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**THE PERMEABILITY OF BINARY ORGANIC
VAPOR MIXTURES THROUGH A BIAXIALLY
ORIENTED POLYPROPYLENE FILM**

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THE PERMEABILITY OF BINARY ORGANIC VAPOR MIXTURES THROUGH A BIAXIALLY ORIENTED POLYPROPYLENE FILM

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ABSTRACT

THE PERMEABILITY OF BINARY ORGANIC VAPOR MIXTURES THROUGH A BIAXIALLY ORIENTED POLYPROPYLENE FILM

By

Taryn Marie Hensley

Permeability studies were carried out as a function of vapor activity for the penetrants, ethyl acetate and limonene, as well as with binary mixtures of these penetrants, by an isostatic method of test. Vapor activity levels between 0.05 to 0.5 were evaluated for the individual penetrants to determine the concentration dependency of the mass transport process. Permeability studies with the binary mixtures allowed consideration of the synergistic effect of a co-permeant.

Permeation of the individual penetrants showed a concentration dependency over the range of vapor activities studied. For the binary mixtures, limonene was found to increase the transmission rate of ethyl acetate by up to 40 times, as compared to pure ethyl acetate vapor, of an equivalent concentration. Ethyl acetate was also found to act synergistically at high vapor levels ($a \geq 0.48$).

These findings were attributed in part to plasticization of the polypropylene by the sorbed penetrants, resulting in polymer chain relaxation and enhancement of free volume.

DEDICATION

Dedicated to my best friend, my husband. Thank you for the incredible patience and understanding. Forever and ever, Amen.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

Symbol	
a	vapor activity = vapor pressure of permeant/saturated vapor pressure of permeant (p/p_o)
A	area of film sample (cm^2)
ANOVA	analysis of varience
b	Van der Waal's molar volume
B	measure of the minimum hole size for the penetrant molecules jump step
c	concentration of permeant
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
cal	calorie
D	differential diffusion coefficient (cm^2/sec)
D_0	pre-exponential diffusion coefficient or limiting diffusion coefficient (cm^2/sec)
E_p	activation energy of permeation
E_d	activation energy of diffusion
f	fractional free volume
f^0	constant describing the fractional free volume of the polymer at zero vapor concentration
GC	gas chromatograph
H_1	partial molar heat of mixing
H_c	molar heat of condensation
H_s	heat of solution
HDPE	high density polyethylene

ID	inside diameter
kg	killogram
L	thickness of film sample before swelling (cm or mil)
mmHg	millimeters of mercury
M	Equilibrium sorption at infinite
m	meter
mil	0.001 inches
μl	microliter
OD	outer diameter
OPP	oriented polypropylene
P	transmission rate
P	permeability coefficient (kg m/m^2 s Pa)
Pa	pascal
P_0	limiting permeability coefficient
p_1	permeant partial pressure at the ingoing side of the film
p^2	permeant partial pressure at outgoing side of the film
ppm	parts per million
Q	quantity of permeant which has passed through area of film
R	ideal gas law constant
RH	relative humidity
S	solubility coefficient
S_0	pre-exponential solubility coefficient
s	second (time)
t	time
$t_{1/2}$	time required for sorption to reach 1/2 equilibrium

T	absolute temperature (°K)
T_g	polymer glass transition temperature
V	volume of permeation cell chamber (cm^3)
wt	weight
γ	concentration coefficient
∞	infinity
θ	lag time
Σ	summation operator
π	pi = 3.14159

INTRODUCTION

Up until the mid 1950's polymeric materials played a minor role in protecting food, beverage, and pharmaceutical products. At that time, packaging materials were mainly comprised of glass and metal (Kelsey, 1978). With the introduction of new polymeric materials and processing techniques, glass and metal soon became the minority. In addition to the variety, convience and economy of polymeric materials drove the transformation. New and improved plastics will play a role in expanding markets (Kelsey, 1978), and at a slow steady rate, plastics are replacing glass, paper, and metal (Enc. Pol. Sci., 1985).

Determination of the appropriate material for a packaging system requires many considerations, of which protection, during both distribution and storage is a major concern. Not only must the product be protected from external factors, but the environment must also be protected from hazards the product may impose upon it. For example, product vapors of concern are often organic, and can include flavor ingredients in foods as well as active ingredients in medical, household, and industrial products, such as vapors from motor fuels, detergents, solvents, etc. (Murray, 1985). The transport of gases and other low molecular weight organic compounds from the product through the polymer, or from the environment through the package to the product must be limited to the smallest amount possible in many cases. Unlike metals and ceramics, polymers are relatively permeable to small molecules such as permanent gases (i.e. hydrogen, carbon dioxide, or other gases that are considered "ideal" in behavior) and organic vapors (Brody, 1970). Knowledge of the transport rate, therefore, plays an important role in the selection of the packaging system. The considerable interest that exists in permeation and diffusion characteristics of polymers arises largely from the fact that a number of important practical applications depend wholly, or in part, on such phenomena. These applications include protective clothing, packaging materials for foods and beverages, selective barriers for the separation of gas and liquid mixtures, biomedical devices, and liners in hazardous waste-containment facilities (Mickelson et al., 1985).

The loss of specific aroma or flavor constituents, or the gain of off odors due to permeation could lead to a reduction in product quality, therefore resulting in a shorter shelf life for the product. Permeation through a polymer film involves three basic steps i) sorption - solution (condensation and mixing) of the permeant in the surface layers, ii) diffusion - migration of the permeant molecules to the opposite surface through step-wise diffusive "jumps" from one sorption site to the next under a concentration gradient; and iii) desorption - evaporation from that surface to the ambient phase (Lebovitz, 1966).

Permeation or transport through a polymer film or slab can be described in terms of its component parts by Equation 1, assuming Henry's law and Fickean diffusion is held:

$$P = DS \tag{1}$$

where S is the solubility coefficient and D is the diffusion coefficient. S characterizes the amount of permeant that can be dissolved into the polymer under unit vapor pressure, and D describes the rate at which the permeant molecules advance through the barrier film. Once again when assuming Henry's law and Fickean diffusion is held, commonly used units for S and D are (Crank and Park, 1968):

$$s = \frac{(cm^3)\,(STP)}{(cm^3)\,(cmHg)} \tag{2}$$

$$D = \frac{cm^2}{s} \tag{3}$$

therefore:

$$P = \frac{(cm^3)\,(STP)\,(cm)}{(s)\,(cm^2)\,(cmHg)} \tag{4}$$

Permeation is 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.

