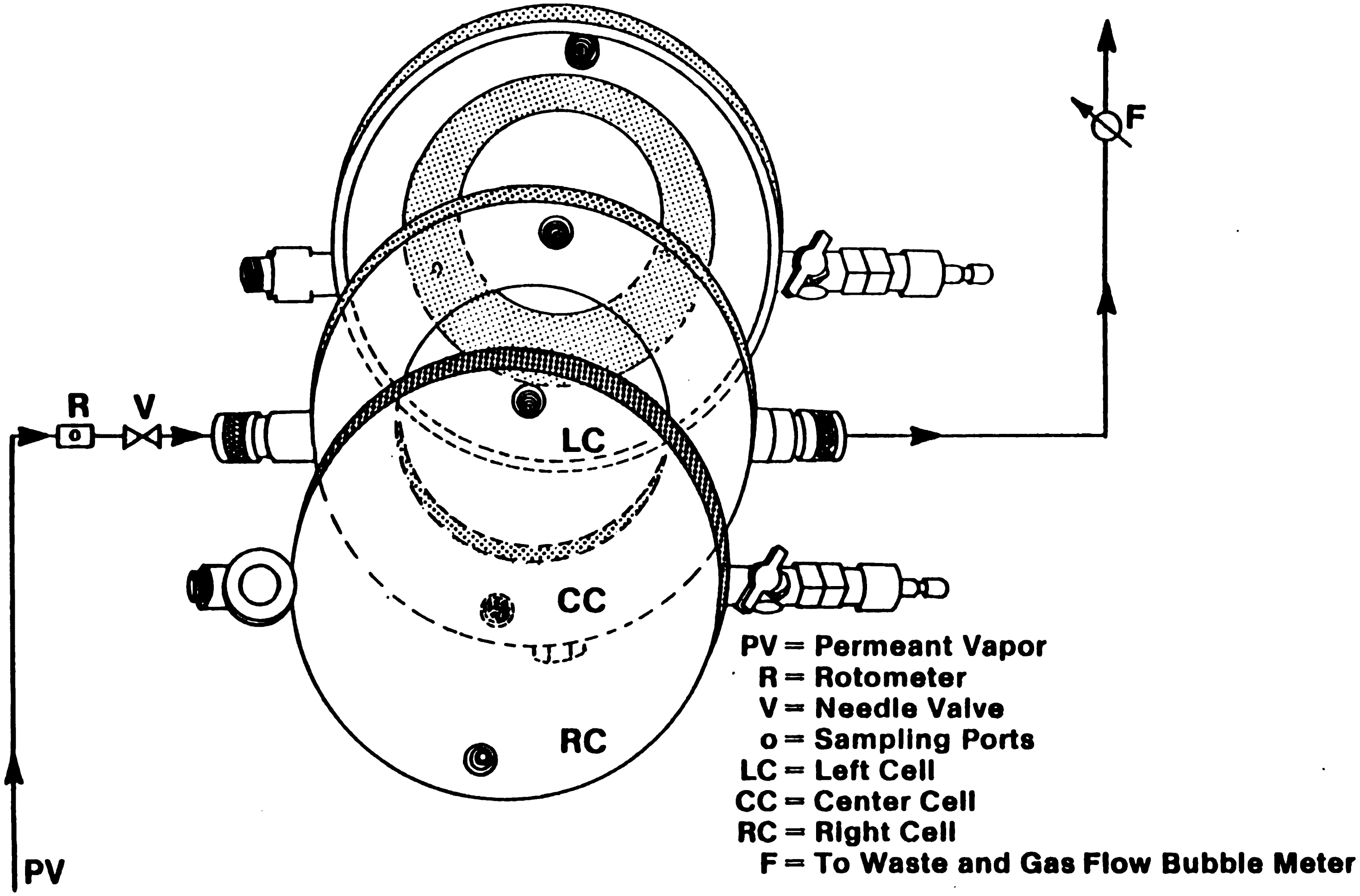

Figure 2. Permeation Cell System

disconnected from the permeant dispensing manifold and to an exhaust line that discharges into a fume hood. The center ring allows the permeant vapor mixture to pass simultaneously over two film samples. Two 4"x4" film samples are held in place and sealed between the two sections of the cell by Viton^R o-rings. Viton^R is a flourocarbon elastomer compound which is resistant to attack and swelling by most organic vapors. The surface area of the film exposed to the permeant is approximentely 50cm^2, determined from the center diameter of the o-rings. The cell sections and film samples are clamped together by tightening two bolts until there is a 0.010" gap, determined by a feeler gauge, between the cell sections. Assembling the cells in this manner ensures reproducing the same headspace volume, for each test.

As shown each section of the cell contains a sampling port with a septum that allows sampling the headspace and center ring permeant concentrations with a gas tight syringe. The sorption of vapor by the septa is minimized by using teflon coated silicone septa and placing the inert teflon side towards the inside of the cell.

A constant permeant vapor concentration in nitrogen carrier gas is generated by bubbling nitrogen through a 100 ml graduated cylinder containing 70 ml of the liquid permeant. The nitrogen is dispersed in the liquid by a fritted glass fitting with an average pore size of 60μm (Fischer Scientific Inc., Pittsburg, Pa.) to ensure saturation of the

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nitrogen with the organic vapor. The top of the cylinder is stoppered with a 100% silicone rubber stopper with two holes for the inlet and outlet of 1/8" o.d. copper tubing. The cylinder is submersed in a 32°C constant temperature water bath which maintains the temperature of the organic liquid above the test temperature (27°C) to ensure that the saturation vapor pressure of the organic permeant in the nitrogen is reached. A 250 ml erlenmeyer flask stoppered with a 100% silicone stopper is placed downstream from the graduated cylinder and acts as a trap for entrained toluene liquid droplets.

The nitrogen stream containing the organic vapor at its saturation vapor pressure can be used as the permeant concentration driving force or it can be mixed with pure nitrogen gas to provide lower penetrant driving force concentrations. The nitrogen flow rates are controlled by Nupro 's' series valves (Crawford Fitting Co., Solon, Ohio) with vernier handles and monitored by Gilmont #1 shielded flow meters (Gilmont Instruments Inc., Great Neck, N.Y.). The nitrogen tank regulator is set at 5 psi.

The permeant concentration supplied to the center ring can also be measured at a sampling port before the mixing chamber (see Figure 2). After the mixing chamber the permeant mixture flows to a dispensing manifold. Up to four permeation cells can be connected to the dispensing manifold by Swagelok quick connects.

The lines carrying the permeant vapor are made from 1/8" o.d. copper refrigeration tubing, with the exception of the dispensing manifold which is constructed from 3/8" o.d. copper tubing. All fittings and tubing connectons used were brass Swagelok fittings.

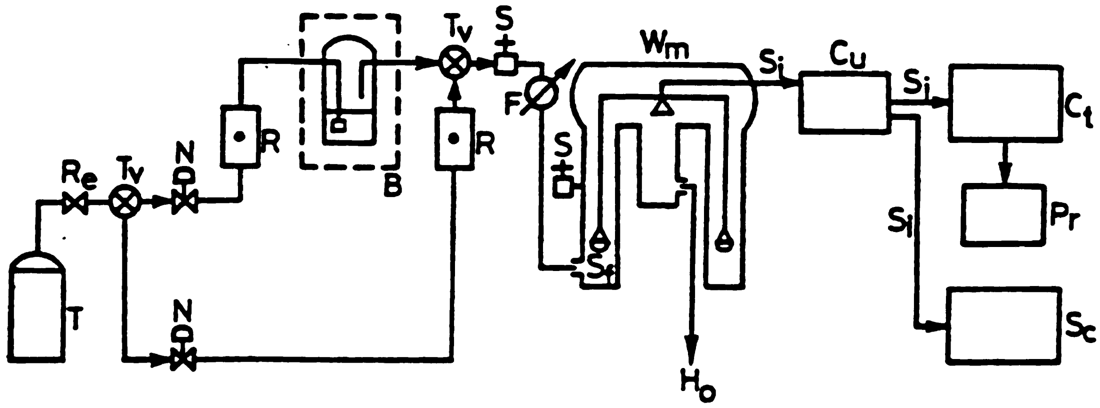
With this apparatus design and set up, permeation tests are limited to ambient temperature testing (i.e. 25^0C). To test at temperatures other than ambient temperature the cell could be placed in a temperature controlled box or chamber (e.g. an oven or refrigerator).

Solubility Studies

Solubility Test Method

The solubility test method used is based on a continuous gravimetric sorption technique using an electrobalance.

Figure 3 shows a schematic diagram of the sorption/desorption test apparatus. The central component of the apparatus is a Cahn Electrobalance model RG (Cahn Instruments, Inc., Cerritos, CA.). The balance may be described as an electric current-to-torque transducer. Initially the polymer sample is suspended on the sample wire on one side of the balance beam arm and counter weights are added to the opposite arm to balance the beam. As the sample absorbs/desorbs vapor its weight increase/decrease produces a torque about the central axis of the balance which is measured by the amount of current needed by the torque converter to keep the beam level. The change in current is transmitted by the balance control unit to a strip chart recorder which also records the time function. The balance output is calibrated in grams of weight sorbed by the polymer. This calibration can be performed by using a calibration weight set purchased from Cahn Instruments. Further description of the balance hardware and operation can be obtained from Cahn Instruments (Berens, 1977, Cahn Instruments,



B - Water bath, generation of permeant
Vapor phase diluted in Nitrogen
C_t-Computer terminal
C_u-Control unit
F - Gas flow bubble meter
H_o-Hood
N - Needle valve
P_r- Printer
T - Nitrogen tank

R - Rotameter
R_e-Regulator
S - Sample port
S_f-Sampling film
S_c-Strip chart
S_i-Electrical input/output signal
T_v-Three way valve
W_m-Cahn electrical balance

Figure 3. Schematic Diagram of Sorption/Desorption Apparatus.

Cerritos, Ca.).

The electrobalance and sample tube were kept in a constant temperature environment of 21 ± 0.5°C. For a sample mass of 10 mg, the sensitivity of the balance is approximately 5 μg. The test system in Figure 3 allows for the continuous collection of sorption data of an organic vapor by a polymer film from time zero to steady state conditions. By performing several experiments at varying vapor concentrations the solubility as a function of penetrant concentration can be determined.

The electrobalance is placed in a vacuum jar that has three hang down tubes attached. As shown in Figure 3, the polymer film sample to be tested is suspended directly on one of the arms of the electrobalance and a constant concentration of dry penetrant vapor in nitrogen is flowed continually through the sample hang-down tube. Using this method the polymer sample is totally surrounded by the penetrant vapor at a total pressure of one atmosphere. A constant concentration of vapor was produced by employing a vapor generator system similar to that detailed for the permeation measurement system. The flow rate of the vapor was kept constant at 10 ml/min and was monitored continuously by a rotometer. All fittings and tubing were brass and copper respectively. The fittings and tubing were washed with methylene chloride and methanol and baked out in a hot oven prior to assembling. The vapor exits the vacuum jar via the middle hang-down tube where it then flows to a fume hood.

The concentration of vapor in contact with the polymer sample was monitored throughout the measurement by removing a gas sample via the sample port in the sample hang-down tube. The gas sample was taken using a gas tight syringe and injecting the sample into a gas chromatograph for quantition (see permeation test method for syringe and gas chromatograph specifications and conditions). In order to begin sorption experiments at the precise permeant vapor concentration of the test the following was developed to introduce the sample into the sample hang-down tube at time zero. The penetrant vapor was flowed through the empty electrobalance apparatus until the concentration of vapor in the electrobalance equilibrated. Then the sample hang-down tube was carefully removed and the preweighed polymer sample was suspended on the sample wire and the hang-down tube placed back on the vacuum jar. The polymer sample of approximately 10 mg was preweighed on a Analytical balance to an accuracy of $1x10^{-4}$ grams. The time when the hang-down tube was replaced was marked on the strip chart recorder as time zero. Problems with electrostatic attraction between the polymer sample and hang-down tube were sometimes experienced. An anti-static spray was obtained Cahn Intruments and applied to the surfaces of the hang-down tube to dissipate electrostatic build up prior to introducing the sample.

The gain in weight of the sample due to penetrant (i.e. toluene vapor) sorption was monitored continually until the system attains steady state or equilibrates. The sample was assumed to reach equilibrium when no further sample weight gain was observed over 24 hours. This procedure was repeated at several penetrant concentration levels. For each concentration level, a new film sample was utilized. All measurements were carried out at 0% relative humidity, using toluene vapor of greater then 99% purity.

Solubility Quantitation and Data Analysis:

The output from the strip chart recorder during a sorption measurement is converted to polymer weight gain over time by calibration. The equilibrium solubility (Cs) in grams of vapor sorbed per gram of dry polymer is obtained by dividing the equilibrium weight gain (M_∞) by the polymer at $t = \infty$, by the dry weight of the polymer. The equilibrium weight gain of the polymer represents the maximum amount of vapor the polymer will sorb at a given vapor concentration.

A simple approximation of the integral diffusion coefficient was made using Equation:

$$D_{t1/2} = 0.04919\ L^2 / t_{1/2} \qquad (22)$$

Where $t_{t1/2}$ is the time required for the sorption curve M(t) versus t to reach one-half the value of M_∞ and L is the thickness of the dry polymer. The use of this expression to determine D is an approximation for penetrant/polymer systems where the diffusion coefficient is concentration independent, Henry's law solubility is followed and the system follows Fickian sorption (Fujita, 1968).

The equilibrium solubility (Cs) for a given vapor concentration corresponds to the concentration of vapor in the outer surface of a polymer film from a permeation experiment. From the equilibrium solubility (Cs) the solubility coefficient, representing an upper bound for the solubility coefficient in a permeation experiment, is obtained. In a permeation experiment there is a concentration gradient of permeant in the film ranging from Cs at the penetrant interface to essentially zero at the opposite side of the film. The solubility coefficient is calculated by dividing Cs by the permeant concentration.

Results and Discussion

Characteristics of Steady State Permeation of Toluene Through Test Films

The Quasi-isostatic permeation measurement method was employed to determine the permeation rates and permeability coefficients for the film-permeant systems investigated at the given test condition of permeant vapor activities. This method also yields the integral diffusion coefficient ($\bar{D}$) by the lag time method (Barrer, 1939). The results of the permeation measurements are summarized in Table 2. In this discussion the permeant vapor activity (a) will be used as a measure of the penetrant concentration in describing the concentration dependence of the diffusion process. The permeant activity is defined as the ratio of the measured test permeant partial pressure over the equilibrium permeant saturation partial pressure at the temperature of the test. A plot showing the variation of toluene equilibrium vapor concentration with temperature can be found in Appendix A, along with sample calculations and the equilibrium vapor pressure references. Because the experiments were run at different temperatures, vapor activity was used in an attempt to correct the effect of temperature on the permeant driving force concentration and to allow a more accurate comparison between data acquired at different temperatures. Vapor activity (a) ranges from 0 to 1.0, where a value of (a) = 1.0 indicates the vapor pressure is equivalent to the equilibrium vapor pressure of the penetrant.

Table 2

Permeation Measurement Results

a^a	$^oF^b$	ppm^c	P^d	P^e	θ^f	$D_{lag}{}^g$
Toluene - Oriented Polypropylene (OPP) 1.0 mil :						
0.11	78.2	16±1	0.24	0.524	2.9	1.03
0.26	81.0	41±3	1.46	1.34	1.81	1.65
0.31	81.0	48±3	2.38	1.85	1.43	2.09
0.52	80.9	81±4	22.5	10.4	1.08	2.76
0.59	81.1	93±3	50.0	20.3	0.66	4.56
0.68	78.7	100±5	109.0	38.6	0.52	6.13
0.71	81.1	112±5	724.0	244.	0.36	8.23
Toluene - High Barrier Saran (PVDC) 1.1 mil :						
0.56	74.2	73±3	0.0016	0.00068	237.6	0.015
0.63	80.1	96±3	0.119	0.045	40.5	0.089
0.77	82.5	125±5	36.6	11.48	5.62	0.64
0.85	83.2	141±5	39.0	11.06	4.97	0.73
Toluene - OPP/PVDC (OPP side towards permeant) 2.0 mil total thickness:						
0.27	78.4	40±2	0.004	0.0035	105.2	0.14
0.36	79.0	54±2	0.035	0.023	35.5	0.34
0.52	79.7	79±2	0.95	0.436	12.2	0.98
0.60	80.0	92±3	43.1	17.2	2.66	4.5
0.62	80.0	94±2	33.6	13.1	2.22	5.4
0.84	81.9	135±3	214.0	61.2	0.66	18.0
Toluene - OPP/PVDC (PVDC side towards permeant) 2.0 mil total thickness:						
0.30	78.9	40±2	0.0034	0.0030	88.3	0.14
0.62	80.0	94±5	48.6	19.6	1.9	6.4
0.67	79.3	97±3	106.6	38.2	1.7	9.0
0.85	85.5	150±5	334.0	94.6	0.44	27.0

All results are averages of four replicate samples

(a) $\underline{a}$ - vapor activity - (p/p_o)

(b) ^oF - temperature of test

(c) ppm - permeant concentration in nitrogen (µg/ml)

(d) $\underline{P}$ - permeability rate $x10^{+2}$ $(g/m^2 \cdot hr)$

(e) $\overline{\underline{P}}$ - permeability coefficient $(g \cdot structure/m^2 \cdot day \cdot a)$

(f) θ - lag time (hour)

(g) D_{lag} - lag time diffusion coefficient $x10^{+10}$ (cm^2/sec)

Permeation Rate

For better illustration of the relationship between vapor activity and permeation rate (P), the values of Table 2 are presented graphically in Figure 4, where the permeation rate (P) is plotted as a function of toluene vapor activity. The permeation rate (P) of these penetrant-polymer systems varied exponentially with the permeant vapor activity. Linear regression analysis of the plot of the log of the permeation rate versus vapor activity gave correlation coefficients (r) ranging from 0.94 to 0.99 for the respective film-permeant combinations. For the oriented polypropylene structure, the relationship between the permeation rate (P) ($g/m^2 \cdot hr$) and toluene vapor activity (a) is given by:

$$P = 5.9\text{x}10^{-4} \exp(11.9 \cdot a) \qquad (43)$$

For the Saran structure the relationship between (P) and (a) is given by:

$$P = 2.5\text{x}10^{-14} \exp(38.2 \cdot a) \qquad (44)$$

For the Saran coated oriented polypropylene the relationship between (P) and (a) is given by:

$$P = 2.8\text{x}10^{-7} \exp(20.8 \cdot a) \qquad (45)$$

$$P = 2.8\text{x}10^{-7} \exp(21.1 \cdot a) \qquad (46)$$

Equation 45 was tested with the OPP layer next to the toluene vapor and Equation 46 was tested with the Saran layer next to the toluene permeant.