It should be noted that the sorption step alone could potentially deem the product unacceptable. Knowing solubility data for essential flavor ingredients in certain polymers is, therefore, of paramount importance in avoiding the effect of "flavor scalping." For example, limonene, a common flavor component present in foods, has a relatively high solubility in high density polyethylene (HDPE) (Mohney et al., 1986). Since the flavor compounds are normally present in low concentration in the foodstuffs, there is a potential risk to "lose" the aroma constituent due to absorption by the package film. DeLassus (1985) has also briefly described this phenomenon. This process depends on the chemical nature of the penetrant molecule and the polymer.

Studies reported dealing with permeation and diffusion of organic liquid mixtures through barrier polymer films show varying degrees of interaction between the components of the mixture. In permeability studies reported by Michelson, et al., (1985), the authors found that for binary organic liquid mixtures of varying composition, three (3) possible modes of interaction between the components of the mixture and the polymer could be described, namely:

1. The mixture may decrease the lag time or breakthrough time

of the components.

2. A component that does not permeate as a pure liquid may be transported through the membrane by another component, when present in the mixture.

3. The collective permeation rate for the mixture may be higher than the transmission rates of either pure component of the mixture.

It has been shown by Stannett and Yasuda (1963) that the permeability of liquid organic mixtures through barrier membranes is equivalent to that of the vapor, at a vapor activity (a) of 1.0 ($a=p/p_0$) (refer to appendix B for a more detailed description of vapor activity). It is likely, therefore, that at high vapor activities (a=1.0) the results of organic vapor permeability studies will be similar to studies conducted with the organic liquid. At lower vapor activities, however, the effects of vapor mixtures on the permeation and diffusion of individual components of the vapor mixture are largely unpredictable. Permeation has been shown to be greatly affected by the gas solubility in a polymer, which, in turn, is dictated by the mutual compatibility of the penetrant and the polymer and is related to the ease of condensation of the penetrant. In general, an organic vapor is more easily condensed than organic gas, and since condensation is a function of pressure, the permeation of organic vapor is more sensitive to concentration (Li et al., 1965). By definition, a vapor is considered to be any substance in the gaseous state thought of in reference to the liquid or solid form, and a gas is not associated with a liquid or solid form. It should be pointed out that permeation studies involving organic liquid mixtures are limited to determining transmission rates and permeability coefficient values at only one concentration of penetrant, namely the vapor pressure of the liquid penetrant at the temperature of test and penetrant concentration in the mixture.

In addition to the lack of data on the permeability of organic vapor mixtures through barrier films, no studies have been reported on the concentration dependency of the permeability of organic vapor mixtures, or on the effect of the relative concentration of individual components of the vapor mixture on the transport of each particular penetrant comprising the mixture.

The present study focuses specifically on determining the permeability of a binary organic vapor mixture through a polymeric barrier film, and considers the concentration dependency of the transport process.

The objectives of the study include:

1. Development of methodology to determine the permeation rates of the constituents of a binary organic vapor mixture through a barrier film, to include developing a test system capable of delivering a constant

concentration ratio and pressure of the multi-component organic vapor mixture.

2. Evaluate the concentration dependency of the transport process of the individual penetrants.
3. Study the effect of co-permeants on the diffusivity of the respective individual penetrants through the test barrier polymer structure.
4. Utilize data obtained from the permeability studies to develop a better understanding of the mechanism and the variables which effect the diffusivity of organic penetrants in barrier polymer films. In particular, the effect of co-permeants, or the effect of penetration (i.e. adsorption) of the barrier polymer by a constituent of the binary organic vapor mixture, on the transport properties of the polymer will be addressed.

In terms of practical importance, from the study of permeation of multi-component organic mixtures through polymeric barrier membranes, a relative comparison of barrier properties of polymeric packaging materials to organic penetrants of varying molecular structure and polarity can be made. In the future, therefore, a means of designing an appropriate barrier structure for a specific end use application would be available for researchers. In terms of theoretical importance, a better understanding of the concentration dependency of the diffusion process and the effect of penetrant/polymer interaction on the transport properties of individual components of a multi-component organic vapor mixture will be known.

LITERATURE REVIEW

Organic Vapors and Their Unique Transport Characteristics Through Polymeric Films

The number of studies describing the mass transport process of organic vapors through polymeric films is limited. However, it is known that concentration as well as time dependent diffusion processes may take place, resulting in swelling of the polymer matrix and a non-ideal Henry's Law relationship (Crank, 1975; Bagley et al., 1958; Berens, 1977; Fujita, 1961). In such cases, the diffusion coefficient, solubility coefficient and permeability constant have to be determined independently, in order to describe accurately the mass transport behavior. This phenomena is not seen with gases that are ideal in nature. When applied to a food product/package system, it is, therefore, important to fully understand the product's characteristics, and what effect its constituents have on the gain or loss of vital flavor or aroma as a result of permeation through the polymeric material, before choosing the appropriate system. Prior to selecting a suitable packaging system, it is important to understand the effect that the constituents of the product have on the permeability characteristics of the polymeric film. Also, determination of the concentration profile of constituents that will lead to a critical loss of aroma or flavor must be made. For example, in the case of a food product, the food's aroma serves as a sensitive and primary indicator of quality (Niebergall, 1978). Because organic vapors can exhibit concentration dependent mass transport and sorption processes, the permeant vapor pressure as well as 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 polymeric packages.

Permeation Mechanism

As shown in Equation (1), the permeability coefficient can be described in terms of its component parts, where D and S are determined separately in a sorption type process, or P is determined from direct measurement of the rate of transfer of a substance through a material, in a permeability study. The mass transfer of a substance through a material occurs by a diffusion process, rather than by a flow process such as Knudsen or Poiseuille flow that occurs through porous materials (Lebovitz, 1966). For a simple permeation process, the sorption and desorption steps are described by Henry's law, which relates the concentration of the penetrant in the polymer, to the penetrant concentration (vapor pressure) in the gas or vapor phase in equilibrium with the polymer. The partial pressure of the penetrant is further related to the penetrant concentration in the gas phase through the ideal gas law. The application of the ideal gas law is justified since the concentration of the diffusant in the gas phase is, in general, very low. The diffusion step is described by Fick's first and second laws of diffusion (Crank, 1975):

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad (5)$$

The experimental techniques for measuring P,D, and S involve one of two procedures, namely: 1) Diffusion (D) and Solubility coefficients (S). These are usually determined by observing the change in weight (i.e. increase or decrease) of a polymer sample during a sorption process; and 2) Diffusion (D) and permeability coefficient (P) values are obtained from permeability studies. In the sorption measurement method, a polymer film of thickness L is placed in a constant bath of diffusant of a given concentration, and the amount of diffusant absorbed into the sample is recorded as a function of time, until it reaches equilibrium. In permeation studies, a diffusant (gas or vapor) of constant pressure p (or concentration c) is introduced to one side of the film (thickness L) at time t=0, and the amount of gas (or vapor) permeating through the film is monitored continually (i.e. isostatic procedure) or by quantifying the amount of permeant that has passed through the film and accumulated as a function of time (i.e. quasi-isostatic procedure). From a single permeation experiment, under certain conditions, all three transport parameters, P,D, and S can be obtained (Crank, 1975).

Factors Affecting the P, D, and S Parameters

The permeability parameters, P,D, and S are dependent upon:

1. The nature of the permeant
2. The nature of the polymer, including morphology and molecular motion of the polymer.
3. Temperature
4. Concentration

Nature of the Permeant

Small diffusant molecules like the fixed gases; oxygen, hydrogen, and carbon dioxide, have almost no effect on the polymer molecules when 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 the film, the frequency of the jumps of the diffusant past the polymer chains gives a net flux of the diffusate molecules through the film (Meares, 1965a). Organic molecules, 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. With increasing molecular size of the permeant, the diffusion coefficient usually decreases. For fixed gases, diffusivity decreases exponentially, and the activation energy of diffusion (Ed), increases linearly with increasing diameter of "spherical" penetrant molecules. For C_4 and larger n-alkanes, and other elongated or flattened molecules, diffusivities are higher, and Ed lower, than for spherical molecules of similar molar volume (Berens 1982). A plot of log D versus the van der Waal's molar volume (b) displays a very systematic trend encompassing ten orders of magnitude in D values, for little more than a two fold change in permeant diameter (Berens and Hopfenberg, 1982). The van der Waal's molar volume (b) is defined as the effective volume of the molecule in one mole of gas (Handbook of Chemistry and Physics, 1966). The activation energy of diffusion (Ed) varies by a factor of about five over the same range. The limiting diffusion coefficient (D_0) decreases and the limiting solubility coefficient (So) increases exponentially with an increase in the overall molecular volume and cross sectional diameter. As a consequence of this compensating behavior, Po is much less dependent on the penetrant size and shape than either So or DO is individually (Roger, 1964). It has also been shown that a penetrant molecule with a branched structure decreases the diffusion coefficient more than the effect 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). In a study reported by Berens (1982) it was noted that with a number of polymer structures, elongated or flattened penetrant molecules showed distinctly greater mobility than nearly spherical molecules of equal molecular volume or mean diameter.

If the permeant is a good solvent for a polymer, and organic vapors tend to be, it will swell and plasticize the polymeric structure when absorbed into the polymer, giving rise to increased mobility of both the polymer chain segments, and the permeant molecules. This in turn results in higher rates and significant concentration dependence of the diffusion process (Laine et al., 1971). The swelling is primarily due to the organic penetrant having a high solubility in the polymer. The solubility is related to the quantitative measure of the attractive forces holding the polymer chains together within the polymer matrix (i.e. the cohesive energy density). The cohesive energy is the square root of the solubility parameter (Billmeyer, 1984). The closer the attractive forces of the solvent and the polymer, the more likely the two components will be soluble. In such a case, the sorbed penetrant is capable of acting as a plasticizer, thus lowering the glass transition temperature of the polymer and increasing the polymer's segmental motions at all temperatures, which results in further plasticization and swelling (Meares, 1965b). It should be clear then that 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).

Nature of the Polymer

With semicrystalline polymers, the existence of crystalline domains has at least three effects on the sorption and diffusion process: (i) The crystalline region is essentially impermeable to permeant molecules (i.e. sorption and diffusion occur almost exclusively through the amorphous component). Hence less polymeric material is available to the diffusing molecules; (ii) The diffusing molecule must take a more tortuous pathway through the semicrystalline polymer in order to avoid the impermeable crystalline domains. This tortuosity depends on the spatial distribution of the crystalline domains in the sample in the sense that; (iii) The crystalline domains, acting like giant crosslinking regions, impose strong constraints on the amorphous phase, and give rise to considerable decreases in the mobility of the amorphous chain segments. Thus, the amorphous phase in a semicrystalline polymer is usually less permeable than in a fully amorphous sample (Enc. Pol. Sci., 1985). It has been shown that the sorption of vapors in polyethylene occurs primarily in the amorphous regions of the polymer, and that there is an approximate linear dependence of sorption on the degree of crystallinity of the film (Rogers et al., 1960). With studies carried out on polyethylene film of varying density (i.e. % crystallinity), a general behavior, indicative of time dependent diffusion, was observed, suggesting that a rearrangement or relaxation of the polymer structure had occurred during the initial stages of the sorption process. This effect is more pronounced in the case of diffusion through the higher density, more crystalline polyethylenes. It may be assumed that the initially sorbed vapor disrupts some of the more imperfectly ordered crystalline regions, which would decrease the average size of the crystallites. The equilibrium number of bonds broken would be proportional to the vapor concentration, and time required to break these bonds would be proportional to the degree of crystallinity and the concentration (Rogers et al., 1960).

The molecular weight of a polymer has little effect on the diffusion rate, whereas chemical modification and morphology of the polymer have a much greater effect (Rogers, 1964). With other factors equal, the permeation of gases and vapors can be expected to decrease as the structural symmetry and cohesive energy density of the polymer increases (Rogers, 1964). Also, the magnitudes of the apparent activation energies, Ed and Ep, increase as the chain rigidity and polarity of the polymer increase. The permeability decreases with an increased degree of crosslinking crystallinity in the polymer (Rogers, 1964). The diffusion coefficient is 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 values of 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 the thermo-mechanical history of the sample (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). The sorption of organic vapors causes the polymer to swell, and so changes the configurations of the polymer molecules. These configurational changes are not instantaneous, but are controlled by the retardation times of the chains. If these are long, stresses may be set up which relax slowly. Thus the absorption of a vapor is accompanied by time-dependent processes in the polymer which are slower than the micro-Brownian motion which promotes diffusion. These processes depend upon the nature of the polymer, the temperature, and the concentration of the sorbed substance (Meares, 1965).