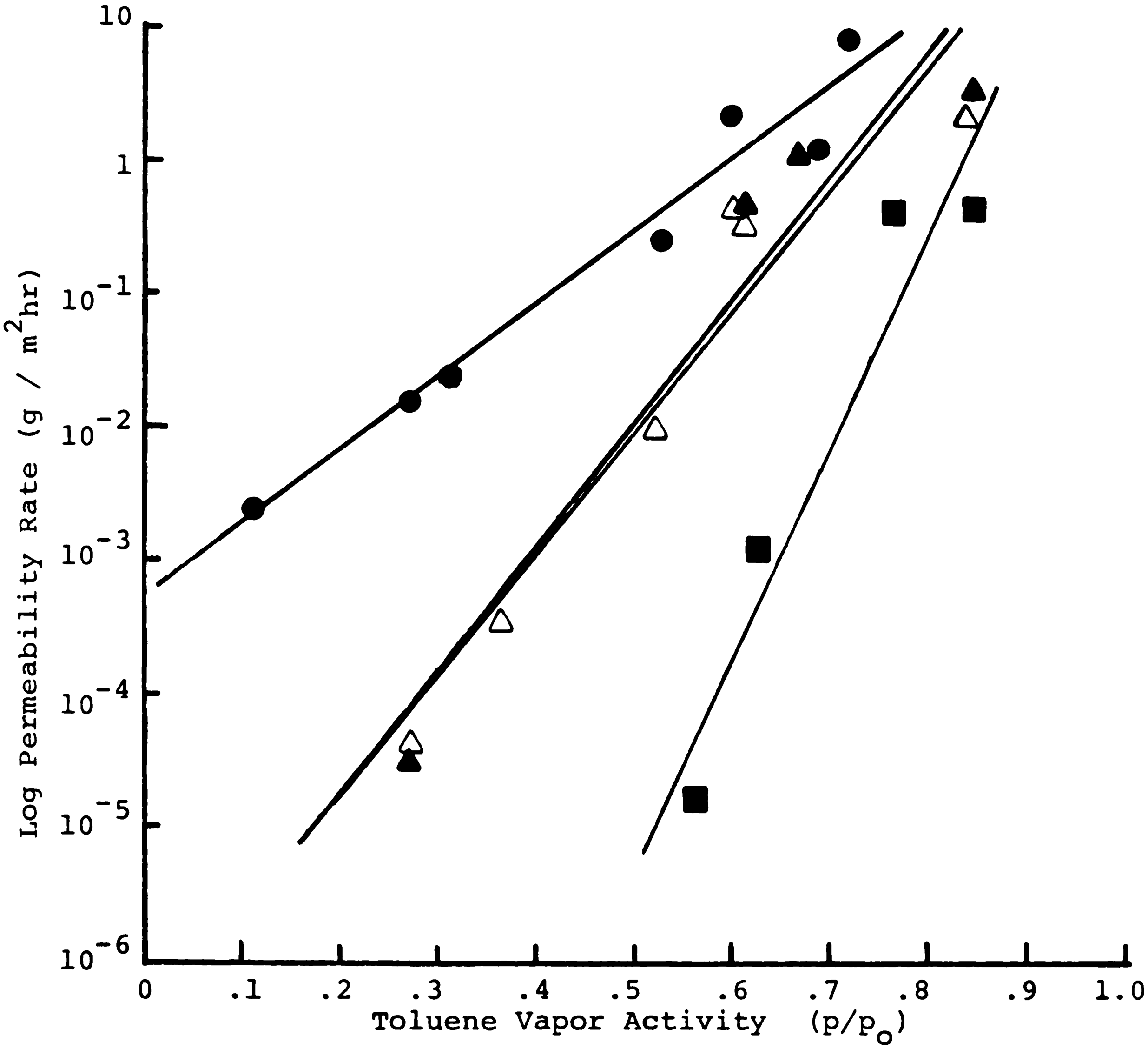


Figure 4. Log Permeability Rate versus Toluene Vapor Activity.

● OPP; ■ PVDC; △ OPP/PVDC (OPP next to toluene vapor); ▲ OPP/PVDC (PVDC next to Toluene vapor).

There was no statistical difference shown between the linear regression line slopes for the OPP/PVDC laminate film structure, regardless of which surface (i.e. OPP or PVDC) is placed next to the toluene permeant at the $\alpha = 0.05$ level of significance. There is almost six orders of magnitude difference between the pre-exponential factor for the permeation rate regression lines for toluene through OPP/PVDC laminate and the PVDC homopolymer. However the slopes of the regression lines of log P vs (a) for the OPP/PVDC and PVDC are not statistically different at the $\alpha = 0.05$ level of significance. The similarity between the behavior of the toluene permeation concentration dependency between these two films suggests that the PVDC layer in the laminate controls the toluene permeation behavior in this film. The difference in the magnitude of the permeation rates can be explained in part by the difference in the thickness of the PVDC layers. The specific molecular structure and processing history of the two PVDC's may also vary and contribute to the differences in observed barrier properties. The thickness of the PVDC in the laminate coating of 0.2 to 0.3 mils and is applied as a latex coating, as compared to 1.1 mils for the high barrier PVDC (Mobil, 1986). The PVDC in the laminate is a latex coating and is not expected to be as good a barrier material as the high barrier PVDC in the homopolymer due to the differences in structure as well as residual surfactants in the latex from processing (Brown, 1986).

Permeability Coefficient

The permeability coefficient ($\bar{P}$), is the permeation rate normalized to the permeant concentration or vapor activity. The permeability coefficient varied exponentially with toluene vapor activity, but was not linear like the permeation rate, as shown Figure 5 where the permeabililty coefficients (g·structure/m^2·day·vapor activity) for OPP, PVDC and PVDC coated OPP are plotted as a function of vapor activity (a). The log $\bar{P}$ vs (a) curves had different convexities and concentration dependencies depending on the film structure and permeant. The OPP-toluene, film-permeant combination, displayed a somewhat convex shaped curve to the activity axis, while the film structures containing the PVDC material were concave to the activity axis. Polypropylene, although it had a higher overall permeabililty coefficient than the PVDC and PVDC containing films, was less concentration dependent. For example, between the experimental vapor activity range of 0.3 to 0.7, the permeability coefficient ($\bar{P}$) for toluene through OPP increased by one and one-half orders of magnitude. For toluene permeation, through PVDC-coated polypropylene, the permeability coefficient increased by almost 4 orders of magnitude over the same range. At a toluene vapor activity of 0.8, the predicted permeability coefficients for toluene permeation through the OPP and PVDC-coated polypropylene are equivalent.

In his chapter Rogers (1964) described the variation of the permeability

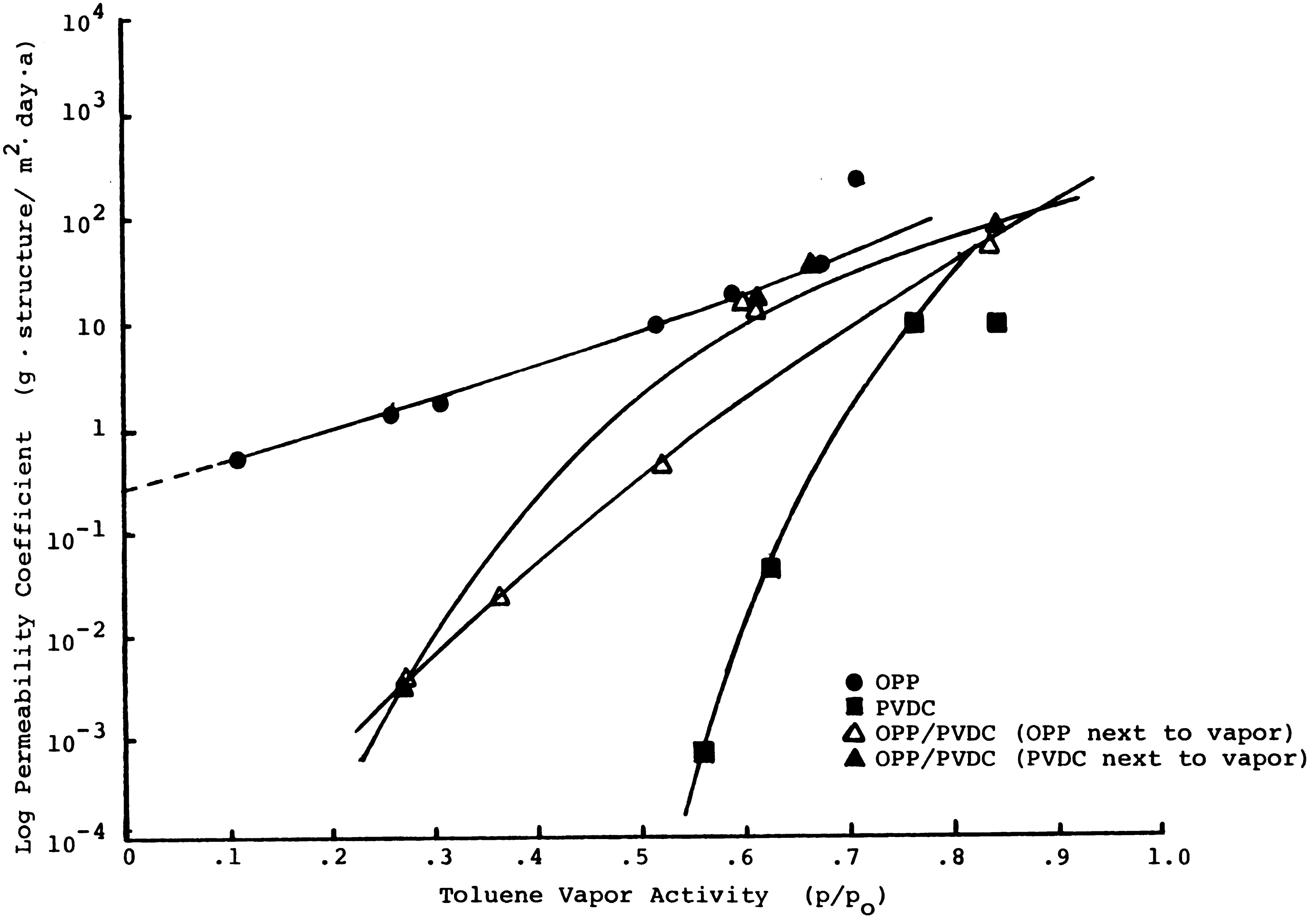


Figure 5. Log Permeability Coefficient versus Toluene Vapor Activity

coefficient with organic permeant vapor activity as an exponential function of vapor activity where the log of $\bar{P}$ becomes progressively non-linear at higher vapor activities. In cases where the solubility of the vapor in the polymer approximates Henry's law, log $\bar{P}$ varies linearly with vapor activity (Rogers, 1964). At very low vapor activities, the permeability coefficient can be reduced to a linear dependence on vapor pressure (Cutler et al, 1951). A curve similar to that obtained for the OPP-Toluene system, was observed for benzene in polyethylene by Rogers et. al. (1960). Log $\bar{P}$ vs (a) curves similar to the concave curves obtained for the PVDC-Toluene, film-permeant combination, were measured by Zobel, (1982) for a PVDC/OPP/PVDC film and benzyl acetate as the permeant. Based on these observations and comparisons to other published data, there is some support for modeling these log $\bar{P}$ vs (a) curves using polynomials. Equations for the four log $\bar{P}$ vs (a) curves found in Figure 5 were fitted using a cubic polynomial curve fitting program. The polynomial equations and least squares regression coefficients for the fit of the line to the points are given in Table 3.

Diffusion Coefficient

The lag time diffusion coefficient (D_{lag}) is derived from Fick's second law of diffusion assuming a constant diffusion coefficient and solving using the boundary conditions of the permeation experiment (page 93 of results) for the concentration in the polymer. Then using the mass

Table 3

Polynomial Equations
$\log_{10}$ Permeability Coefficient ($\bar{P}$) versus Vapor Activity

OPP - Toluene

$\log \bar{P} = 1.316557(a)^3 - 0.6758886(a)^2 + 3.100905(a) - 0.6156436$
experimental vapor activity range: 0.1 - 0.7
least squares polynomial fit (r): 0.9559

PVDC - Toluene

$\log \bar{P} = 130.3141(a)^3 - 306.1882(a)^2 + 253.6787(a) - 72.15646$
experimental vapor activity range: 0.55 - 0.85
least squares polynomial fit (r): 0.9438

OPP/PVDC - Toluene (OPP next to vapor)

$\log \bar{P} = 1.60863(a)^3 - 5.775069(a)^2 + 12.29352(a) - 5.412251$
experimental vapor activity range: 0.27 - 0.84
least squares polynomial fit (r): 0.9454

OPP/PVDC - Toluene (PVDC next to vapor)

$\log \bar{P} = 13.27179(a)^3 - 34.3645(a)^2 + 32.64957(a) - 9.089249$
experimental vapor activity range: 0.27 - 0.85
least squares polynomial fit (r): 0.9964

$\bar{P}$ = permeability coefficient (g·structure/m^2·day·vapor activity)
a = vapor activity (p/p_o)

balance to describe the flow of permeant through the film the result obtained from solving Fick's second law is applied. At steady state conditions Equation 17 then describes the lag time for the flow of permeant to reach steady state.

$$\Theta - L^2/6D_{lag}$$

Equation 17 assumes that the diffusion coefficient in the expression is independent of concentration, spatial coordinates in the polymer and time. For the laminate structure the diffusion coefficient is more appropriately referred to as an effective diffusion coefficient composed of the different diffusion processes from each of the polymer layers. A plot of the log of the diffusion coefficient versus toluene vapor activity for the respective test films is presented in Figure 6. As shown, the lag time diffusion coefficient follows a linear exponential dependence on the vapor activity for the test film structures. Linear regression analysis of the log of the lag time diffusion coefficient (D_{lag}) versus vapor activity produced correlation coefficients ranging from 0.94 to 0.98. The regression lines and data for the lag time diffusion coefficients are given in Table 4. The inverse log of the y intercept of the linear regression equation gives the theoretical limiting diffusion coefficient which is the diffusion coefficient at zero vapor concentration where there would be no sorbed permeant in the polymer and thus no penetrant polymer interaction (Rogers, 1965). It is necessary to extrapolate the curves outside of the experimental vapor activity region to find the limiting diffusion coefficient.