Temperature

The permeant molecules are able to diffuse through the polymer matrix by "jumping" from one sorption site or "hole" to the next under a pressure gradient. The amorphous sections of the polymer, provide units of stable free volume which corresponds to the maximum volume or "holes" required to accommodate a permeant molecule, and must have the capacity to create enough "holes" to form a pathway to allow for successive "jumps" or diffusion of the permeant molecule. For a polymer above its glass transition temperature (Tg), vibrational, rotational and translational motions of the polymer chain segments continually create temporary "holes" in the polymer matrix. 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, plays a large role in the amplitude of the permeation process. Defined, the glass transition process at temperature Tg (K) marks the freezing in (on cooling) or the unfreezing (on heating) of micro-Brownian motion of chain segments 20-50 carbon atoms in length. This micro-Brownian motion is a semi-cooperative action involving torsional oscillation and/or rotations about backbone bonds in a given chain, as well as in neighboring chains. Torsional motion of side groups about the axis connecting them to the main chain may also be involved (Boyer, 1977). Below the Tg of a polymer, not enough energy is provided to produce the micro-Brownian motion, and the chains are fixed in a specific conformation related to processing conditions. With permanent gases, diffusion will only occur if the free volume is above the critical size required to accomodate the molecules. Diffusion and permeation in polymers at temperatures below the polymer's Tg consist of more complex behaviors, and are not well understood at this time (Hernandez, 1984). Above the Tg, an increase in polymer chain segmental mobility creates more channels for the diffusion jumps, resulting in an increase in permeability and diffusion. Since many organic molecules may have considerable solubility in a polymer, the organic penetrant is capable of disrupting the polymer matrix, thus swelling the polymer and acting as a plasticizer. The Tg is then lowered and segmental motion is increased at all temperatures, resulting in further plasticization and swelling (Meares, 1965b).

Within a limited temperature range, the temperature dependence of transport process can be represented as follows, (Barrer, 1936; Rogers, 1964; Van Amerongen, 1946),assuming the polymer does not pass through a thermal transition within the temperature range studied:

$$D = Do \exp(-Ed/RT) \qquad (6)$$

$$S = So \exp(-Hs/RT) \qquad (7)$$

where Ed is the activation energy of diffusion, Hs is the heat of solution, R is the gas constant, T is temperature, and Do and So are pre-exponential factors related to entropy.

The activation energy of diffusion (Ed) 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 (Do), can be thought of as being related to the frequency and magnitude of the holes or "looseness" within the polymer in the absence of permeant. The activation energy of the polymer increases at temperatures above the polymer's Tg (Rogers, 1964).

The heat of solution (ΔHs) can be expressed as the sum of the molar heat of condensation (ΔHc) and the partial molar heat of mixing (ΔH_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, ΔHs is slightly positive so that solubility increases slightly with temperature. However for the more condensable vapors, such as organic compounds, ΔHs is negative due to the relatively large heat of condensation. The solubility therefore decreases with increasing temperature (Rogers, 1964).

Combination of the two equations gives:

$$P = Po \exp(-Ep/RT) \qquad (8)$$

where Po is the pre-exponential term of permeability at zero degrees Kelvin (Rogers, 1964), and Ep is the apparent activation energy for permeation. On passing through polymer transition temperatures (Tm, Tg, etc.), discontinuity in the above relationships will occur. Polymers at temperatures below the glass temperature, and those polymers with long relaxation times usually exhibit anomalous non-Fickian diffusion behavior (Rogers et al., 1960).

Concentration

For gases and some vapors of very limited solubility, the diffusion coefficient can be thought of as a constant, independent of the permeant concentration (i.e. Fickian in nature). For permeants with relatively high solubility in polymers, such as organics the concentration dependence of D becomes important, since the organic penetrants are capable of plasticizing the polymer chain segments, resulting in a rapid increase of D with increasing permeant concentration. Studies involving the diffusion of organic vapors in barrier polymer films have established that in a number of cases the diffusion process is strongly dependent upon the concentration of the penetrant (Rogers et al., 1960). The solubility coefficient often is essentially constant at low vapor activities for the more volatile vapors, and only the diffusion coefficient exhibits significant concentration dependence (Rogers et al., 1960). For systems in which the solubility does not conform to Henry's Law, both the diffusion and the solubility parameters are concentration dependent. In general, D depends on the permeant concentration in an exponential manner (Rogers, 1964):

$$D - D_o \exp(\gamma c) \tag{9}$$

where γ is the concentration coefficient, and c the concentration of the permeant. γ is closely related to the nature of the polymer, and provides information about the morphological features of the polymer. In the case where the diffusion coefficient is time dependent, the diffusion process is said to be non-Fickian (Fujita, 1961; Meares, 1965; Crank and Park, 1968). The diffusion of any given vapor becomes more concentration dependent as the degree of crystallinity of the polymer increases. An increase in crystalline content undoubtedly decreases the natural mobility of the remaining amorphous chain segments, and thus the plasticizing effect of small incremental increases of penetrant.

Permeation of Mixtures

The phenomena of the transport of non-interactive penetrant molecules through polymer materials has been studied thoroughly (Chern, et al., 1983; Crank, et al., 1988; Meyer, et al., 1957; Pasternak, et al., 1970; Pye, et al., 1976; and Stannett, et al., 1972). However, research involving the permeation process of organic vapors has been limited, and has focused primarily on single component organic vapor/polymer systems. Studies describing the permeation of organic vapors and liquids through barrier polymers include those by Rogers et al., 1960; Gilbert et al., 1983; Niebergall et al., 1978; Zobel, 1982; Rogers, 1964; Baner et al., 1986; Hernandez et al., 1986; Mohney et al., 1988; and Liu et al., 1986. These studies were very important in providing a better understanding of the mechanism of the permeation process, involving organic penetrants. However, only a limited number of studies have been reported on the permeation of multi-component mixtures of organic liquids and vapors through barrier membranes (Li et al., 1965; Huang et al., 1968; Weinberg, 1977; Mickelson et al., 1985). Much of this is because of the complexities involved with organic vapors exposed to plastics. DeLassus et al., (1988) alluded briefly to the permeation of multi-component mixtures of organic vapors in the transport of apple aroma in polymer films, where permeation of a binary organic vapors mixture in low density polyethylene was studied. Such studies would be more representative of an actual product/package system, where the product aroma profile contains numerous volatile components. For example, it is known that a natural aroma is generally composed of several hundred to over a thousand individual components (Niebergall et al., 1978). The most varied classes of organic compounds are represented here. Aromatic and aliphatic, saturated and unsaturated hydrocarbons are found, together with alcohols, acetals, esters, phenols, sulphides and amines, among others, often of a more complex structure (Niebergall et al., 1978).