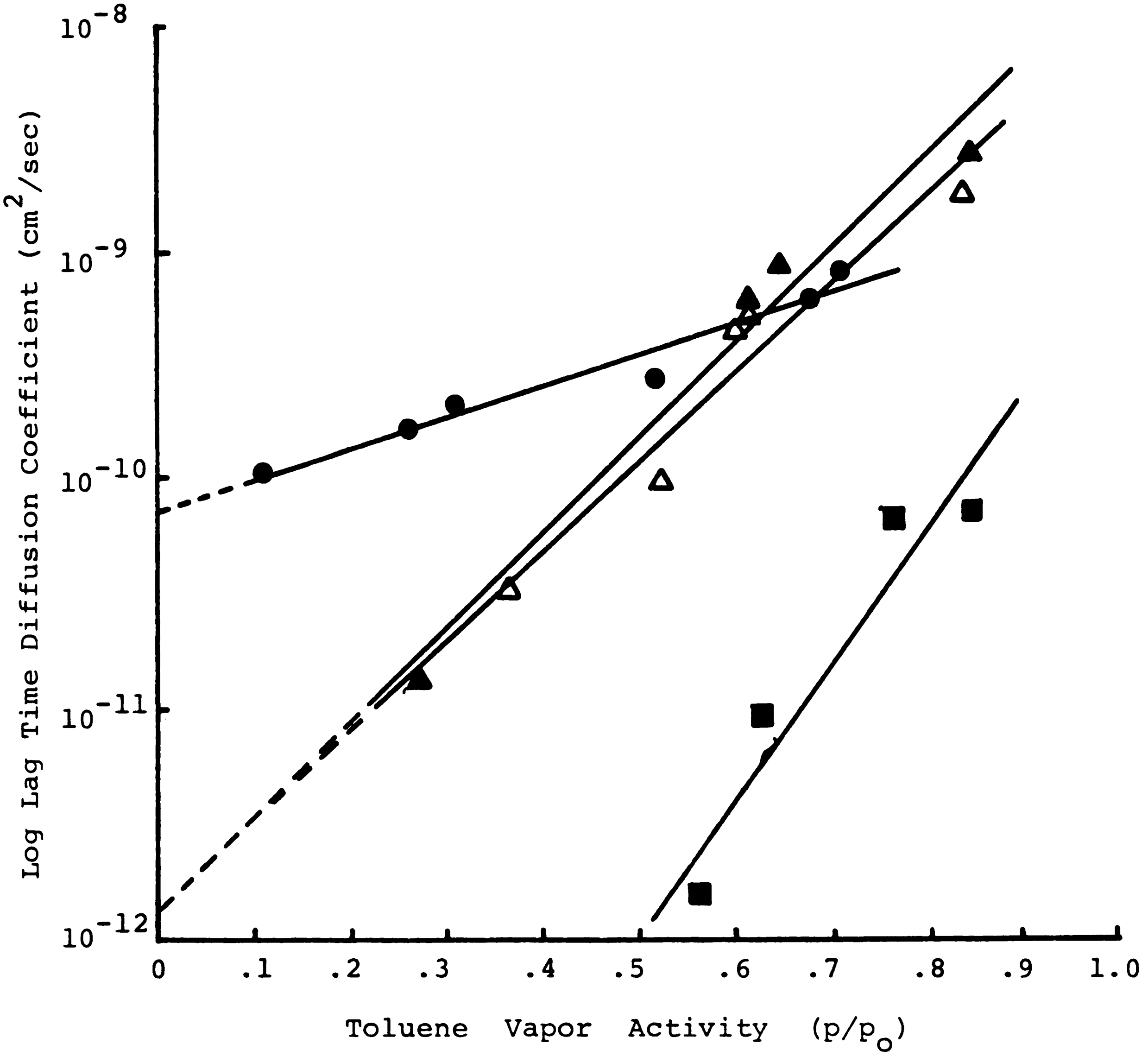


Figure 6. Log Lag Time Diffusion Coefficient versus Toluene Vapor Activity

● OPP; ■ PVDC; △ OPP/PVDC (OPP next to vapor); ▲ OPP/PVDC (PVDC next to vapor)

Table 4

Linear Regression Equations $\log_{10} D_{lag}$ vs Vapor Activity

OPP - Toluene

$\log D_{lag} = 1.39(a) - 10.15$

experimental vapor activity range: 0.1 - 0.7

correlation coefficient (r): 0.98

PVDC - Toluene

$\log D_{lag} = 5.93(a) - 14.96$

experimental vapor activity range: 0.55 - 0.85

correlation coefficient (r): 0.94

OPP/PVDC - Toluene (OPP towards vapor)

$\log D_{lag} = 3.90(a) - 11.87$

experimental vapor activity range: 0.27 - 0.84

correlation coefficient (r): 0.979

OPP/PVDC - Toluene (PVDC towards vapor)

$\log D_{lag} = 4.12(a) - 11.87$

experimental vapor activity range: 0.27 - 0.85

correlation coefficient (r): 0.985

D_{lag} = lag time diffusion coefficient (cm^2/sec)
a = vapor activity = (p/p_o)

The slopes of the regression lines for the diffusion of toluene through the OPP/PVDC film with either the OPP or the PVDC layer next to the toluene permeant are not significantly different from one another at the $\alpha = 0.05$ level of significance. This indicates that the effective diffusion coefficient for this film is not significantly affected by which side of the polymer is in contact with the vapor. The OPP/PVDC-toluene diffusion coefficient versus vapor activity regression line slopes are not significantly different at the $\alpha = 0.05$ level of significance from the PVDC homopolymer film regression line. The slopes of these curves are however, significantly different than the OPP-Toluene diffusion regression curve slope. The pre-exponential factors for the PVDC film is three orders of magnitude lower than the OPP/PVDC laminate film curves. This difference between the films is partly explained by the differences in the thickness of the PVDC layers in the films and the differences in the PVDC material used. These results suggest the PVDC is the polymer in the OPP/PVDC laminate that controls the diffusion process of Toluene.

Sorption Studies

The results of the studies on the sorption of toluene vapor by the OPP and PVDC film samples are summarized in Table 5, where the equilibrium solubility (Cs, g vapor/g polymer), solubility coefficient (S, g vapor/(g polymer•vapor activity)) and the half time diffusion coefficient ($D_{t1/2}$, cm^2/sec) are tabulated. The half-time diffusion coefficient was calculated from the sorption curve for each sorption run, by substitution into Equation 22 (Crank and Park, 1968). Only the half-time diffusion coefficients for the OPP film were calculated. It can be seen that acceptable agreement was obtained between the lag time diffusion coefficient from the permeation measurements and half-time diffusion coefficient obtained from the sorption studies. Presented in Figure 7 is a plot of log $D_{t1/2}$ as a function of toluene vapor activity for the OPP film. The lag time diffusion coefficient values (D_{lag}) for OPP and Saran are plotted versus vapor activity and are superimposed in Figure 7 for comparison. For the oriented polypropylene structure the relationship between the lag time diffusion coeffcient and toluene vapor activity (a) is given by:

$$D_{lag} = 7.0x10^{-11} \exp(3.1 \bullet a) \quad (47)$$

The relationship between the half time diffusion coefficient and toluene vapor activity for the polypropylene is given by:

Table 5

Toluene Solubility As A Function of Vapor Activity

ppm[a]	a[b]	Cs[c]	S[d]	$D_{t1/2}$[e]	D_{lag}[f]
Oriented polypropylene (OPP) 1.0 mil :					
21.4	0.14	0.7	5.0	0.58	1.1
39.7	0.26	1.06	4.1	1.2	1.6
55.0	0.36	1.43	4.0	3.1	2.2
111.5	0.73	4.42	6.1	6.3	6.8
Saran (PVDC) 1.1 mil :					
84.0	0.55	3.45	6.3	-	0.020
85.5	0.56	3.66	6.5	-	0.023
111.5	0.73	5.04	6.9	-	0.24
135.9	0.89	7.04	7.9	-	2.1

(a) Toluene ppm (Ìg/ml)

(b) a = vapor activity (p/p_o)

(c) Cs $x10^{+2}$ Equilibrium solubility (g/g)

(d) S $x10^{+2}$ Solubility Coefficient (g/g a)

(e) $D_{t1/2}$ $x10^{+10}$ Half time Diffusion Coefficient (cm^2/sec)

(f) D_{lag} $x10^{+10}$ Lag time Diffusion Coefficient (cm^2/sec)

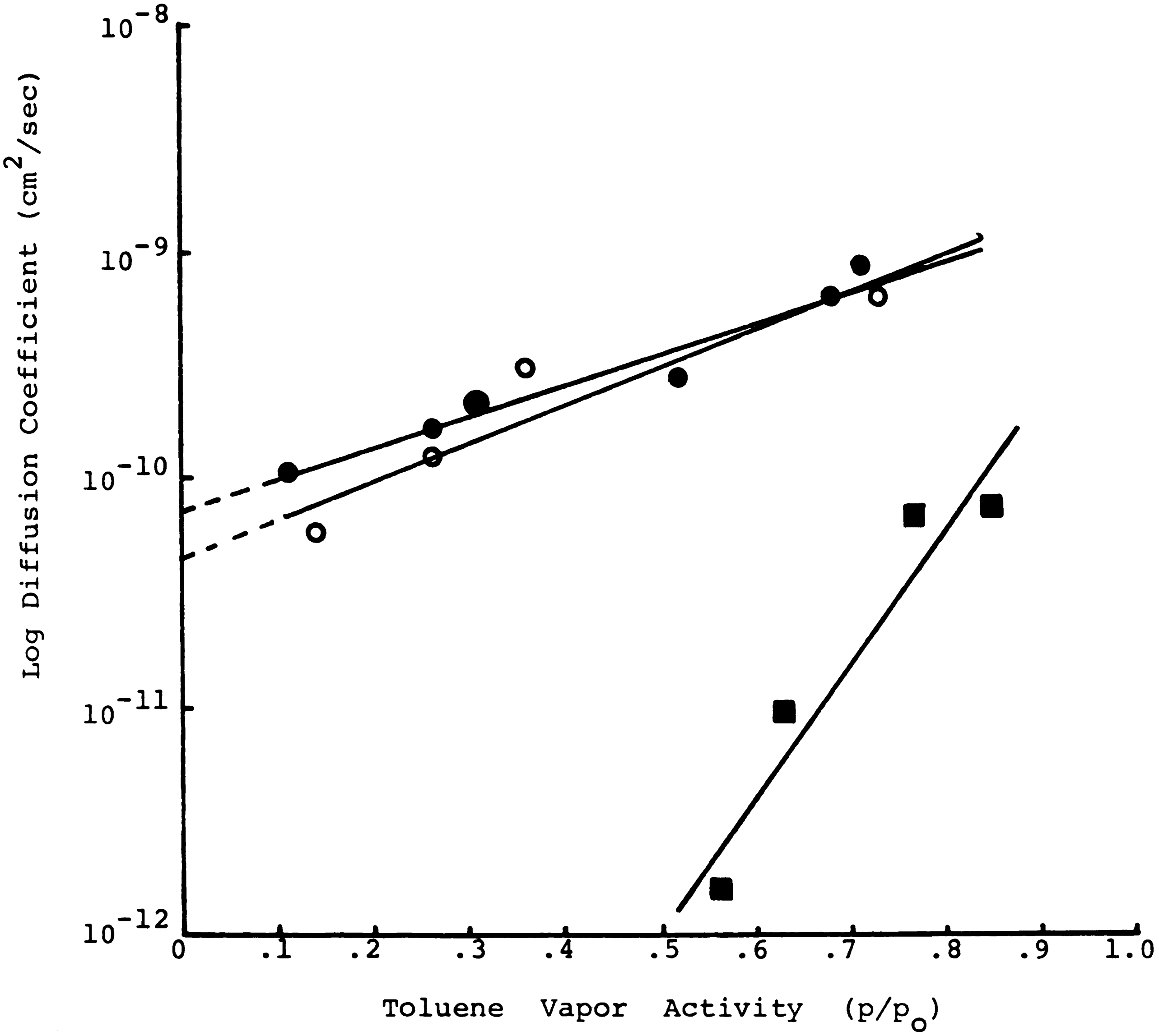


Figure 7. Lag Time and Half Time Diffusion Coefficients versus Toluene Vapor Activity

● OPP, ■ PVDC Lag Time Diffusion Coefficients
○ OPP Half Time Diffusion Coefficients

$$D_{t1/2} = 4.6\text{x}10^{-11}\ \exp(3.9 \cdot a) \quad (48)$$

As shown good agreement was obtained for the two diffusion coefficient regression lines for the OPP. Agreement is expected since both the expressions for calculating the diffusion coefficient are derived from Equation 6 using slightly different boundary conditions at the surfaces of the film. For the half time sorption diffusion coefficient the film surfaces are maintained at a concentration that is in equilibrium with the contacting vapor phase and the boundary conditions are:

for $t = 0$

$c = 0$ for $0 \leq x \leq L$

for $t > 0$

$c = c_1$, @$x = 0$ and $x = L$

For the lag time diffusion coefficient from the permeation experiment one film surface is in equilibrium with the contacting vapor phase and the other surface is assumed to be maintained free of vapor and the boundary conditions are:

for $t = 0$

$c = 0$ for $0 \leq x \leq L$

for $t > 0$

$c = c_1$ @$x = L$

$c = 0$ @$x = 0$

For better illustration, the equilibrium solubility Cs (in grams of

toluene absorbed per gram of polymer) is plotted as a function of toluene vapor activity in Figures 8 and 9 for the OPP and PVDC films respectively. The equilibrium solubility values reported correspond to the concentration at the surface of the polymer film directly in contact with the permeating vapor in the permeation experimemt. This value represents c_1 in a permeation experiment and is the maximum solubility of the permeant in the film. It can be seen from Figure 8, that up to a vapor activity of 0.4, the solubilitiy of toluene in the OPP may be approximated by Henry's law, $c = 4.35\text{x}10^{-2}(g/g\cdot a)\cdot p$. However, at vapor activities greater than 0.4, deviation from the linear Henry's law is observed and the solubility behavior for toluene in the OPP may be expressed by a second order or greater polynomial expression. Similar observation for toluene sorption behavior in oriented polypropylene were made by Choy et al (1984). Figure 9 shows the equilibrium solubility for toluene in PVDC in a vapor activity region from 0.5 to 0.9. Based on the limited vapor activity range measured for the equilbirium solubility for toluene in PVDC, the data was fitted by a second order polynomial. The polynomial expressions describing the variation of the equilibrium vapor solubility with the toluene vapor activity for the OPP and PVDC respectively are:

$$Cs = 0.04168\cdot a^3 - 0.008543\cdot a^2 + 0.04\cdot a \qquad (48)$$

$$Cs = 0.04141\cdot a^3 - 0.01314\cdot a^2 + 0.058\cdot a \qquad (49)$$

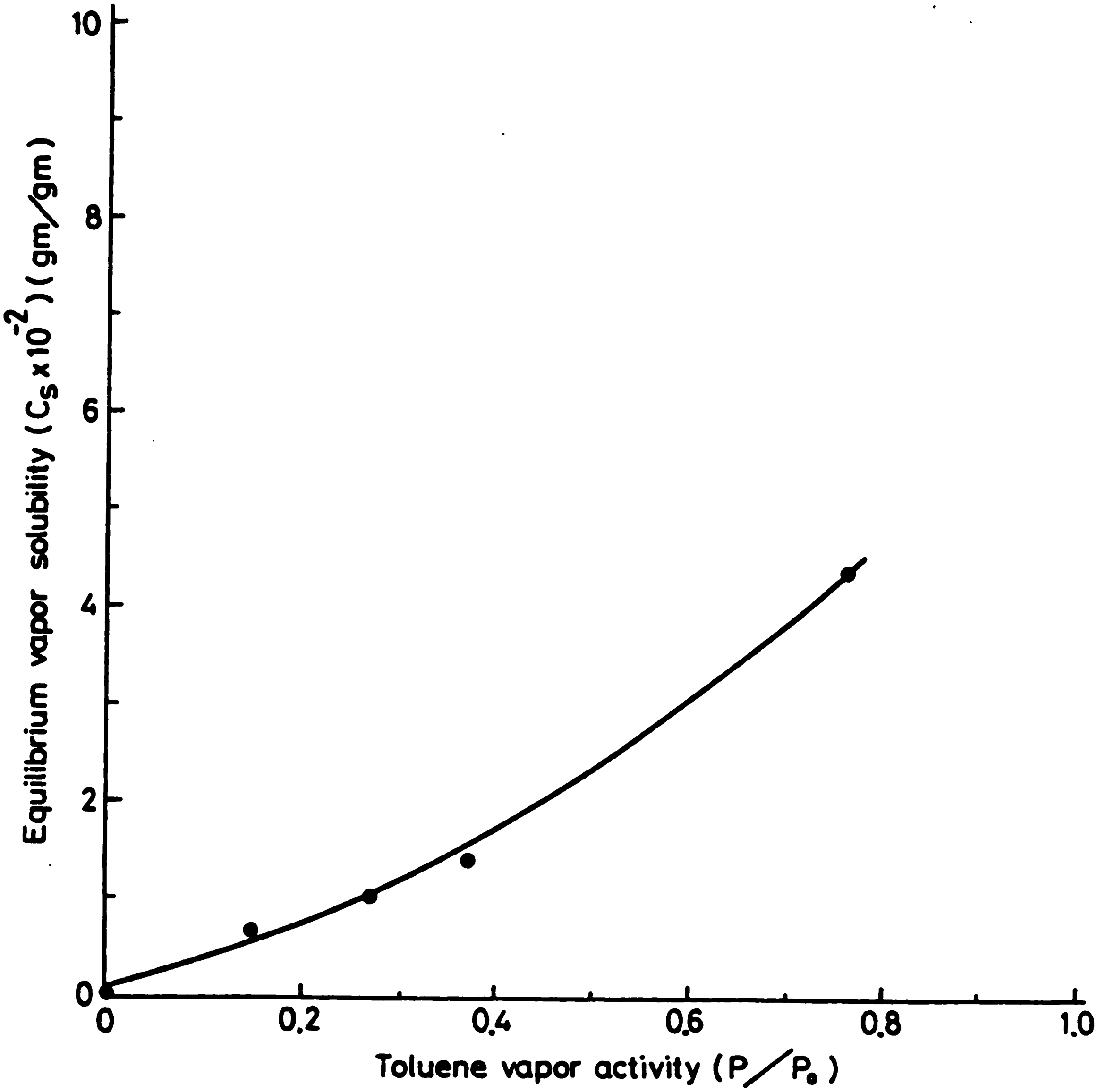


Figure 8. Toluene Solubility versus Vapor Activity In Oriented Polypropylene

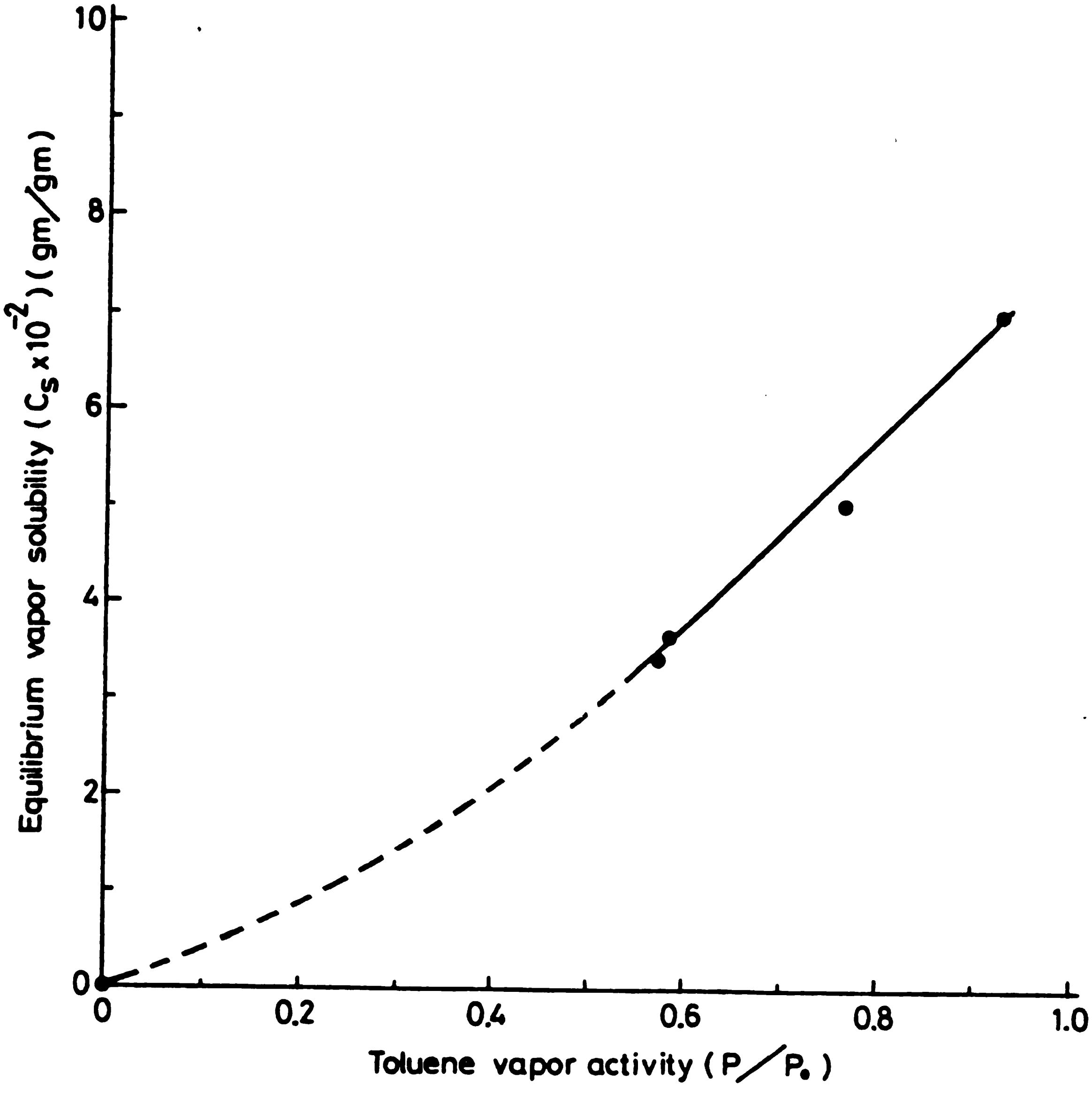


Figure 9. Toluene Vapor Solubility versus Vapor Activity In PVDC

Penetrant/Polymer Interaction and Consideration of Free Volume Effects

The permeability coefficient ($\bar{P}$) is related to the diffusion coefficient (D) and the solubility coefficient (S) by Equation 5:

$$\bar{P} = D \cdot S$$

The derivation of this equation follows from Fick's first law of diffusion. This expression assumes that D is a constant, independent of spatial coordinates, time and concentration of penetrant in the polymer. The solubility coefficient is also assumed to be a constant with concentration i.e. there is a linear relationship between the external vapor pressure and the corresponding equilibrium concentration within the polymer. This relationship is well known to be applicable to gas-polymer systems (Crank and Park, 1968).

It has been shown for the organic penetrant - polymer systems studied (see Table 3) that the permeability coefficient is not a constant but rather varies exponentially with the vapor activity of the penetrant (toluene). If Equation 5 is to be applied to the penetrant/polymer systems studied, the diffusion coefficient and/or the solubility coefficient must also vary with vapor activity. By direct measurement of the equilibrium solubility (see Table 5 and Figures 8 and 9) it was shown that the equilibrium solubility versus vapor activity did not follow the linear Henry's law relationship over the entire vapor activity range studied. As shown for OPP and toluene vapor, Henry's law is followed up to a vapor activity of 0.4, but at higher vapor activities (> 0.5) the curve can be fit by a quadratic expression. The deviation of the solubility coefficient from Henry's law does not explain in total the logarithmic increase of the permeability coefficient with vapor activity. The diffusion coefficient must therefore also be concentration dependent and contribute to the logarithmic increase in the permeability coefficient observed.

Using the polypropylene film data as an example, the permeability coefficient of toluene increased 70 fold going from a vapor activity of 0.15 to 0.7 while the solubility coefficient increased by six fold in this same vapor activity range. To account for this 70 fold increase in the permeability coefficient, the diffusion coefficient for toluene through OPP must have increased by an order of magnitude over the vapor activity range studied. Similarly, the polyvinylidene chloride film also showed that the diffusion coefficient for toluene increased exponentially with vapor activity. Within a toluene vapor activity range of 0.55 to 0.75 the permeability coefficient increased over four orders of magnitude, while the solubility coefficient only increased 1.1 times. Assuming the relationship given in Equation 5 is valid, a possible explanation for the dramatic increase in the permeability coefficient with vapor activity lies with the high vapor concentration dependency of the diffusion coefficient.

Starting with Fick's first law for permeation at steady state:

$$P = -D\, \partial c/\partial x = \text{constant}$$

the flux, P, is a constant at steady state and is measured experimentally with the following boundary conditions:

at $t = 0$ $c = c_1 = c_2 = 0$

for $t > 0$

at $x = 0$, $c = c_1$

at $x = L$ $c = c_2 \approx 0$

Based on the boundary conditions of the experiment, the concentration of permeant in the polymer must vary with the distance (x) in the polymer. It follows then that the diffusion coefficient must be a function of concentration and vary with position. Fick's second law takes into account the change in the diffusion coefficient with concentration at different locations within the polymer.

$$\partial c/\partial t = \partial/\partial x\, (D(c)\, \partial c/\partial x)$$

An integral value of the diffusion coefficient, over the concentration range of the permeation experiment, is given by Equation 8:

$$\bar{D} = (1/c_1)\int_{o}^{c1} D(c)\, dc \qquad (8)$$

Since the diffusion coefficient, as a function of the spatial coordinates cannot be measured, the integral diffusion coefficient ($\bar{D}$)

is used here to represent an average value of the diffusion coefficient over the thickness and concentration profile present in the film.

Further, the change in concentration of the permeant in the film with position cannot be determined, so a linear approximation is made using the boundary conditions described above. From solubility experiments the equilibrium solubility (Cs) can be measured, which is the concentration c_1 at $x = 0$. At the position $x = L$, the concentration of permeant in the film is small enough that it can be assumed to be zero. Therefore $\partial c/\partial x$ is approximated by:

$$\partial c/\partial x = (0 - c_1)/(L - 0)$$

Fick's first law can now be approximated by:

$$P = \bar{D} \cdot Cs/L \qquad (50)$$

Now solving for the permeability coefficient by dividing both sides of Equation 50 by the permeant driving force, $p_1 - p_2 = p$, and multiplying through by L gives the following equation:

$$\bar{P} = \bar{D} \cdot Cs/ p \qquad (51)$$

When the ratio, Cs/p, in Equation 51 is constant it can be replaced by the solubility coefficient. By taking experimental measurements for $\bar{P}$ and Cs at different permeant vapor activities the integral steady state diffusion coefficient (Dss) can be estimated from equation (51). By determining the steady state diffusion coefficient, Dss, at several permeant vapor activities the dependence of Dss on vapor activity can be determined. Hence, Equation 51 is equivalent to Equation 13, given in the literaure review.

Steady state diffusion coefficient values at several vapor activities were calculated for the diffusion of toluene vapor through the oriented polypropylene and polyvinylidene chloride films using Equation 51. The log of Dss versus toluene vapor activity is plotted in Figure 10 for the two film structures. The lag time diffusion coefficient (D_{lag}) versus the toluene vapor activity for the respective films has been superimposed for comparison. The variation of the log of Dss with toluene vapor activity can be approximated by the linear exponential expressions for OPP and PVDC by equations (52) and (53) respectively:

$$Dss = 1.6x10^{-11} \exp(7.1 \cdot a) \qquad (52)$$

$$Dss = 1.2x10^{-22} \exp(33.3 \cdot a) \qquad (53)$$

The variation of the log of D_{lag} with the toluene vapor activity can be expressed by Equations (54) and (55):

$$D_{lag} = 7.0x10^{-11} \exp(3.1 \cdot a) \qquad (54)$$

$$D_{lag} = 1.0x10^{-15} \exp(13.3 \cdot a) \qquad (55)$$

for the OPP and PVDC films respectively. As shown in Equations 52 and 54 for the OPP film and Equations 53 and 55 for the PVDC film, the slopes of the steady state diffusion coefficient regression lines in Figure 10 are more than two times greater than the slopes of the lag time diffusion coefficient regression lines. The difference in the slopes of the regression lines suggests that the steady state diffusion coefficient is more dependent on the toluene vapor activity than the lag time diffusion coefficient. The pre-exponential factor for the

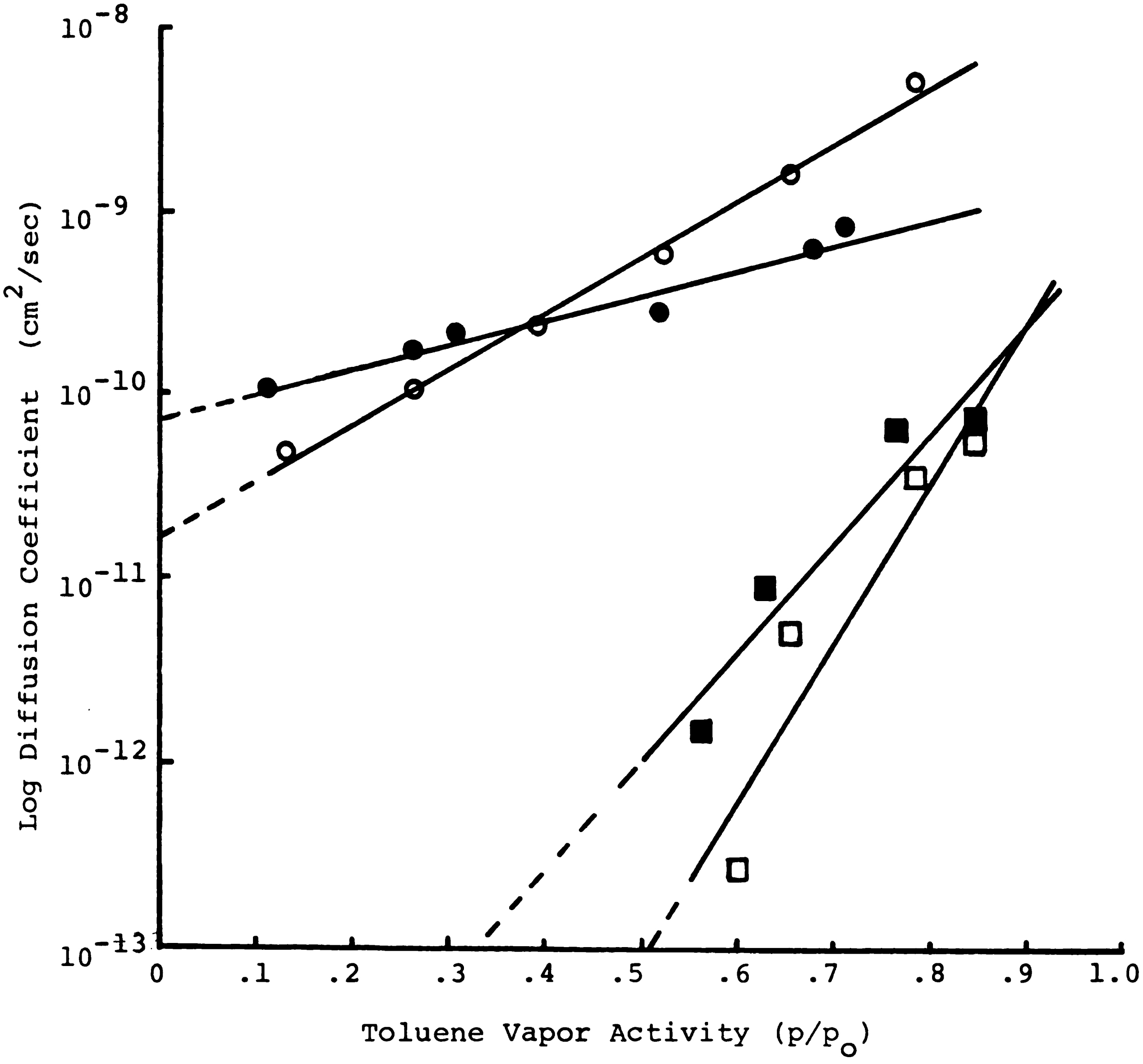


Figure 10. Comparison of Lag Time and Steady State Diffusion Coefficients versus Toluene Vapor Activity

- ● OPP Lag Time Diffusion Coefficient
- ○ OPP Steady State Diffusion Coefficient
- ■ PVDC Lag Time Diffusion Coefficient
- □ PVDC Steady State Diffusion Coefficient

steady state diffusion coefficient expression, as compared to the lag time diffusion coefficient expression is significantly different at the $\alpha = 0.05$ level of significance for both films The lag time diffusion coefficient, determined from transient state permeation data, and the steady state diffusion coefficient, determined at steady state permeation conditions are both integral diffusion coefficients. From the definition of the integral diffusion coefficient, the integral diffusion coefficient represents an average of the diffusion coefficients throughout the polymer thickness. Thus the integral diffusion coefficients are assumed to be independent of time effects and are defined for the given boundary conditions of the permeation experiment, even though the concentration distribution of permeant in the polymer is not explicitly known. The integral diffusion coefficient is fickian in nature meaning that the diffusion coefficient is independent of time effects.

The lag time diffusion coefficient and steady state diffusion coefficient are defined using the same boundary conditions using similar equations. Analytically the only difference between these diffusion coefficients are the time periods during the permeation process from which they are determined. While not fully understood, one possible reason for the lag time diffusion coefficient showing a lesser dependency on the contacting vapor concentration, as compared to the steady state diffusion coefficient, may be the changing permeant

concentration gradient in the polymer during the transient period. The lag time diffusion coefficient method assumes the diffusion coefficient is a constant with vapor concentration. However, given the exponential dependence of the diffusion coefficient on vapor activity this assumption is not valid for the penetrant barrier systems studied. At steady state, the concentration gradient of permeant is fully established and is assumed to no longer vary with time.

Part of the increase in the concentration dependency of the diffusion coefficient, as permeation progresses from transient to steady state conditions, may also be due to relaxation effects occurring within the polymer matrix. The absorption of organic vapors can result in polymer swelling and thus can change the conformation of the polymer chains. These conformational changes are not instantaneous but are controlled by the retardation times of the polymer chains. If these times are long, stresses may be set up which relax slowly. Thus, the absorption and diffusion of organic vapors can be accompanied by concentration as well as time-dependent processes within the polymer bulk phase, which are slower than the micro-Brownian motion of polymer chain segments which promote diffusion (Meares, 1965).

From sorption studies at low vapor activities of vinyl chloride monomer in polyvinyl chloride powder, Berens (1977) proposed that above the glass transition temperature, the relaxation process is sufficiently rapid to be complete within the time scale of the fickian diffusion process. However for PVC polymer films, Berens (1977) found that the separation of relaxation and diffusion phenomena is not possible. The results of Blackadder and Keniry (1973) support Berens observation of a longer time scale for relaxation phenomena in polymer films. These investigators found that it took 8 to 24 hours for a true steady state rate of permeation of p-xylene through a 0.75 mil polyethylene film to be attained. Their conclusion was that there are long stress relaxation times occurring in the polyethylene film, which are longer than the time required for diffusion. Other researchers have developed expressions accounting for polymer chain relaxation effects on the diffusion of penetrants. Vrentas et. al. (1975) and Vrentas (1977) have used a Deborah number, which is a ratio of polymer mean relaxation time to a characteristic diffusion time, for characterising diffusional transport in amorphous polymer-solvent systems. Jäckle and Frisch (1985) have developed a generalized diffusion equation that accounts for the effect of slow structural relaxation in a solvent of high viscosity (the polymer matrix) on the chemical potential driving the diffusion of penetrant molecules.

On the basis of the studies of Berens (1977) and Blackadder and Keniry (1973) there is supportive evidence for long time period relaxation effects occurring in polymer films above their glass transition temperature. Thus there may be relaxation effects occurring during the diffusion of toluene in both the OPPand PVDC films investigated. From the work of Berens (1977) the relaxation effects are expected to be more severe at higher vapor activities. Both the OPP and PVDC films were studied at temperatures well above their glass transition temperatures, over a range of vapor activities up to 0.85. In addition to the proposed changing concentration gradient within the polymer bulk phase during the transient state, long time relaxation effects may also occur and contribute to the differences in the magnitudes and concentration dependencies of the lag time and steady state diffusion coefficients.

The relaxation processes which occur over a longer time-scale than diffusion may be related to a structural reordering or redistribution of the free volume elements in the polymer. Thus providing additional sites of suitable size and accessability to accomodate more penetrant molecules (Berens, 1978). The difference between the transient and steady state diffusion coefficient values may therefore also be related to the change in the free volume of the polymer matrix. The free volume model for diffusion in polymers may be used to analyze the differences observed between the transient and steady state rates of diffusion in the polymers studied; and is described below..

From the free volume theory of Fujita (1961), the relationship between the diffusion coefficient (D) and the equilibrium solubility concentration (Cs) for a penetrant/polymer system can be expressed by

Equation 30.

$$D- D_o \exp (\gamma Cs) \qquad (30)$$

Where D_o is a pre-exponential factor, sometimes referred to as the limiting diffusion coefficient, and γ is a lumped proportionality factor, related to free volume parameters by Equation 35.

$$\gamma - B \beta / f^2_o \qquad (35)$$

Where f_o is a constant describing the fractional free volume of the polymer at zero vapor concentration, B is a measure of the minimum hole size for the penetrant molecules jump step in the polymer matrix and β denotes the effectiveness of the penetrant molecules for increasing the free volume of the polymer (Choy et al., 1984). In Equation 35, the γ term (g polymer/g penetrant) is a function specific for each penetrant/polymer pair and temperature.