The first study which involved measuring the effect of mixed gases on one another, was carried out by Alexejev et al., (1927), who studied the permeation of carbon dioxide, oxygen, acetylene, Nitrogen and air, both alone and as mixtures through rubber membranes. They established that for wide differences in compositions, the rate of permeation of a gas mixture was equal to the sum of the rates of its constituents. Pye et al., (1976) reported that noninteractive penetrants permeated independently of a co-permeant, even at low partial pressures, and also that a decrease in selectivity of H_2 over CH_2 occurred with an increase in temperature. It was found that, within experimental error, no effect of one penetrant gas on another was observed, but the time taken to establish the steady state increased when mixed gases were used (Meyer, et al., 1957). Stannett et al., (1957) conducted permeability studies with nitrogen, oxygen, and carbon dioxide through various plastic films. They confirmed that no difference in the permeability constant was found, whether the gas diffused alone or in the presence of another gas, provided the gases were adequately mixed. Robeson (1969), presented data for CO_2 permeation in polycarbonate, in which both solubility and diffusivity are reduced due to antiplasticization caused by the presence of the strongly interacting 4,4'-dichloro diphenyl sulfone. Conversely, sorption of a less strongly interacting penetrant, such as a hydrocarbon, may primarily affect only the solubility factor, without significantly changing the inherent mobility of the penetrant in either of the two modes. Flux reduction in this latter context occurs simply because the concentration driving force of penetrant A is reduced. This results from exclusion of A by component B from sorption sites that were previously available to penetrant A in the absence of B (Robeson, 1969).

The results described by Mickelson et al., (1985) have also been observed by other investigators in studies where the effects of polymer morphology, degree of penetrant-polymer interaction, and temperature on the permeation of organic liquid mixtures through polymer membranes were evaluated (Binning et al., 1971; Li et al., 1965; Huang et al., 1968; Weinberg, 1977). It is interesting to note that while the studies reported on the permeation of multi-component organic liquid mixtures through barrier polymer films were conducted with a total pressure differential across the membrane, the effect of the total pressure differential on the transmission rate of the organic liquid penetrants was minimal (Binning et al., 1971).

Polymer systems have been investigated for their ability to separate liquid mixtures. A variety of polymeric films can be used in the liquid permeation process to separate mixtures of organic compounds (Binning et al., 1961). The choice of film depends on the chemical nature of the mixture being separated, and the stability of the polymer at the required operating temperature. Permeation and efficiency of separation are governed by a number of factors, including the chemical nature, molecular size, and molecular shape of the diffusing species, the composition of the permeating mixture, and the physio-chemical properties of the polymer. For a given polymer, the temperature dependence of the permeation rate for both pure liquids and their mixtures exhibit an Arrhenius behavior, and the separation efficiency varies inversely with the temperature (Huang et al., 1968). According to Eyring's hole theory of diffusion, the thermal motion of polymer chains randomly produces "holes" through which the permeating molecules can diffuse. As the temperature is increased, the thermal agitation increases and the diffusive "holes" become larger (Huang et al., 1968). More of the less diffusive molecules can therefore diffuse through the membrane, and the separation factor is decreased. Huang et al., (1968) found that several of the mixtures studied permeated faster than either of the pure components alone, and attributed this to a combined internal plasticizing and solubility effects. Aminabhavi et al., (1989), reported that with mixtures of toluene/isopropyl alcohol;o-xylene/isobutyl alcohol; and n-hexane/n-octane, the rate of permeation through polyethylene membranes, and the selectivity in separating the mixtures, decreased with increasing pressure on the membrane. The same authors found that for alcohol-hydrocarbon mixtures, a concentration dependence was observed, which led to an increased rate of alcohol permeation with increasing pressure. In such mixtures, the hydrocarbon selectivity decreased with increasing pressure and with increasing hydrocarbon content in the mixture. Sweeny and Rose (1965) concluded that binary liquid mixtures of different polarity were selectively permeated and that the component whose polarity most closely matched that of the membrane was preferentially permeated. For members of a homologous series in a common solvent, higher degrees of separation are achieved for the higher molecular weight members, and better separation from a common solvent is also achieved with molecules of larger cross sections (Huang et al., 1970).

In the sorption study performed by Weinberg (1976), which utilized organcic vapor mixtures in Barex 210 film, it was noted that for the co-permeants of 1,1,2-trichloroethane and 1,1,2-trichloroethylene, the weaker penetrant lags behind the stronger penetrant but that the difference decreases as sorption proceeds. It was found in these studies, that the co-permeants "break through" the film at essentially the same time. In addition, the permeation rates of the two components are nearly in the same ratio as the concentration of the components in the binary phase, with a somewhat enhanced rate for the stronger penetrant, resulting in a slight enrichment of the permeating vapor in this compound. It is also apparant that the weaker penetrant more effectively reduces the steady state permeation rate, as compared to the sorption rate of a mixture. Presumably this is the result of the greater role of film plasticization in the former case. As noted by Binning et al., (1961), the phenomena of reversal of selectivity of the permeation rate can be observed by changing the type of film. For example, if two permeants 1 and 2 are introduced to two films A and B, and permeant 1 is more soluble in film A, then permeant 2 will be selectively permeated. On the other hand, if permeant 2 is more soluble in film B, then permeant 1 will be selectively permeated. The authors proposed, that this type of phenomenon can be correlated with the Flory-Huggins parameter for the interaction of solvents with polymers.

Permeability Theory for Organic Vapor Permeation in a Sheet

Work done by Rogers (1964) proposed the general theory of permeation, which can be described in a series of mathematical expressions. Further detail can be found in the work by Crank (1973). The permeation rate (P) or transmission rate is defined as the amount of penetrant passing, during unit time, through a surface of unit area normal to the direction of flow:

$$P = \frac{Q}{A\,t} \tag{10}$$

Where Q is the total amount of permeant which has passed through area (A) during time (t). When a penetrant is exposed to a given unit area of film thickness, L (cm) at a 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 + (∂P/∂x)dx. The amount retained per unit volume of polymer is therefore equal to the rate of change of concentration with time:

$$\frac{-\partial P}{\partial x} = \frac{\partial c}{\partial t} \tag{11}$$

If the steady state rate of flow ∂c/∂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:

$$F = \frac{-D\partial c}{\partial x} \tag{12}$$

Where:

F=flux

D=differential diffusion coefficient

Assuming D to be constant, it can then be integrated between the two concentrations c_1 and c_2:

$$P\int_{x=0}^{x=L} = -D\int_{c2}^{c1} dc \tag{13}$$

which gives:

$$P = \frac{D(c_1-c_2)}{L} \tag{14}$$

By utilizing Henry's Law, c = Sp, the equilibrium concentration c_1 and c_2 of penetrant in the surface layer of the polymer can be related. 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. This leads to:

$$P = \frac{D\,S\,(p_1-p_2)}{L} \tag{15}$$

or:

$$P = D\,S = \frac{P\,L}{(p_1-p_2)} \tag{16}$$

P is the quantity of permeant permeated through a film of thickness L per unit membrane area, per unit permeant driving force, which is defined as the permeability coefficient.