The values of D_o and γ can be obtained from a linear best fit of a plot of log D versus the corresponding equilibrium solubility values (Cs), obtained at the same vapor activity. Plots of D_{lag} versus Cs and Dss versus Cs for the OPP and PVDC film samples are presented in Figure 11. As shown, a linear relationship was obtained which gave correlation coefficients of 0.98 and 0.99 for OPP, and 0.92 and 0.92 for PVDC for

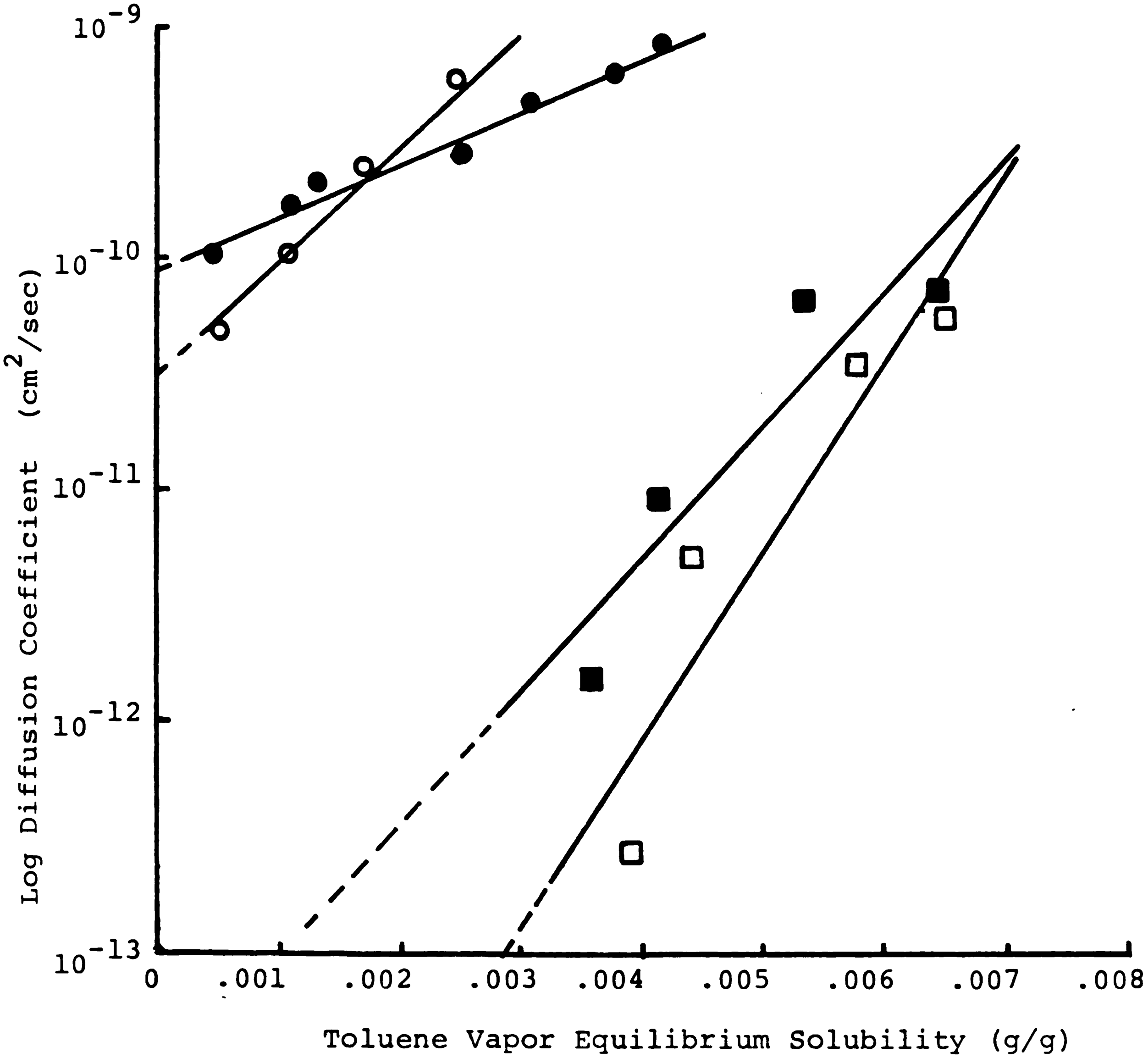


Figure 11. Comparison of Lag Time and Steady State Diffusion Coefficients versus Equilibrium Solubility Of Toluene

● OPP Lag Time Diffusion Coefficient
○ OPP Steady State Diffusion Coefficient
■ PVDC Lag Time Diffusion Coefficient
□ PVDC Steady State Diffusion Coefficient

D_{lag} and Dss respectively. For OPP/toluene the free volume expressions for D_{lag} and Dss are:

$$D_{lag} = 9.3x10^{-11} \exp(48.0 \cdot Cs) \qquad (56)$$

$$Dss = 3.1x10^{-11} \exp(113.7 \cdot Cs) \qquad (57)$$

For PVDC/toluene the free volume expressions for D_{lag} and Dss are:

$$D_{lag} = 2.5x10^{-14} \exp(132.7 \cdot Cs) \qquad (58)$$

$$Dss = 4.6x10^{-16} \exp(187.6 \cdot Cs) \qquad (59)$$

The pre-exponential terms obtained from graphical analysis of Equation 30 were not significantly different at the $\alpha = 0.05$ level of significance for the OPP. The pre-exponential terms for D_{lag} versus Dss for PVDC where found to be significantly different. However, the terms for D_{lag} and Dss are significantly different at the $\alpha = 0.05$ level of significance for both the OPP and PVDC films.

From Equation 35, it is assumed that B and f_o are constants for the penetrant/polymer system and are independent of penetrant concentration, while, the β term is interpreted as an interaction parameter which describes the effectiveness of the penetrant molecule for increasing the free volume of the polymer. The β term is also assumed to be a constant for a specific penetrant/polymer combination. However it was found here that its numerical value was not constant, but depended upon whether the diffusion process was determined from transient or steady state data.

From the theory of Fujita (1961) the diffusion coefficient (D) in

Equation 30 is, by definition, a Fickian diffusion coefficient and is not a function of time. Therefore, in application of the free volume theory it may be incorrect to employ the diffusion coefficient measured during the transient state for systems where there is a changing permeant concentration gradient over the period of measurement and during a time period when polymer chain relaxations are occurring. When applying the lag time diffusion coefficient to the free volume model, the assumption must be made that the lag time diffusion coefficient represents a time averaged value, taken over the entire transient permeation stage.

In addition to time dependent effects, the expression for the lag time diffusion coefficient was derived for the case where the diffusion coefficient is constant and is not dependent on the concentration of the permeant in the polymer. Therefore it may be incorrect to apply the lag time method to these penetrant/polymer systems. However, Pollak and Frisch (1959) have shown that the inequality:

$$1/6 \leq \Theta D/L^2 \leq 1/2 \qquad (18)$$

holds for a large class of functional dependencies of D on c. Thus an estimate of the magnitude of the lag time diffusion coefficient may differ at worst by a factor of three when the expression for the lag time diffusion coefficient is substituted into Equation 18. Frisch (1958) and Pollack and Frisch (1959) have shown that the lag time diffusion coefficient can be an indicator of the magnitude and form of

concentration dependency of the diffusion coefficient on the penetrant concentration.

Based on the results of Pollack and Frisch (1959) for the magnitude of the lag time diffusion coefficient and the assumption of the lag time diffusion coefficient being a time averaged value and thus being independent of time, the lag time diffusion coefficient can be related to the free volume. The steady state diffusion coefficient is a fickian diffusion coefficient and the free volume model can be applied because the polymer system is in an equilibrium condition, where all time and relaxation effects have occurred prior to its measurement.

In order to take in account the time dependent concentration gradient within the polymer bulk phase and polymer chain relaxation when going from the transient state to a steady state rate of diffusion, it is proposed that the β term be comprised of two parameters, phi (ϕ) and epsilon (ϵ):

$$\beta = (\phi + \epsilon) \qquad (60)$$

The ϕ term describes the penetrant polymer interaction parameter associated with the Fickian diffusion process and is independent of a changing penetrant concentration gradient and molecular reorientation (i.e. relaxation). The ϵ term takes into consideration the effect of time dependent interaction and relaxation which occur as the system goes to steady state. It includes the simulataneous relaxation of the polymer chains due to plasticization by the penetrant and the resulting increase in the concentration gradient of the penetrant in the polymer. These time dependent processes will lead to an increase in the diffusion coefficient for a penetrant polymer system with a concentration dependent diffusion coefficient. The ϵ term describes the time, and spatial effects, as well as concentration changes occurring in the polymer bulk phase due to the presence of penetrant molecules.

For Equation 30, when D_{lag} values are substituted, the β interaction term associated with γ could be interpreted to be the fickian diffusion interaction effects (ϕ). When steady state diffusion coefficient values are applied, the β interaction term reflects the interaction effects of both fickian diffusion (ϕ) and relaxation (ϵ). No attempt is made here to derive numerical values for the ϕ and ϵ terms, as it is beyond the scope of this study and mor experiments are necessary.

The lag time diffusion coefficient for the PVDC film was found to have a greater concentration dependency, as shown by the larger γ term as compared to the D_{lag} value for OPP. Conversely the PVDC film shows a smaller increase in the γ term than the OPP film, when comparing D_{lag} and Dss values for solution of Equation 30. A 1.4 times increase for the PVDC versus a 2.4 times increase for the OPP was observed. These results suggest that relaxation effects may be more important in the OPP film than in the PVDC film. The larger apparent relaxation effects in the OPP may be a result of the internal tension present in in the polymer matrix because the OPP film is biaxially oriented. An estimation of the strength of the intermolecular forces between the polymer chains is given by the cohesive energy density. The smaller apparent relaxation in the PVDC due to sorbed toluene vapor may be due to its higher solubility parameter of 22-30 $MPa^{1/2}$ versus 16.6 $MPa^{1/2}$ for OPP (Brandrup and Immergut, 1975). Toluene has a solubility parameter of 18.3 $MPa^{1/2}$ which makes it more soluble in the OPP than the PVDC thus leading to larger relaxation effects in the OPP.

Experimental Error Analysis

Permeation Measurements:

Interpreting the transmission profile curve properly to obtain the equation for the straight line describing the steady state permeation region can be a major source of error in the data analysis of this method. From this steady state equation the permeation rate and lag time are determined from which the permeability, diffusion, and solubility coefficients are then derived. Errors and uncertainties in determining the steady state permeation line on the transmission profile curve come from: (i) individual measurement error and variability; (ii) interpretation of the transmission profile curve shape; (iii) fundamental errors in the experimental design and execution. The folowing error analysis describes some sources of error in this particular experiment and makes estimations of the magnitude of these errors and their effect on experimental results.

The estimated error or uncertainty in a single headspace syringe sample measurement is shown in Table 6. The relative error is the percent error where the amount of variation or uncertainty in a measurement is divided by the best estimate of the true value for the parameter which is an average of several experimental values (Taylor, 1982).

Table 6

Estimates of Measurement Uncertainty

relative error	description of error
± 1%	Syringe volume accuracy
± 1%	G.C. Detector accuracy
± 2%	Sampling error from leaking septa, sample volume, and mixing problems
-2%	Decrease in permeant concentration in cell headspace due to sample removal
± 6%	Total estimated sample measurement error

Error in Sampling Time

absolute error	time interval	relative error
±10 seconds	1 minute	17%
±10 seconds	10 minutes	5%
±30 seconds	1 day	0.03%
1 minute	1 week	1.6x10-4%

The relative uncertainty or error of the quantity of permeant as seen in Table 6 is estimated to be ±6% for a single syringe sample. The sample measurement error is considered to be an average uncertainty for each syringe sample and is composed of several identifiable sources of error. The syringe accuracy of ±1% was obtained from the syringe manufacturer and assumes this accuracy if the syringe is working properly and there is no operator error. The gas chromatoraph flame ionization detector accuracy accounts for the inherent variability in the response of the detector from sample to sample. The sample error comes from leaks in the GC and cell septa, changes in the sample volume with pressure and mixing problems within the cell's headspace. This error can be quite large and depends on the operators skill and experience in recognizing if there are leakage or some other problems when sampling. The 2% decrease in the permeant headspace concentration occurs because a 0.5 ml sample is removed from the 50 ml headspace volume this removes 2% of the total permeant present in the headspace at the time of sampling which is then replaced with an equivalent volume of nitrogen. If the amount of permeant removed by sampling is calculated and added back into the measured final concentration the measured concentration in the cell is approximentely 2% lower than what actually has permeated. The total estimated error is the sum of all the component errors.

This uncertainty for each sample is depicted on the transmission profile curve in Figure 12 as vertical error bars. As the quantity of permeant in the headspace increases the error bars representing the absolute error increase while the relative error remains at ±5%. The relative error of meaurement is considered to remain constant for all syringe samples and for all film samples. The relative error in the sampling time becomes negligible at longer times and generally can be ignored for data taken after a time interval over 10 minutes.

Another source of error for a film-permeant measurement is interpreting where the steady state permation region begins. Often times the only way to be sure the permeation is in the steady state is to plot the transmission profile curve and visually examine the data. If the data appears to be following steady state behaviour then the permeation rate and lag time is calculated using points that lie in the steady state region. The data should be collected for a time period equivalent to at least two or three lag times to ensure the permeation is steady state (Siegal and Coughlin, 1970).

Linear regression analysis is a statistical technique that can be used to determine the best fitting linear line for a given set of data points (see Steel and Torrie, 1980). This is the preferred method for obtaining the equation of the line for the steady state region. Linear regression analysis gives a reproducible and statistically sound way of deriving the equation for the steady state permeation region. The

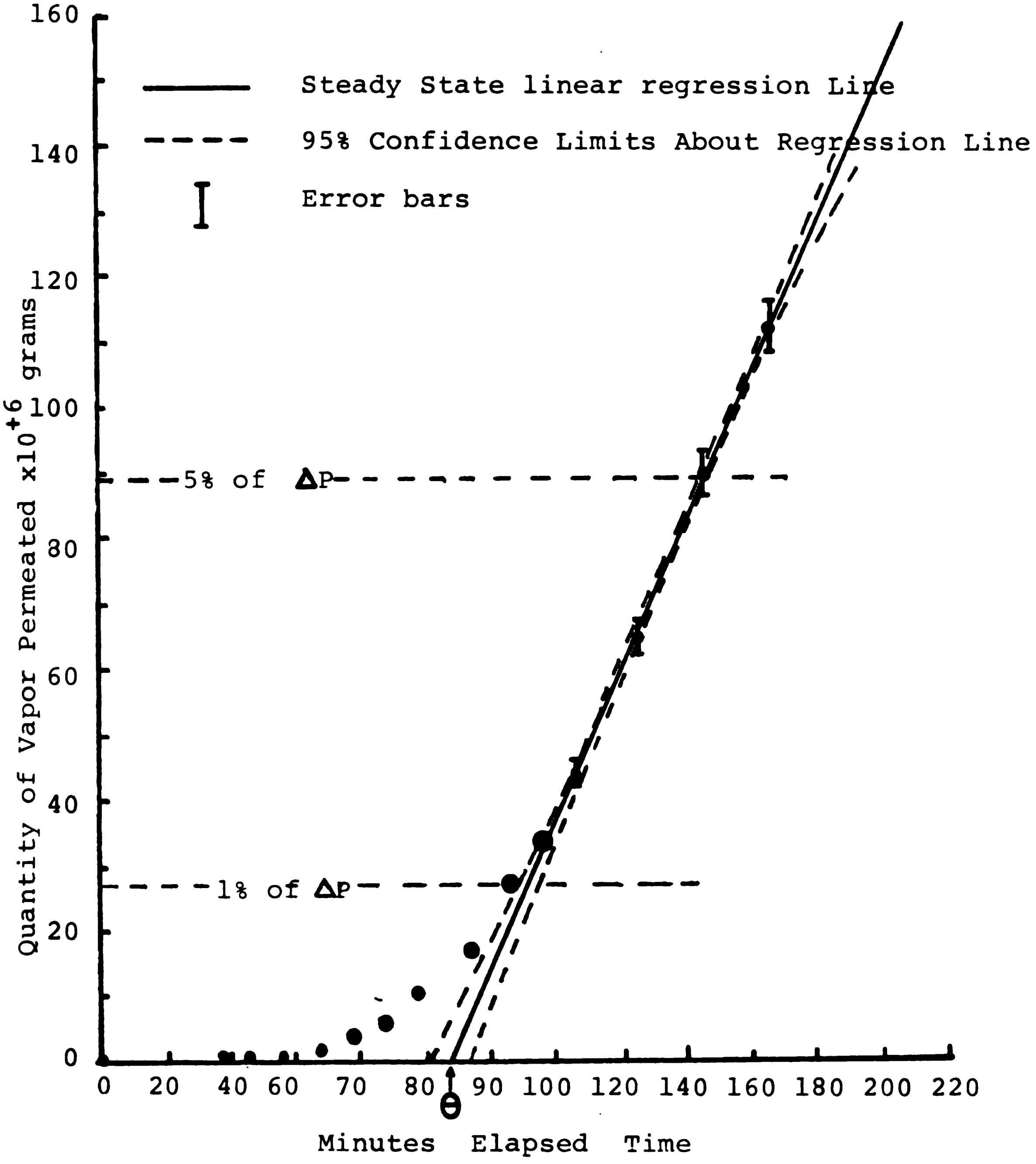


Figure 12. Transmission Profile Curve Error Analysis

Transmission profile curve of Toluene permeation through Oriented Polypropylene at a driving force vapor activity of 0.261.

correlation coefficient (r) can also be calculated which indicates how the variation in y (the headspace permeant quantity) varies with x (time) (Steel and Torrie, 1980). A correlation coefficient of ±1 indicates a perfect fit of the line with the data points and coefficient of $r = 0$ indicates there is no linear correlation between the variation in the headspace quantity with time. Table 7 shows the correlation coefficients of the steady state regression lines for the data presented. The correlation coefficients ranged from 0.9800 to 0.9998, with an average correlation coefficient around 0.9960. A good correlation coefficient is not a guarantee that the true steady state regression line has been determined although it is a strong indication. Data collection over a long enough period of time to positively identify the steady state permeation region is the surest way to avoid errors of this type.

Table 7 also shows the variation between the permeation rates for film samples tested under the same conditions. There is a variation of 8 to 50% in these permeability rates. Table 8 lists estimates for different sources of variation that affect the comparison of permation rates between equivalent film samples. The variation in cell volume can occur when the film is not placed in the cell properly due to error in clamping the cell parts together, the film sags due to the force of gravity or is distended because of unequal pressures in the cell compartments. This error is minimized by using good technique. The 8%

Table 7

Variation of Toluene Permeation Rate

Film	runs	ppm	P	s.d.	range of P	r	range of r
OPP[1]							
	4	16±1	1.23	.2	1.09-1.51	.9960	.9903-.9999
	2	41±3	7.26	-	6.88-7.63	.9971	.9946-.9995
	2	48±3	11.9	-	10.6-13.3	.9998	.9997-.9999
	4	81±4	112.	21.	96.7-143.	.9958	.9895-.9986
	4	93±3	251.	21.	227.-268.	.9960	.9940-.9975
	4	100±5	543.	148.	413.-754.	.9977	.9955-.9973
	4	112±5	3630.	578.	285.-414.	.9983	.9955-.9998
PVDC[2]							
	4	73±3	.0084	.0037	.0042-.010	.9830	.9800-.9860
	4	96±3	5.95	.33	5.19-6.16	.9989	.9985-.9995
	2	125±5	183.	-	181.-186.	.9953	.9938-.9967
	2	141±5	195	-	194.-195.	.9978	.9964-.9993
OPP/PVDC[3]							
	4	40±2	.020	.008	.0086-.029	.9919	.9884-.9951
	2	54±2	.175	-	.169-.181	.9824	.9797-.9850
	4	79±2	4.75	1.15	3.89-6.42	.9974	.9946-.9995
	2	92±2	215.	-	206.-224.	.9985	.9983-.9987
	2	94±2	168.	-	140.-195.	.9957	.9938-.9973
	4	135±3	1070.	340.	780.-1480.	.9988	.9973-.9998

1) OPP 1.0 mil
2) PVDC 1.0 mil
3) OPP/PVDC 2.0 mils OPP towards vapor

runs - number of replicate samples measured

ppm - concentration of toluene vapor (g/ml)

P - average permeation rate $x10^{+5}$ (gm/hr 50cm^2)

s.d. - standard deviation of permeation rate $x10^{+5}$ (gm/hr 50cm^2)

range of P - range of permeation rates measured $x10^{+5}$ (gm/hr 50cm^2)

r - average correlation coefficient for slope of steady state permeation portion of transmission profile curve

range of r - range of correlation coefficients measured

Table 8

Table of Uncertainties For Permeation Experiment Quantities

Description of Parameter	Relative uncertainty
Estimated measurement error for a single syringe measurement (grams)	± 5%
Cell Volume (cm^3)	± 4%
Film Surface Area (cm^2)	± 8%
Permeation Rate (g/hr•50cm^2)	± 5%
Permeant Concentration (ppm)	± 5%
Film Thickness (cm)	± 10%
Permeability Coefficient (g·structure/cm^2·day.ppm)	± 21%
Lag Time Diffusion Coefficient (cm^2/sec)	± 28%
Integral Solubility Coefficient (moles/cm^3· atm)	± 35%

relative error in the true surface area exposed to the penetrant is due to the uncertainty of the area of the compression seal of the o-rings. This error is inherent in the design of the cell. The o-rings reduce the exposed area of the film as the cells are clamped together. Using a feeler gauge to measure the gap between the cell sections can control this variability. Within this o-ring error is any permeation or sorption of vapor by the o-rings themselves which would decrease the measured permeation rate. The sample measurement uncertainty of ±6% may not always be this great but some error will always be present. This 2% error due to sample removal from the headspace can be minimized by taking smaller headspace sample volumes. For example, a 0.25 ml gas headspace sample from the 50ml cell headspace would give an error around 1%.

The variation in the permeant driving force concentration is due mainly to the temperature fluctuation of the environment changing the saturation vapor pressure of the permeant. This error can be controlled by performing these permeation tests in a room with good temperature control to with ±0.5°C. The uncertainty of the film thickness is due to the limitations of the measuring equipment which is accurate only to ±0.1 mil. There are also variations in thickness of the sample itself. The variations in the film sample can be compensated for when measuring thickness by taking an average of several measuremnts over the surface area of the film sample.

The calculated permeability coefficient reflects the uncertainties listed in Table 8. The cell volume, film surface area, permeation rate, film thickness and permeant driving force parameters are all multiplied or divided by one another to give the permeability coefficient. Because these uncertainties are all multiplied and divided by one another they can be combined by quadrature in Equation 61 to give an estimate of the uncertainty of the permeability coefficient (Taylor, 1982). For example:

$$\sqrt{(4)^2 + (8)^2 + (5)^2 + (5)^2 + (10)^2} = 21\% \qquad (61)$$

The 21% uncertainty calculated for the permeability coefficient is approximetely the average variation observed for the permeability rates for duplicate film samples. This is not surprising because the permeability coefficient is directly related to the permeation rate. The permeability coefficient "normalizes" the variation effects of thickness, surface area and penetrant driving force of the permeation rate. Stern et. al. (1983) reported the maximum error of permeability coefficients using an isostatic permeation measurement procedure to be ±12% by the method of propagation of errors for their measurements of the permeation of a gas mixture.

Extrapolation of the steady state regression line on the transmission profile curve to the x-axis gives the lag time from which the lag time diffusion coefficient is calculated. The accuracy of the lag time value depends on how well the regression line approximates the true steady state conditions. It has been shown that the relative error of the lag time is several times larger than the error in the permeation rate (Siegel and Coughlin, 1970). A relative error of 10% in the permeation rate can result in a relative error of up to 50% in the lag time (Siegel and Coughlin, 1970).

An estimate of the uncertainty of the lag time can be made by calculating the confidence limits for the steady state regression line. These limits show the possible uncertainty of the x-intercept due to the fit of the regression to the steady state data points. The accuracy of the steady state regression line and the lag time and hence the diffusion coefficient is increased by extending the transmission profile curve to at least 2 to 3 lag times (Siegel and Coughlin, 1970). Table 9 shows the experimental variation of the lag times.

The lag time diffusion coefficient's uncertainty is composed of ±10% relative uncertainty for the film thickness and ±20% relative uncertainty for the observed permeation rate. These uncertainties can be combined by quadrature to give a relative uncertainty of ±28% for the lag time diffusion coefficient. The actual variation of the experimental lag time diffusion coefficients are usually less than the calculated uncertainty. The variation of the experimental D_{lag} values for a film/permeant combination ranged from 0.5% to 50% with an average variation around 25%.

Table 9

Variation of Lag Time

film	runs	ppm	θ	s.d.	range of	temperature
OPP[1]						
	4	16±1	2.90	10	2.77-2.99	25.4-25.9
	2	41±3	1.81	-	1.81-1.83	27.2
	2	48±3	1.41	-	1.42-1.44	27.2
	4	81±4	1.08	.13	.91-1.19	26.9-27.4
	4	93±3	.65	.01	.64-.66	26.7-27.8
	4	100±5	.52	.04	.49-.57	25.8-26.1
	4	112±5	.36	.03	.32-.39	27.2-27.4
PVDC[2]						
	4	73±3	237.66	51.52	187.-284.	23.0-23.9
	4	96±3	40.49	.92	39.2-41.3	26.7
	2	125±5	5.62	-	4.91-6.33	27.5-28.6
	2	141±5	4.45	-	3.93-4.97	27.1-29.8
OPP/PVDC[3]						
	4	40±2	105.21	10.22	92.0-115.	25.0-26.6
	2	54±2	35.46	-	34.79-36.12	23.9-28.3
	4	79±2	12.22	.12	12.1-12.4	26.3-26.7
	2	92±2	2.66	-	2.50-2.81	26.7
	2	94±2	2.22	-	2.13-2.31	26.7
	4	135±3	.66	.09	.57-.78	27.4-28.0

1) OPP 1.0 mil
2) PVDC 1.0 mil
3) OPP/PVDC 2.0 mil OPP towards the toluene vapor
runs - number of replicate samples measured
ppm - toluene vapor concentration (g/ml)
θ- lag time in hours
s.d. - standard deviation of lag time (hours)
range of - range of lag time values measured (hours)
temperature - temperature variation of test (°C)
minimum to maximum temperature

The average temperature for these experiments was 26.6°C with an average day to day temperature variation of ±1.6°C (see Table 10). The effect of this temperature variation on the permeability, diffusion and solubility was not determined in this experiment. However some estimation of the variation in these parameters due to temperature can be made using equations 25,29, and 37 which predict an exponential dependence of the solubility,diffusion and permeability coefficients respectively on temperature. The activation energy for the permeation process, E_p, has been shown to be highly dependent on the polymer-penetrant system studied and the temperature range used (Laine and Osburn, 1971). It has been found in some film-organic penetrant systems, Benzene and Hexane in Polyethylene, that the energy of activation (Ep) around a room temperature range is zero (Cutler et al, 1951). An E_p of zero indicates that the permability coefficient is unaffected by changes in temperature within a given temperature range. As an example of the possible temperature effect on permeability DeLassus (1985) determined the permeation activation energy for d-Limonene at saturation vapor pressure in OPP and a medium barrier Saran to be 11.2 and 14.8 Kcal/mole respectively. Using DeLassus' data for a 1.6°C variation in temperature there is a 11.1% and 16% increase in the permeability coefficient for the OPP and Saran films respectively. Similar behaviour may be anticipated for the film-permeant combinations tested here.

The diffusion coefficient will increase with temperature and with the sorbed vapor content. The activation energy for the diffusion process, E_d, for a polyethylene film and butylene permeant at 25°C and butylene vapor activity of 0.5, was found to be 15.1 kcal/mole (Rogers, 1965). Using equation 29 and this E_d value it can be shown that for each 1°C increase in temperature the diffusion coefficient will increase by 8.9%. It is possible that the diffusion coefficient may increase by as much as 14.5% for a temperature increase of 1.6°C using the E_d of 15.1 kcal/mole. It is possible that similar behavior may be exhibited in the film-permeant systems studied here.

The solubility coefficient decreases with as increase in temperature. The activation energy for the sorption process, Hs, for benzene and hexane in a polyethylene film was reported to be -12 kcal/mole (Cutler et al, 1951). This activation energy coupled with the expected exponential dependence of the solubility coefficient to temperature (equation 25) would give a decrease of approximentely 7% in the solubility coefficient for each 1°C increase. Similar variation of the solubility coefficient with temperature may have occured for the film-permeant combinations tested here.

A decrease in the solubility coefficient coupled with a concurrent increase in the diffusivity of organic vapors with temperature suggests that the permeation process for organic vapors in polymers is less dependent on fluctuations in temperature than either the solubility or diffusion coefficients (Rogers, 1964).

The temperature fluctuations in this experiment followed a diurnal cycle so that the effect of the temperature variations tended to average out to 27°C over a 24 hour time period. This suggests that the effect of temperature variations on these results may be negligible except in cases where there was a significant temperature change during a test run.

A more serious problem with the temperature variations in the environment is its effect on the permeant vapor concentration. Increases in temperature raise the permeant concentration by increasing the saturation vapor pressure of the permeant in the nitrogen as well as changing the flow rate of the nitrogen. The increase (or decrease) in vapor concentration has been shown to have a much greater effect on the permeation process than temperature effects (Rogers, 1964).

The estimated uncertainties for the calculated parameters in this study are summarized in Table 8. There are some refinements in the method and apparatus that can be done to reduce the uncertainty of these measurements. More accurate physical measurements in cell volume, film thickness and film surface are some measurements that can be easily improved. Some uncertainties and errors in the permeation rate, permeability coefficient and lag time diffusion coefficient can be minimized by careful and conscientious data collection of the complete transmission profile curve to ensure accurate determination of the steady state permeation rate, lag time and transient permeation region. Other uncertainties such as the decrease in the slope of the permeation rate due to sampling the cell headspace are inherent in the method but can be corrected for by developing a correction factor. This correction factor is determined by calculating how much permeant vapor is removed per sample and adding it back into the raw transmission profile curve data then recalculating the parameters. The difference between the corrected parameters and the uncorrected ones will determine the size of the correction factor. The error of a single syringe headspace sample can be minimized by proper sampling technique with the syringe, taking smaller sample sizes and redesigning the permeation cell to increase the headspace volume.

The results from this error analysis suggest that this permeation data has an estimated accuracy of ±20% for the lag time diffusion coefficient and permeability coefficient. This may be acceptable error because often the variation between the diffusion coefficient and permeability coefficients between different films, permeants and permeant concentrations is larger than this error. Furthermore these films have not experienced any damage due to handling and package forming that one would expect to find in packaging applications for these films. This method will find its greatest utility in evaluating potential packaging films for a specific application because it produces data accurate enough for comparison purposes. This method may not be accurate enough or sensitive enough when comparing film-permeant systems where differences between the film sample morphology or test conditions are too small to give statistically significant results. However, it has been shown that this method can be used to predict the permeant concentration dependence of the permeability, diffusion and solubility coefficients for different films.

From the error analysis it was determined that the experimental values of the permeability coefficient and lag time have the greatest accuracy because they were directly calculated from experimental results.

Sorption Error Analysis

The major sources of measurement error in the sorption experiment are the initial weighing of the polymer sample, 1%, (due to sensitivity of analytical balance 1xE-4 g) and the measurement of the permeant concentration, 5%. The electrobalance has an error of 0.05% based on a limit of sensitivity of 5 micrograms for a 10 milligram sample of polymer. The strip chart recorder has an accuracy of approximately 1%. These errors combined in quadrature gives a solubility value estimate of variability of 1.4% and a solubility coefficient variability of 5.2%. Measuring the half time diffusion coefficient has several analytical problems such as introducing the film into a constant vapor concentration environment at exactly time zero. Assuming the analytical measurements have minimized any chance of error the major sources of error are in measuring the film thickness at 10% uncertainty and the weight gain as a function of time at 1% uncertainty. A smaller source of error is the 0.001% error due to simplifications made to the diffusion equation. The combined error for the half time diffusion is 14.2%. This is a smaller uncertainty than the lag time diffusion coefficient of 28%.

Combining the uncertainty of the permeability coefficient from the permeation experiment with the uncertainty of the sorption coefficient results in an uncertainty of 21.6% for the steady state diffusion coefficient value.

There is an additional error in the steady state diffusion coefficient value due to the different average temperatures at which the permeability coefficients and solubility coefficients are determined. The average temperature for the permeation experiments was 26.6°C and the average temperature for the solubility experiments was 21.1°C. The temperature dependence of the diffusion coefficient is given by Equation 29. Values for the activation energy for diffusion, E_d, can be estimated using data from DeLassus (1986). DeLassus (1986) reports activation energies for d-Limonene diffusion through OPP and a medium barrier Saran film of 24.9 and 29.2 kcal/mole respectively. Using these activation energies a temperature variation from 21.1°C to 26.6°C produces a 2.2 and 2.3 fold increase in the diffusion coefficients for OPP and Saran films respectively.

The effect of temperature variation on the steady state diffusion coefficient increases the uncertainty of the steady state diffusion coefficient to 47% uncertainty.

Conclusions

Notes On Permeation Cell Design And Usage

As a result of these tests there are some design changes or considerations that should be made in future permeation cell designs. One potential source of error which was not quantified in this study was the sorption of organic vapors in the permeation cell headspace by the cell, o-ring and septa. The cell's headspace chamber should have a smooth inert surface to minimize the adsorption of permeant by the cell. Polished inert and nonporous metals should be used like stainless steels or a layer of nickel chromium plated onto less expensive metals could be used. The sorption by the o-ring in the cell sections with the headspaces can be eliminated by using a polished flat surface and relying on the o-ring in the center ring section of the cell to supply the necessary sealing pressure to seal the film to this metal surface. The sampling port septa is another source of permeant sorption. Teflon coated silicone septa work well until the teflon coating is punctured repeatably by the syringe. Other researchers have placed a ball valve between the septa and the headspace to minimize the time of contact between the septa and permeated vapor (Murray and Dorschner, 1983).

From these studies it is apparant that there are optimum ratios of the film surface area (cm^2) to the cell headspace volume (cm^3) depending on the permeation rate of the film-permeant combination and the permeant concentration used. For example a film which is a poor barrier at a given permeant concentration needs to have a smaller surface area to headspace volume so that there is time to measure the equivalent of two to three lag times before the permeant concentration in the headspace reaches 2-3% of the permeant driving force concentration. Conversely a film that is a good barrier to a permeant concentration may need a larger surface area to volume ratio so that a low permeation rate can be detected easily. The cell design here has a area to volume of one ($50cm^2/50cm^3$) which was adequate for most test situations except for tests of the polypropylene film at high toluene vapor concentrations and the saran film tested at low toluene vapor concentrations. A simple way to increase the surface area to volume ratio when measuring high barrier films, without modifying the permeation cell design, is to flow the permeant through the upper and lower permeation cell chambers and measure the accumulation of permeant in the center ring chamber thus effectively doubling the surface area of film exposed.