Unlike permeant\polymer systems involving "ideal" or fixed gases, 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), a new expression is used which takes into account the change in the diffusion coefficient with concentration at different locations within the polymer:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(\frac{D(c)\partial c}{\partial x}\right) \tag{17}$$

A mean or integral value of the diffusion coefficient, D, over the concentration range c_1 to c_2, can be calculated for a range of permeant concentrations:

$$D = \frac{\int_{C_2}^{C_1} D(c)\ dc}{\int_{C_2}^{C_1} dc} = \frac{\int_{C_2}^{C_1} D(c)}{C_1 - C_2} \tag{18}$$

The estimation of the dependence of D on concentration can be made over several consecutive ranges of concentration. Equation (18) simplifies to Equation (19) when c_2=0 (as in the case of most permeation experiments) and D is determined for a number of values:

$$D = \frac{1}{c_1 \int_{c_2}^{c_1}} D(c)\ dc \tag{19}$$

When experimental conditions are such that c_2 is always zero and 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 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:

$$P = -D\ \left(\frac{dc}{dx}\right) = a\ constant \tag{20}$$

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. Integration between c_1 and c_2, the two surface concentrations of the membrane of thickness (L), gives:

$$P = \left(\frac{1}{L}\right) \int_{c_2}^{c_1} D(c)\ dc = \frac{D\ (c_1 - c_2)}{L} \tag{21}$$

Where D is the integral diffusion coefficient defined by Equation (19). When $c_1>>c_2\tilde{}0$ equation 21 reduces to:

$$P\,L = \int_{c_2}^{c_1} D(c)\;dc\;,\quad D(c) = \frac{d(L\,P)}{dc} \tag{22}$$

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).

D can also be estimated from the definition of the permeability coefficient as the product of the diffusion and solubility coefficients. When the diffusion process is concentration dependent:

$$P = \frac{D(p_1-p_2)}{L} \tag{23}$$

Where 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 coefficient. From Rogers, (1964):

$$P = \left(\frac{1}{(c_1-c_2)\int_{c_2}^{c_1} D\,dc}\right)\left(\frac{c_1-c_2)}{(p_1-p_2)}\right)\left(\frac{(p_1-p_2)}{L}\right) \tag{24}$$

so that, $$P = D\ S \tag{25}$$

and $$D = P/S \tag{26}$$

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

The above permeability theory derivation only considers the case where D and P are functions of concentration and S is constant. However in many organic permeant-polymer systems the solubility coefficients (S) is also a function of the concentration of permeant in the polymer and does not always follow Henry's Law, particularly at high permeant concentrations.

As the permeant diffuses through a polymer membrane, there is an interval of time from when the permeant is introduced to the membrane surface, and when it reaches steady state permeation. During this interval 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):

$$\frac{Q_t}{LC_1} = \frac{Dt}{L^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum \frac{-1^n}{n^2 \exp \frac{-Dn^2\pi^2 t}{L^2}} \tag{27}$$

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 is represented by:

$$Q_t = \frac{Dc_1}{L} \left(\frac{t-L^2}{6D}\right) \tag{28}$$

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

$$\Theta = \frac{L^2}{6D} \tag{29}$$

This is known as the lag time, and from this the diffusion coefficient can be deduced from Equation 29. The solubility can then be obtained from Equation 26 (Daynes, 1920; Barrer, 1941).

Frisch (1957,1958,1959) and Pollack and Frisch (1959) have developed expressions which allow the calculation of the diffusion coefficients 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. This method can be quite complex, as the concentration as a function of x is necessary, and can be very complicated (Crank and Park, 1968).

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

$$\frac{1}{6} \leq \frac{\Theta D}{L^2} \leq \frac{1}{2}$$

Thus an estimate of the integral diffusion coefficient can be made using the time-lag expression derived for a constant D. Equation (29) is at worst too small by a factor of three (Rogers, 1964).

Organic Permeation Measurement Techniques

Permeation data for organic vapors in polymers are limited and has mainly been targeted towards polymers above their glass transition temperature or glassy polymers. Initially, manometric or volumetric techniques were used to measure the permeant in the absolute pressure method (Stannett et al., 1972). More recently, researchers have employed both the quasi-isostatic and isostatic methods for studying the diffusion of organic vapors through barrier films using gas chromatographic analysis for quantification (Stannett et al.; 1972, Zobel, 1982; Baner et al., 1986; Hernandez et al., 1986; DeLassus, 1986). The partial pressure differential of the test vapor provides the driving force, with the total pressure of one atmosphere on both sides of the film.

In the quasi-isostatic method, the permeated gas or vapor is accumulated in the lower concentration chamber of the cell, and monitored as a function of time. The total quantity of penetrant transmitted through the film is plotted as a function of time. Numerous authors have reported studies based on the quasi-isostatic method of permeation measurements (Hilton et al., 1978; Murray et al., 1938; Murray, 1985; Gilbert, 1983; Baner, 1986; Peterlin, 1975).

The isostatic test system allows for the continuous collection of permeation data of an organic vapor or gas through a polymer membrane from the initial time zero to steady state conditions, as a function of temperature and permeant concentration. A constant concentration of permeant vapor is continually flowed through the high concentration cell chamber. At the same time, a constant flow of carrier gas is passed through the lower cell chamber, removing permeant vapor at a constant rate and conveying it to the detector apparatus. At pre-selected time intervals the concentration of penetrant in the carrier stream flowing through the low concentration cell chamber is determined, and the transmission rate is monitored continually until steady state conditions are attained. The steady state permeation rate is equal to the steady state concentration of permeant in the sweep gas stream times the sweep gas flow rate.

Numerous authors have developed isostatic permeation systems with various detection devices. Davis (1946) developed a system that utilized chemical sorption of the permeating gases, but the system lacked sensitivity. Ziegel et al., (1969) and Pasternack et al., (1970) used thermal conductivity detectors to measure the increasing amount of permeant in the lower sweep stream. Yasuda et al., (1970) and Giacin et al., (1981) incorporated small thermistors in the detection system. Both systems worked well for single permeants, but were unable to detect co-permeants. Photoionization and atmospheric pressure ionization techniques were used by DeLassus (1986) to study the transport properties of penetrants through polymeric membranes. Zobel (1982), Pye et al., (1976), Hernandez (1984), and Baner et al., (1986) used a flame ionization detector (FID) to detect the permeants. Niebergall et al., (1978) used an isostatic system to measure the permeation characteristics of mixed organic vapors through polymeric membranes as a function of penetrant concentration, temperature and relative humidity (RH).