The limit of detectability for the permeation rate of toluene permeation through a film in this quasi-isostatic method is between 4.0×10^{-10} and 4.0×10^{-11} g/day.cm^2 for a 50 cm^2 film surface area exposure and 2.0×10^{-10} to 2.0×10^{-11} g/day.cm^2 for a $100cm^2$ film area exposure. The calculation of this limit can be found in appendix D. The limit is based on what is the measurable and quantifiable increase in permeant concentration in the cell headspace over time.

Aside from the problem of the lower limit of detectability for the permeation rate is the amount of time it may take to measure the steady state permeation rate. This problem is especially acute in testing permeation of low permeant concnetrations through barrier film materials. It may take two or more weeks to reach steady state due to the exceptionally low diffusion coefficients sometimes found. Once the steady state permeation is obtained the rate may be so low that only one measurement can be taken every 24 hours in order to detect the change in permeant concentration without a large sampling error that will obscure the small amount of permeation that is occuring. Conversely when measuring the permeation of a high permeant concentration through a low barrier material, the permeation and diffusion may occur so rapidly that it may appear there is no lag time and one cannot take samples fast enough to adequately characterize the steady state permeation region before the permeant concentration in the headspace reaches 10% of the permeant driving force concentration.

To reduce the error in the permeation rate due to sample removal it is desirable to make the cell headspace volume larger. With a larger headspace volume a smaller percentage of the permeant is removed with each sample.

When designing a permeation cell the amount of 'dead volume' created in the cell headspace due to holes for the inlet and septa holes should be minimized by making the holes as shallow as possible. Minimizing the dead volume of the cell headspace will help ensure uniform mixing of the permeating vapor in the headspace.

The volume of the center ring of the permeation cell should be minimized to allow the permeant vapor at the beginning of a run to reach its desired concentration as quickly as possible. The larger the volume in the center section of the cell the larger the volume of nitrogen the permeant has to displace before reaching the incoming vapor stream concentration, thus contributing to lag time error.

Concentration Dependent Diffusion in Organic Vapor-Polymer Systems

The film-permeant combinations tested have shown exponential increases in permeability, diffusion and solubility, with increasing organic vapor concentration or vapor activity. The degree of organic vapor concentration dependency of these parameters depended on the film-permeant combination tested. In addition to the vapor concentration dependency observed these test films are also known to be affected by temperature. These factors which can influence the permeability, diffusion and solubility of organic vapors in polymer films, must be considered when selecting a film for a specific application or when testing a film for vapor barrier properties. It would be ideal to be able to predict the barrier properties of a film-permeant system using published data on the vapor barrier properties of the films or by predicting the systems behavior based on the physical and chemical characteristics of the film and permeant. Unfortunately there is very little published data on vapor permeability through polymers and there is not a complete enough understanding of film and permeant interactions to predict the barrier properties a given film-permeant system will have.

Currently the only way to determine the organic vapor barrier properties of a polymer film is to measure them experimentally. This can be very tedius and time consuming process and may give potentially misleading information if the behavior of the film-permeant combination over a range of vapor concentrations is not known. For example a film may have a concentration dependency such that it is a better barrier to a given permeant at a low vapor concentration than another film but a poorer barrier to the permeant a high vapor concentrations. Two films may also show completely different permeability concentration dependencies depending on the nature of the permeant.

Characterizing the behaviour of a film to a given permeant over a wide concentration range can take a long time. At low vapor concentrations it may take several weeks before a steady state rate of permeation is reached or can be measured. In cases like this a way is needed to reliably predict the film's permeability and diffusion behavior at low vapor concentrations. It has been shown here and in the literature that for these and other film-permeant combinations, the diffusion coefficient and permeation rate have a linear exponential increase with the increase in organic vapor concentration or activity. It is suggested here that P and D at low vapor concentrations, which are very difficult to measure, can be estimated by measuring P and D at high vapor concentration levels and extrapolating down to low vapor concentrations.

Conclusions On The Usefulness of The Method

This quasi-isostatic method has been shown to have the ability to control and test for several important variables in organic vapor testing. The permeability of a film can be easily measured for any film thickness or polymer softness using this technique. Thin or soft films do not need supports underneath the film because there is no total pressure differential across the film during testing like there is with the high vacuum volumetric/manometric techniques. High barrier materials can also be tested without the added complication of maintaining vacuum over long periods of time which is necessary in the high vacuum techniques. This method permits testing the permeability of a film at permeant vapor concentrations ranging from practically zero to saturation vapor pressure concentrations. This allows evaluation of the permeant concentration dependence of the permeation and diffusion processes. This is also an advantage over static test methods which can only test at one concentration.

This method has an advantage over other methods using different types of detectors because it has the ability to test the effects of copermeants including relative humidity on permeability and diffusion. This was not an important consideration in this study however it will be important in future work. The ability to test the effects of copermeants is important because very few products packaged contain only one vapor or aroma. In addition to organic copermeants, water vapor can also function as a copermeant. The importance of copermeating water vapor was demonstrated by the effect of relative humidity on the OPP/PVDC-toluene and the PVDC/OPP/PVDC-toluene film-permeant combinations. Tan (1986) and Liu (1986) have also shown the importance of evaluating the effects of relative humidity on organic vapor permeation. Most packages will be exposed to external environments with an average relative humidity of 50%. The internal package environment can range from range from 32% to 50% equilibrium relative humidity for dry products like plain chocolate and dehydrated vegetables and up to 100% relative humidity for aqueous products (Weurman, 1974). The use of the flame ionization detector with the gas chromatograph allows separation and quantitation of individual components in the cell headspace without interferance from the inert gases and/or water vapor present in the cell headspace. The advantage of testing the effects of copermeants with this method is compromised somewhat by the increase in error and inconvenience created by the manual sampling procedure.

Another advantage of this method is its adaptability to use in most labs and its relatively simple design and low cost compared to other test systems. In most systems the permeant detection part of the apparatus is one of the most expensive test apparatus components. It is assumed here that most analytical labs have a gas chromatograph with a flame ionization detector. This method does not require the gas chromatograph to be dedicated only for permeability testing.

One of the problems of this method and other methods such as the manometric/volumetric method is that the measurements required are very labor intensive. People must be present to periodically collect sample points for the transmission profile curve. The accuracy of the sampling is dependent in part on the operators experience and skill. A host of problems can occur when taking gas headspace samples. Some common problems include leaking GC and permeation cell septa and leaky or plugged syringes. Isostatic techniques that use a sweep gas to carry the permeant to a detector avoid these sampling and operator problems but are usually limited to testing only pure vapor permeants. An adaptation of this apparatus to make it an isostatic method and which uses an automated gas sampling valve on a gas chromatograph has been developed by Hernandez (1984). Ultimately the choice of a suitable test method for measuring permeation rates depends on the needs and resources of the testing lab.

Conclusions: Theoretical Importance

These studies were designed to develop a better understanding of the mechanism of diffusion of organic penetrants though polymer membranes, for penetrant/polymer systems demonstrating strong thermodynamic interaction of penetrant with the polymer. The results obtained are of both theoretical and practical importance. In terms of theoretical importance the concentration dependency of the permeability coefficient $(\bar{P})$ was considered in terms of the two fundamental mass transport parameters, the diffusion coefficient and the solubility coefficient. For the penetrant /polymer systems studied, toluene/OPP and toluene/PVDC, the variation of the equilibrium solubility of toluene in the polymers with the contacting vapor activity only accounted for less than 5% of the increase of the permeability coefficient in the same vapor activity range. The diffusion coefficient was found to account for most of the increase of the permeability coefficient with toluene vapor activity for both the OPP and PVDC films. The calculated integral diffusion coefficients increased exponentially with penetrant vapor activity.

An integral diffusion coefficient calculated during the transient state of permeation using the lag time method was compared to an integral steady state diffusion coefficient which was determined from steady state permeation measurements and equilibrium solubility measurements.

The transient diffusion coefficient was found to be significantly less concentration dependent than the steady state diffusion coefficient. The differences between the transient and steady state diffusion coefficients was interpreted as being mainly caused by the changing concentration gradient in the polymer matrix brought on by time dependent polymer structural relaxations. The free volume model for diffusion was used to describe the exponential increase in the diffusion coefficient with penetrant driving force and to interpret the differences between the transient and steady state diffusion coefficients. The free volume model polymer/penetrant interaction term (γ) was interpreted as being composed of a term associated with the fickian diffusion process and a term describing the effect of time dependent pentrant/polymer interactions and relaxations that occur as the system goes from transient to steady state. Characterization of the magnitudes of these fickian diffusion and time dependent interaction paramters in the context of the free volume model remains for future work.

Appendices

Appendix A

Saturation Vapor Concentration Versus Temperature

Saturation pressure (mmHg) versus temperature (^{o}C) data was obtained from Perry's Chemical Engineers Handbook. The saturation pressure was converted to its corresponding saturation vapor concentration using the ideal gas law, $PV = nRT$, solving for the number (n) of moles of vapor contained in 1 ml of gas at the saturation vapor partial pressure and temperature. The saturation concentration is reported in ppm (grams vapor/ ml).

The curve of saturation ppm versus ^{o}F was fitted using a two point cubic spline curve fitting program by Tan (1986). The relationship between the saturation vapor concentration and temperature is given by the following equation:

$$\text{ppm} = 2.100191\text{x}10^{-4} \cdot (^{o}F)^{3} - 6.627369\text{x}10^{-3} \cdot (^{o}F)^{2} + 1.1 \cdot (^{o}F)$$

Vapor activity is calculated by dividing the experimentally determined vapor concentration (p) by the saturated vapor concentration at the test temperature (p_o).

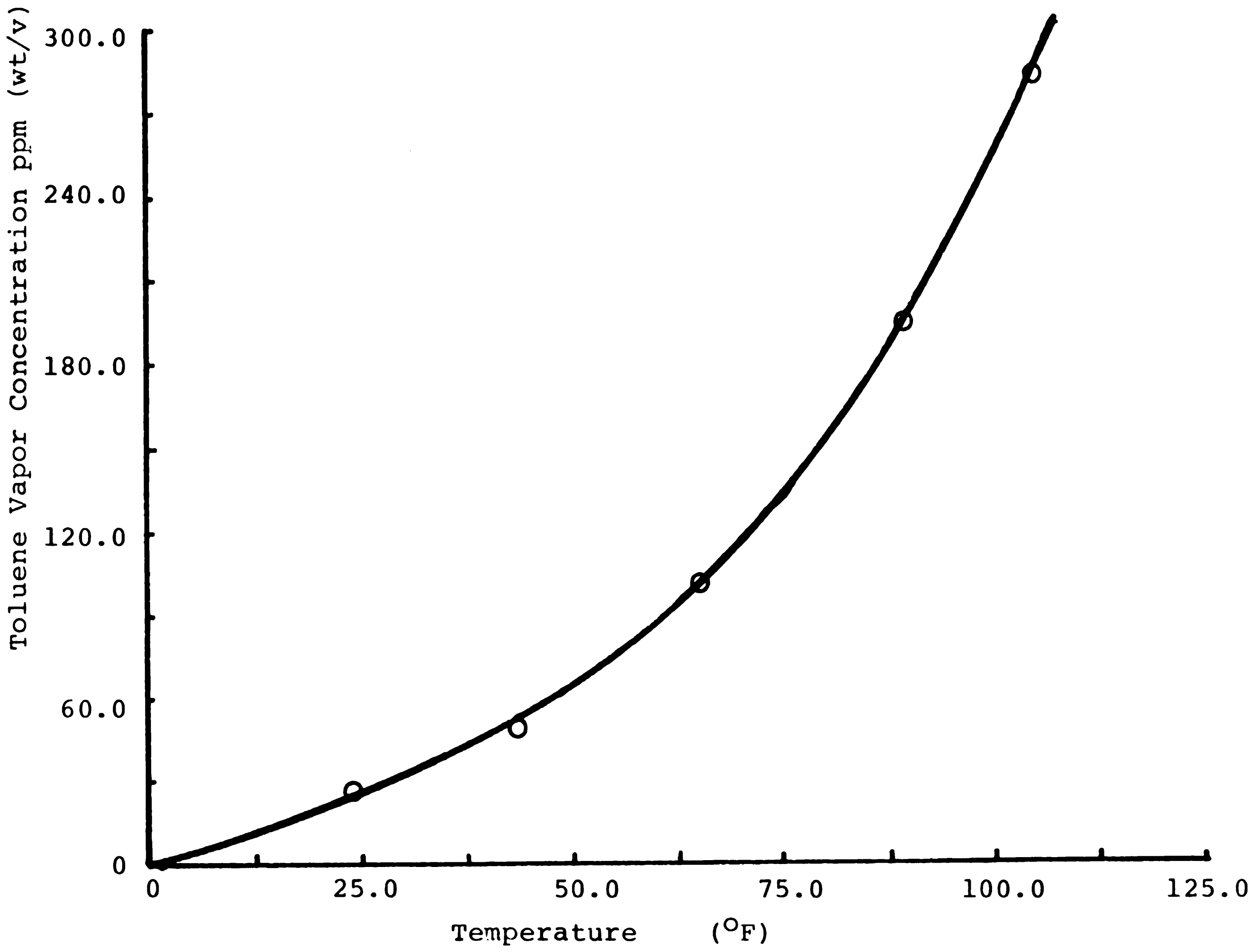


Figure 13. Toluene Saturation Vapor Concentration versus Temperature

Appendix B

Test For the Validity of Assuming Toluene Vapor Behaves As An Ideal Gas

Ideal Gas Law: PV=nRT

T = 300°K

R = .08206 liters-atm/mole-degree

V = .001 liter

Concentration Range of Toluene Used in This Study:

16 ppm (μg/ml) = 1.738×10^{-7} mole/ml

partial pressure = 4.281×10^{-3} atm using the ideal gas law

150 ppm (μg/ml) = 1.630×10^{-6} mole/ml

partial pressure = 4.0127×10^{-2} atm using the ideal gas law

Calculation of the partial pressure at these two concentrations using Van der Waals equation to correct for nonidealities of toluene vapor.

reference: Page D-195 Handbook of Chemistry and Physics, R.Weast (ed). 1982-1983.

$$(P + n^2a/V^2)\ (V - nb) = nRT$$

$a = 24.06\ L^2\text{-atm/mole}^2$

$b = .1463\ L/\text{mole}^2$

at 16 ppm (μg/ml) the partial pressure calculated using Van der Waals equation = 4.2807×10^{-3} atm.

at 150 ppm (μg/ml) the partial pressure calculated using van der Waals equation = 4.0007×10^{-2} atm.

The difference of the partial pressures for Toluene vapor in this concentration range between the ideal gas equation and Van der Waals equation is less than one percent.

Appendix C

Gas Chromatograph Calibration Procedure

Equipment

(5) 10 ml volumetric flasks with stoppers

(1) 5 μl liquid sampling syringe

(1) 10 μl liquid sampling syringe

(1) 50 μl liquid sampling syringe

Analytical balance

Materials

HPLC grade Toluene

HPLC grade ortho-Dichlorobenzene solvent

Procedure

1) Bake out vials and syringes in oven prior to use to remove any residual solvent or permeant. Cool to room temperature.

2) Evaluate the purity of the solvent using the gas chromatograph to ensure there are no interfering peaks at the permeant retention times.

3) Prepare a dilution scheme for the permeant standards.

a) partially fill volumetric flasks with solvent.

b) tare the flask and solvent

c) add desired quantity of permeant

d) reweigh flask to determine the actual amount of permeant added to flask

e) fill flask to volumetric line with solvent

f) mix flask's contents

4) Set Gas Chromatograph conditions:

column: 5% SP2100 on 100/120 Supelcoport
(Supelco, Inc., Bellefonte, Pa.)
1/8inch o.d. x 6 ft. SS column

analysis conditions:

He carrier gas	30 ml/min.
col. temp.	175°C
FID temp.	350°C
Injection port	200°C
Time 1	3 min.
Column Temp. Program rate	25°C/min.
Final Col. Temp.	225°C
Time @ 225°C	2 min.

permeant retention times:

Toluene	1.33 min.

5) Approximately 0.5 μl sample size used. A method of injecting that allows accurate determination of the actual sample volume injected is required.

6) Plot the Gas Chromatograph area unit response versus the number of grams injected per sample. The slope of this curve equals the calibration factor.

7) Sample calculations:

Dilution #1 : 0.80 g permeant diluted in 10 ml solvent.
concentration = .08 g/ml.

typical injection :
0.08 g/ml x .0005ml injection volume =
4×10^{-5} g permeant injected

Appendix D

Limits of Detectability For Toluene Permeation In Quasi-Isostatic Permeation Cell

Estimate based on experience and error analysis minimum permeation rate of 10 to 100 gas chromatograph integrator area units per day. Measurements made over the period of a month.