Isostatic Permeation Methods

Since the isostatic permeation method was utilized in the present study, a detailed discussion of the equations describing the permeation process follows.

Summarizing from Hernandez et al., (1986), solution to the following equation:

$$P = -D \frac{\partial c}{\partial x} \qquad (30)$$

depends on the boundary conditions of the experiment, which in this study is given by:

$c = c_1$ at $x = 0$ $t = 0$

$c = c_0$ at $x = L$ $t > 0$

$c = c_2\ (L-x)/L$ at $0 < x < L$ $t = \infty$ (31)

where L is the thickness of the film, c_0 is the concentration at x = L in equilibrium with the penetrant flow. These boundary conditions represent the change from one steady state, t = 0 and c_1 to the final concentration c_2 at $t = \infty$, with the partial pressure of the permeant on the downstream side of the membrane always at zero, since pure carrier gas is continuously flowed.

A solution to Equation 30 subject to boundary conditions given by Equation 31 was presented by Pasternak et al., (1970), and is given as a first approximation in Equation 32:

$$\frac{\frac{(\Delta M)}{(\Delta t)_t}}{\frac{(\Delta M)}{(\Delta t)_\infty}} = \left(\frac{4}{\sqrt{\pi}}\right) \left(\frac{(L^2)}{(4Dt)}\right) \exp\left(\frac{-L^2}{4Dt}\right) \qquad (32)$$

where $(\Delta M/\Delta t)_t$ and $(\Delta M/\Delta t)_\infty$ are the transmission rate of the penetrant at time t and at steady state, respectively, t is time and L is the thickness of the film.

For each value of $(\Delta M/\Delta t)_t/(\Delta M/\Delta t)_s$ a value of $L^2/4Dt$ can be calculated, and by plotting $(4Dt/L^2)$ as a function of time, a straight line is obtained. From the slope of this graph, the diffusion coefficient (D) is calculated by substitution in Equation 33:

$$D = \frac{slope\ L^2}{4} \qquad (33)$$

From a different general expression for $(\Delta M/\Delta t)\infty$, Ziegel et al., (1969), derived Equation 34 to solve for D:

$$D = \frac{L^2}{7.199\, t_{1/2}} \qquad (34)$$

where $t_{1/2}$ is the time required to reach a rate of transmission $(\Delta M/\Delta t)^t$ equal to half the steady state $(\Delta M/\Delta t)_s$ value.

The permeability coefficient P can be determined from the isostatic method by substitution into Equation 35:

$$P = \frac{(a)\,(G)\,(f)\,(L)}{(A)\,(b)} \qquad (35)$$

where:

a = calibration factor to convert detector response units of mass of permeant/unit of volume [(mass/volume)/signal units]
G = response units from detector output at steady state

(signal units)
f = flow rate of sweep gas conveying penetrant to detector (volume/time)
A = area of the film exposed to permeant in the permeability cell (area units)
L = film thickness (thickness units)
b = driving force given by the concentration or partial pressure gradient (pressure or concentration units)

MATERIALS AND METHODS

Materials

Film Sample

A 2 mil biaxially oriented polypropylene film provided by the Mobil company was used for all studies. The level of elongation was 430% (machine direction) and 800% (cross machine direction), based on the initial dimensions. Ethyl acetate and limonene were selected as the organic penetrants, and nitrogen served as the carrier gas.

Limonene

Used as a permeant.

Supplied from Aldrich Chemical Co.(Milwaukee, WI).

Density	0.840
Molecular Weight	136.24
Boiling Range	175.5-176°C
Refractive Index	1.4715
Purity	97%

Ethyl Acetate

Used as a permeant.

Supplied from Aldrich Chemical Co. (Milwaukee, WI).

Density	0.894
Molecular Weight	88.11
Boiling Range	77.1°C
Refractive Index	1.37
Purity	99.9%

Dichlorobenzene

Used as a solvent for constructing a calibration curve for ethyl acetate analysis.

Dichloromethane

Used as a solvent for constructing a calibration curve for limonene analysis.

Nitrogen

Used as the carrier gas. High purity dry nitrogen 99.98% by the Union Carbide Corporation, Linde Division (Danbury, CT).

Experimental Procedure

Permeability studies were carried out with the individual components of the mixture at numerous concentrations, along with binary organic vapor mixtures of varying composition. The isostatic method of measurement was utilized for all studies conducted. The permeability cells and test apparatus are of a design developed and used for the studies of Baner et al., 1986 and Hernandez et al., 1986. The cells are composed of two stainless steel disk shaped plates that, when clamped together, form the complete cell. The volume of each cell chamber is 5 cc.. The surface area of the film exposed to the permeant is 50 cm^2. Each cell chamber contains an inlet and outlet port for the continuous flow of vapor and carrier gas streams. Analysis for penetrant concentration was based on a gas chromatographic procedure, with flame ionization detection (FID). The gas chromatograph is interfaced to the permeation cell via a computer aided stream selection and a gas sampling valve, which allows continuous monitoring of the permeation of the organic penetrant through the membrane, from initial time zero to steady state conditions, as a function of penetrant concentration. The system is designed to test two polymer/penetrant samples concurrently.

The film samples to be tested were conditioned at the temperature of test for at least 24 hours. All studies were carried out at 23°C +/ 1°C. The influence of temperature and relative humidity on the barrier properties of the polypropylene were not considered in this study.

A schematic diagram of the system utilized is presented in Figure 1. All permeation cells, cell parts, and O-rings were baked out in an oven at 135°C for a period of at least 24 hours to remove any residual sorbed permeant from the previous experiment prior to initializing a run. For each permeation cell, a sample approximately 5" x 5" was cut and placed between the two stainless steel disks, which were then clamped together. Hermetic isolation of the chambers from the environment was achieved by the compression of overlapping Viton "O" rings on the film (Viton is a fluorocarbon elastomer which is resistant to attack and swelling by most organic vapors).