(50 ml headspace volume) • (1/0.5 ml injection volume) • (2.0026×10^{-12})
CALIBRATION Factor gm/au
• ($1/50 cm^2$ surface area of film) • (10 to 100 au/day) =

4.005×10^{-11} to 4.005×10^{-10} ($g/day \cdot cm^2$)

Appendix E

Experimental Data

Toluene Vapor Permeation Data

ppm (μg/ml)	Temp. range (^{o}C)	run #	Permeation Rate ($x10^{-6}$ g/hr 50cm^2)	Lag Time (θ) (hours)
Oriented Polypropylene				
112±5	27.2-27.4	1	28,496.0	.380
		2	41,400.5	.364
		3	35,352.2	.391
		4	39,827.6	.317
100±5	25.8-26.1	1	4128.7	.514
		2	4832.9	.487
		3	5218.56	.572
		4	7540.0	.522
93±3	26.7-27.8	1	2659.25	.655 average
		2	2813.0	
		3	2614.49	
		4	3084.1	
81±4	26.9-27.4	1	1120.49	1.044
		2	967.1	.914
		3	1150.27	1.169
		4	705.99	1.194
48±3	27.2	1	106.14	1.419
		2	132.6	1.438
41±3	27.2	1	68.75	1.806
		2	76.34	1.822
16±1	25.4-25.9	1	12.31	2.989
		2	10.85	2.768
		3	10.91	2.875
		4	15.06	2.979

ppm (µg/ml)	Temp. range (°C)	run #	Permeation Rate (x10^{-6} g/hr 50cm^2)	Lag Time (θ) (hours)
Polyvinylidene Chloride				
141±5	27.1-29.8	1	1952.0	3.931
		2	1940.8	3.943
125±5	27.5-28.6	1	1805.8	6.328
		2	1859.9	4.907
96±3	26.7	1	61.61	39.230
		2	58.75	40.407
		3	55.29	41.302
		4	62.51	41.032
73±3	23.0-23.9	1	0.1015	284.590
		2	0.1268	279.175
		3	0.04154	199.114
		4	0.06734	187.778
PVDC Coated OPP: OPP towards vapor				
135±3	27.4-28.0	1	7979.1	.689
		2	14,894.0	.528
		3	7,828.8	.782
		4	12,072.6	.614
94±2	26.7	1	1,407.3	2.309
		2	1,948.2	2.126
92±3	26.7	1	2,063.5	2.816
		2	2,242.0	2.508
79±2	26.3-26.7	1	41.72	11.986
		2	45.11	12.248
		3	38.96	12.062
		4	64.27	12.232
40±2	25.0-26.6	1	0.2078	111.220
		2	0.0856	92.050
		3	0.2933	115.040
		4	0.2218	102.520

ppm (μg/ml)	Temp. range (°C)	run #	Permeation Rate ($\times 10^{-6}$ g/hr 50cm^2)	Lag Time (θ) (hours)
PVDC coated OPP: PVDC towards Vapor				
150±4		1	15,058.2	.473
		2	18,295.3	.380
		3	16,196.0	.527
		4	17,629.0	.392
97±3	26.7	1	4,999.6	1.364
		2	5,657.2	1.294
94±5	26.7	1	1,857.5	2.100
		2	2,827.8	1.690
40±2	25.0-26.6	1	0.1133	91.202
		2	0.154	79.740
		3	0.1907	86.381
		4	0.2408	95.832

Bibliography

Bibliography

Amerongen, G.J.van, 1946, J.Applied Physics 17:972

ASTM, 1982, D-1434-82 Gas Transmission Rate of Plastic Film and Sheeting. Annual Standards. ASTM, Philadelphia, Pa.

Baner. A.L., 1986, Diffusion and Solubility of Toluene In Polymer Films. presented at the 13th Annual IAPRI Symposium, Oslo, Norway May 26-28, 1986.

Baner, A.L., Hernandez, R.H., Jayaraman, K., Giacin, J.R., 1986, Isostatic and Quasi-Isostatic Methods For Determining The Permeability of Organic Vapors Through Barrier Memebranes, Current Technologies In Flexible Packaging, ASTM STP 912.

Barrer, R.M., 1939, Trans. Faraday Soc. 35:628

Barrer, R.M. and Skirrow, G. Transport and Equilibrium Phenomena In Gas-Elastomer Systems.I. Kinetic Phenomena. 1948. J. Polymer Sci. 3(4):549.

Becker, K. ,Koszinowski, J., and Piringer, O. 1983. Permeation of Scenting and Flavoring Substances Through Polyolefins. Deutsche Lebensmittel-Rundschau. 79(8): .

Bent, H.A. 1957. J. Polymer Sci. 24:387.

/Berens, A.R., 1977, Diffusion and Relaxation In Glassy Polymer Powders: 1 Fickian Diffusion of Vinyl Chloride In poly(vinyl chloride) Polymer. 19(7):697.

Berens, A.R., and Hopfenberg, H.B., 1978. Diffusion and Relaxation in Glassy Polymer Powders: 2 Separation of Diffusion and Relaxation Pararmeters. Polymer, 19(5):489.

Berens, A.R., 1979. The Diffusion of Gases and Vapors In Rigid PVC. Journal of Vinyl Technology, 1(1):8.

Berens, A.R. and Hopfenberg, H.B., 1981. Diffusion of Organic Vapors at Low Concentrations In Glassy PVC, Polystyrene, and PMMA. Journal of Membrane Sci. 10:283.

Blackadder, D.A. and Keniry, J.S. 1972. The Measurement of the Permeation of Polymer Memebranes to Solvating Molecules. J. Applied Polymer Sci. 16:2141.

Blackadder, D.A. and Keniry, J.S. 1973. Difficulties Associated With the Measurement of the Diffusion Coefficient of Solvating Liquid or Vapor In Semicrystalline Polymer: I Permeation Methods. J. Applied Polymer Sci. 17:351.

Boyer (ed) 1977. "Encyclopedia of Polymer Science and Technology, Supplement no. 2". J. Wiley & Sons, New York.

Brandrup, J. and Immergut, E.H. (eds.) 1975. Polymer Handbook. 2nd ed. Wiley Interscience, N.Y.

Brown, W. 1986. Private Communication. Private Consultant, Midland, MI.

Caskey, T.L. 1967. Modern Plastics. 4:168.

Choy, C.L. Leung, W.P., Ma, T.L. 1984. Sorption and Diffusion of Toluene In Highly Oriented Polypropylene. Journal of Polymer Science: Polymer Physics Edition. 22:707.

Crank, J. and Park, G.S. 1968. "Diffusion In Polymers". Academic Press, N.Y.

Crank, J. and Park, G.S. 1968b. Methods of Measurement. Ch. 1 in Diffusion In Polymers. Crank, J. and Park, G.S. (eds). Academic Press, N.Y.

Cutler, J.A., Kaplan, E., McLaren, A.D., and Mark, H. 1951. The Permeation of Vapors Through Polyethylene. TAPPI. 34(9):404.

Davis, D.W. 1946. Gas Permeability, An Isostatic Test Method. Modern Packaging. May:145.

Daynes, H.A. 1920. Proc. Roy. Soc. (London) A97:273.

DeLassus, P.T. 1986. Transport of Unusual Molecules In Polymer Films. TAPPI Proceedings Polymers. Lamination and Coatings Conference. September 1985.

Doolittle, A.K. 1951, Studies in Newtonian Flow. II. The Dependence of the Viscosity of liquids on Free Space. J. Applied Physics. 22:1471

Doolittle, A.K. 1952. Studies In Newtonian Flow. III. The Dependence of the Viscosity of Liquids on Molecular Weight and Free Space (in homologous series). J. Applied Physics. 23:236.

Frisch, H.L. 1957. The Time Lag In Diffusion. J. Phys. Chem. 61(1):93.

Frisch, H.L. 1958. The Time Lag In Diffusion. II. J. Phys. Chem. 62(4):401.

Frisch, H.L. 1959. The Time Lag In Diffusion. IV. J. Phys. Chem. 63(8):1249.

Fujita, H. 1961. Diffusion In Polymer-Diluent Systems. Fortschr. Hochpolym.-Forsh. 3(9):1.

Fujita, H. 1968. Organic Vapors Above the Glass Transition Temperature. ch. 3. in "Diffusion In Polymers", Crank, J. and Park, G.S. (eds). pg. 75. Academic Press, N.Y.

Giacin, J.R. and Gyeszly, S.W. 1981. The Permeability of Organic Vapors Through Barrier Packaging Materials: Theoretical and Practical Considerations. Plastic Materials in Food Packaging. Proceedings of a Symposium In Polymerteknisk Selskab. #2. May 5, 1981, pg 74.

Gilbert, S.G. and Pegaz, D. 1969. Package Engineering. 14:661.

Gilbert, S.G.,Hatzidimitiu, E., Lai, C., and Passey, N. 1983. The Study of Barrier Properties of Polymeric Films to Various Organic Aromatic Vapors. Instrumental Analysis of Foods. 1:405.

Haring, H.G. 1974. Vapor pressures and Raoult's Law Deviations In Relation To Odor Enhancemant and Suppression. in "Human Responses To Environmental Odors. Turk, A., Johnston, J.W. and Moulton, D.G. (ed). pg 199. Academic Press, N.Y.

Hernandez Macias, R. J. 1984. Permeation of Toluene Vapor Through Glassy Poly(Ethylene) Terephthalate Films. M.S. Thesis. Michigan State University. E. Lansing, MI.

Hernandez, R. J. 1985. Personnal Communication, School of Packaging, Michigan State University, E. Lansing, MI.

Hernandez, R. J., Giacin, J.R., Baner, A.L. 1986. The Evaluation of the Aroma Barrier Properties of Polymer Films. Journal of Plastic Film and Sheeting. 2(3):187

Hilton, B.W. and Nee, S.Y. 1978. Permeability of Organic Vapor Through Packaging Films. Ind. Eng. Chem. Prod. Res. Dev. 17(1):80.

Jäckle, J., Frisch, H.L. 1985. Relaxation Of Chemical Potential and Generalized Diffusion Equation. Journal of Polymer Science: Polymer Physics Ed. 23:675

Jacques, C.H.M. and Hopfenberg, H.B. 1974. Kinetics of Vapor and Liquid Transport In Glassy Polyblends of Polystyrene and Poly(2,6 Dimethyl 1,4 Phenyloxide). Part II. Polymer Eng. Sci. 14(6):449.

Kishimoto, A. and Enda, Y. 1963. Diffusion of Benzene In Polyacrylates. Journal of Polymer Science. Part A. 1:1799.

Kwei, T.K. and Huang, T.T. 1972. Macromolecules 2:128

Laine, R. and Osburn, J.O. 1971. Permeability of Polyethylene Film To Organic Vapors. J. Applied Polymer Sci. 15(2):327.

Lebovits, A. 1966. Permeability of Polymers To Gases, Vapors and Liquids. Modern Plastics. 43:139.

Liu, K. 1986. Evaluation of the Effect of Relative Humidity on the Permeation of Toluene Vapor Through Barrier Films. M.S. Thesis. Michigan State University, E. Lansing, MI.

Lockhart, H.E. 1963. Development of Apparatus and Method For Measuring Gas Permeability. Technical Report #2 project #56. Michigan State University, School of Packaging, E. Lansing, MI.

Martinovich, R.J. and Boeke, P.J. 1957. Performance of A New Polyethylene. Modern Packaging. 31(2):167.

Meares, P. 1958a. Diffusion of Allyl Chloride in PVA. Part I. The Steady State of Permeation. J. Polymer Sci. 27:391.

Meares. P. 1958b. Diffusion of Allyl Chloride in PVA. Part II. The Transient State of Permeation. J. Polymer Sci. 27:405.

Meares, P. 1965a. " Polymers: Structure and Bulk Properties". Van Nostrand & Co. LTD, London.

Meares, P. 1965b. Transient Permeation of Organic Vapors Through Polymer Membranes. J. Applied Polymer Sci. 9:917.

Meyer, J.A., Rogers, C., Stannett, V. and Szwarc, M. 1957. Studies In Gas and Vapor Permeability of Plastic Films and Coated Papers. Part III. The Permeation of Mixed Gases and Vapors. TAPPI. 40(3):142.

Mobil Chemical Co. 1986. Plastic Films Division, Macedon, N.Y.

Murray, L.J. and Dorschner, R.W. 1983. Permeation Speeds Tests, Aids Choice of Exact Material. Package Engineering. March:76.

Murray, L.J. 1984. An Organic Vapor Permeation Rate Determination For Flexible Packaging Materials. TAPPI Proceedings, 1984 Polymers Laminations and Coatings Conference. p. 521.

Niebergall,W., Humeid, A. and Blochl, W. 1978. The Aroma Permeability of Packaging Films and Its Determination By Means of A Newly Developed Measuring Apparatus. Lebensm-Wiss U. Technol. 11(1):1.

Ng, H.C., Leung, W.P., and Choy, C.L. 1985. Sorption and Diffusion of Toluene In Isotropic and Ariented Linear Polyethlyene. J. of Polymer Sci. : Polymer Physics Ed. 23:973.

Park, G.S. 1950. Trans. Faraday Soc. 46:684.

Pasternack, R.A., Schimsheimer, J.F. and Heller, J. 1970. A Dynamic Approach To Diffusion and Permeation Measurements. J. Polymer Sci. Part A-2. 8:467.

Peterlin, A. 1977. J. Applied Physics. 48:4099.

Pollack, H.O. and Frisch, H.L. 1959. The Time Lag In Diffusion. III. J. Phys. Chem. 63:1022.

Prager, S. and Long, R.A. 1951. Diffusion of Hydrocarbons In Polyisobutylene. J. Am. CHem. Soc. 73:4072.

Pye, D.G., Hoehn, H.H., Panar, M. 1976. Measurement of Gas Permeation of Polymers II. Apparatus for Determination of Permeation of Mixed Gases and Vapors. J. Applied Polymer Sci. 20:1921.

Rodriguez, F. 1970. "Principles of Polymer Systems". McGraw-Hill Book Co., N.Y.

Rogers, C.E., Meyer, J.A., Stannett, V. and Szwarc, M. 1956. Studies In The Gas and Vapor Permeability of Plastic Films and Coated Papers. Part I. Determination of the Permeability Constant. TAPPI. 39(11):737.

Rogers, C.E., Meyer, J.A., Stannett, V. and Szwarc, M. 1956. Studies In The Gas and Vapor Permeability of Plastic Films and Coated Papers. Part II. Some Factors Affecting The Permeability Constant. TAPPI. 39(11):741.

Rogers, C.E., Stannett, V. and Szwarc, M. 1960. The Sorption, Diffusion and Permeation of Organic Vapors In Polyethylene. J. Polymer Sci. 45:61.

Rogers, C.E. 1964. Permeability and Chemical Resistance of Polymers. ch 9. in "Engineering Design For Plastics". Baer, E. (ed). Rheinhold, N.Y.

Rogers, C.E. 1965. Solubility And Diffusivity. ch 6 in "Physics and Chemistry of The Organic Solid State vol.2". Fox, D., Labes, M.M. and Weissberger, A. (ed). J. Wiley & Sons. N.Y.

Roger, N.A., Buritz, R.S. and Alpert, D. 1954. Diffusion Coefficient, Solubility and Permeability For Helium In Glass. J. Applied Physics. 25:868.

Rouse, P.E. 1947. J. Am. Chem. Soc. 69:1068.

Salame, M. 1984. Prediction Of Gas Barrier Properties of High Polymers. presented at the Second International Ryder Conference. Dec. 3-5, 1984.

Salame, M. 1980. A Correlating Parameter for Liquid Permeability In Polyethylene. Presented at the 183rd Meeting Am. Chem. Soc. Div. of Organic Coatings and Plastics. pg 224.

Siegel, R.D. and Coughlin, R.W. 1970. Errors in Diffusivity as Deduced From Permeation Experiments Using The Time-Lag Technique. J. Applied Polymer Sci. 14:3145.

Stannett, V., Hopfenberg, H.B. and Petropoulos, J.H. 1972. Diffusion In Polymers. Ch. 8 in "Macromolecular Science". Baum, C.E. (ed). 8:329.

Stern, S.A., Mauze, G.R. and Frisch, H.L. 1982. Tests of a Free-Volume Model for the Permeation of Gas Mixtures Through Polymer Membranes. CO_2-C_2H_4, CO_2-C_3H_8 and C_2H_4-C_3H_8 Mixtures In Polyethlene. J. of Polymer Sci.: Polymer Physics Ed. 21:1275.

Steel, R.G.D. and Torrie, J.H. 1980. "Principles and Procedures of Statistics". 2nd ed. McGraw-Hill Book Co. N.Y.

Talwar, R. 1974. Plastic in Packaging: Gas and Vapor Permeability. Package Development. Sept/Oct:29.

Tan, S. 1986. Personnal Communication, School of Packaging, Michigan State University. E. Lansing, MI.

Taylor, J.R. 1982. " An Introduction to Error Analysis". University

Science Books. Mill Valley, Ca.

Van Amerongen, G.J. 1946. J. Applied Physics. 17:972.

Vrentas, J.S., Jarzebski, C.M., Duda, L. 1975. A Deborah Number for Diffusion In Polymer-Solvent Systems. Journal of AICHE, 21:894.

Vrentas, J.S. 1977. Diffusion In Polymer-Solvent Systems. III. Construction of Deborah Number Diagrams. Journal of Polymer Science: Polymer Physics Ed. 15:441.

Weast, R.C. (ed). 1983. " Handbook of Chemistry and Physics". 63rd ed. The Chemical Rubber Co., Cleveland, Ohio.

Weurman, C. 1974. Sampling In Airborne Odorant Analysis. pg. 263 in "Human Responses to Environmental Odors". Turk, A., Johnston, I.W. and Moulton, D.G. (ed). Academic Press, Inc., N.Y.

Williams, M.L., Landel, R.F. and Ferry, J.D. 1955. The Temperature Dependence of Relaxation Mechanisms In Amorphous Polymers and other Glass-forming Liquids. J. Am. Chem. Soc. 77:3701.

Yasuda, H. and Stannett, V. 1962. Permeation, Solution and Diffusion of Water In Some High Polymers. J. Applied Polymer Sci. 57:907.

Yasuda, H. and Rosengren, K. 1970. Isobaric Measurement of Gas Permeability of Polymers. J. Applied Polymer Sci. 11(14):2839.

Zobel, M.G.R. 1982. Measurement of Odour Permeability of Polypropylene Packaging Films At Low Odourant Levels. Polymer Testing. 33:133.

Zobel, M.G. 1985. The Odour Permeability of Polypropylene Packaging Film. Polymer Testing. 5:153.

Ziegel, K.D., Frensdorff, H.K., Blair, D.E. 1969. Measurement of Hydrogen Isotope Transport in PolyVinyl Flouride Films by Permeation Rate Mehtod. J. Polymer Sci. A2. 7:809.