The assembled cells (two) were placed horizontally in an oven (on a rack in the middle of the oven). Although elevated temperatures were not utilized in this study, the oven provided a chamber where the cells were maintained at a

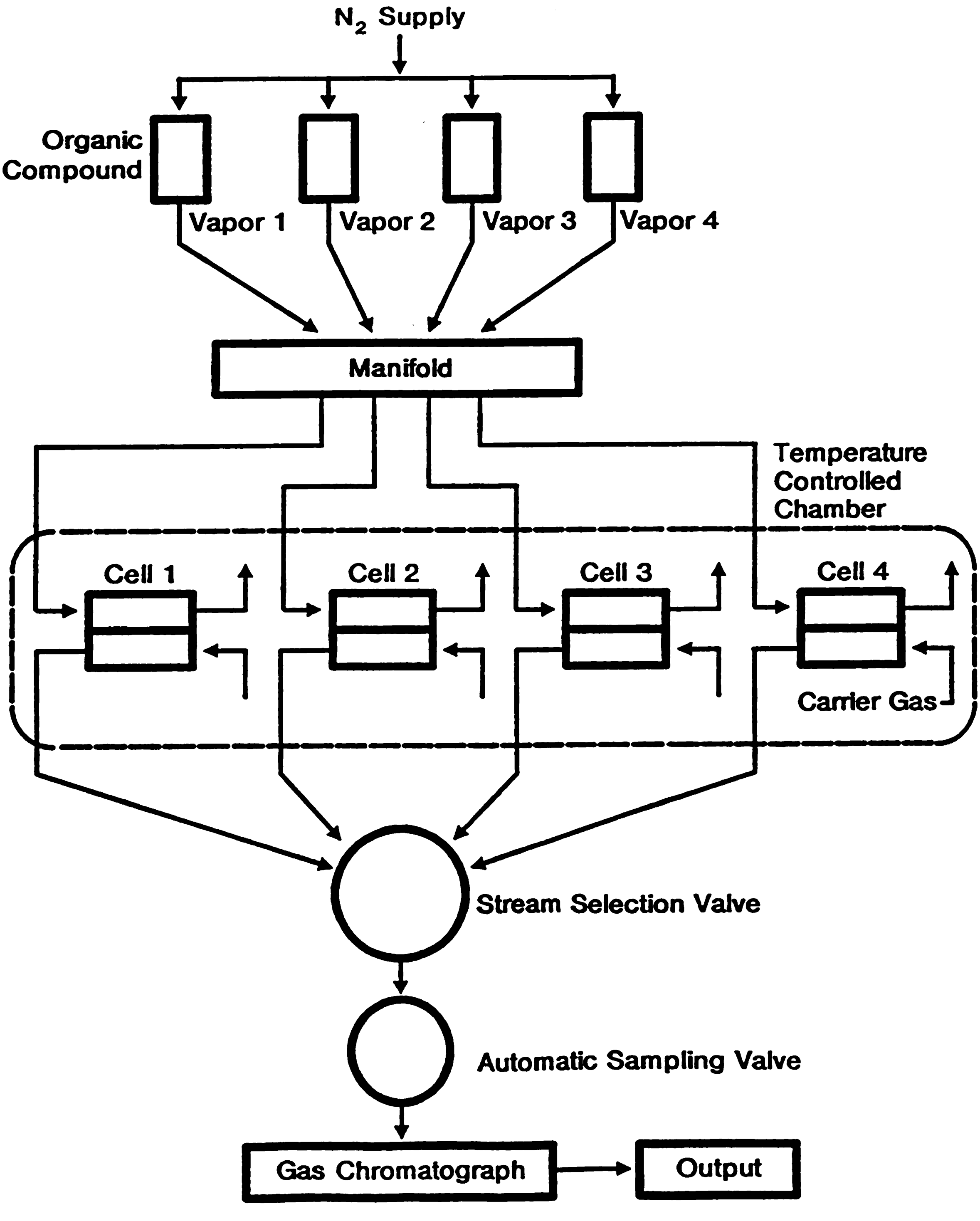

Figure 1. Schematic of isostatic permeation test apparatus

constant temperature, and were not affected by minor fluctuations in the environmental conditions. A constant flow of permeant (i.e. the "high concentration" permeant) is flowed into the top portion of each cell and then vented from the opposite side of the cell. A constant flow of carrier gas (nitrogen) is introduced into the low concentration chamber of each cell, which then transports any permeated penetrant (i.e. the "low concentration" permeant) to the GC and detector apparatus.

The high concentration stream was directed to another permeation cell before being vented to the hood (see Figure 1). This cell has three chambers, with the center one being isolated from the top and bottom chambers by aluminum foil. The center chamber contains a sampling port from which aliquots were taken for the determination of vapor activities (the volume in the center chamber is approximately 50cc).

A constant concentration of permeant vapor for the "high concentration" was produced by bubbling nitrogen through the liquid permeant. The liquid permeant is contained in a vapor generator consisting of a Pyrex glass gas washing bottle, 250mm long and 50mm wide, with a fritted dispersion tube. The organic vapor stream can then be mixed with another source of pure nitrogen, if further dilution is needed.

Before actual testing was conducted, flowmeter settings were determined to provide vapor activity (a) values of approximately 0.05, 0.1, 0.2, 0.3, and 0.5, respectively.

Included in Appendix B are the concentrations utilized for both the individual penetrants and the binary mixture. Rotameters were used to provide an indication of settings required for the desired vapor activities. The gas flows to the rotameters were regulated by Nupro "M" series needle valves. Electronic mass flowmeters, (Manufactured by Sierra Instruments, Top-Trak 821 model, 0-10 SCCM with an accuracy of 2% of full scale and 0.5% repeatability), were incorporated between the dispensing manifold and the test cell, to provided a continuous indication that a constant rate of flow was maintained. The mass flowmeters were used to monitor flow through the low concentration cell chamber, before it reached a stream selection valve.

The low concentration stream, through a 1/16" OD stainless steel tubing, is introduced from the cell to the stream selection valve (Multiposition automatic gas sampling valve model no. ACSF8P, Valco Instruments Co. Inc., Houston, TX) which allows one stream at a time to flow to the gas sampling valve, through a common outlet. A stream was selected in the clockwise direction every time the valve was actuated. With this valve, a sample will be taken from cell #1 and then at a predetermined time interval, a sample was taken from cell #2. The valve will continue to take samples at predetermined time intervals until the program is terminated.

A 1/16" stainless steel tubing connected the stream selection valve to the automatic gas sampling valve, which is a 6 port valve located inside the GC housing. The sampling loop in the valve has a volume of 0.5 ml. The stream selection valve and automatic gas sampling valve are both pneumatically operated.

The connections between the cell and the stream selection valve, and from the stream selection valve to the automatic gas sampling valve on the GC were made with stainless steel capillary tubing 1/16" OD and 0.762mm ID. Except for the 1/16" SS tubing noted above, all of the components of the test system were connected by 1/8" x 1.65mm copper refrigeration tubing. All fittings and tubing connections used were brass Swagelok fittings. The column packing material and GC calibration data are stated in appendix A.

A Hewlett Packard 5830A gas chromatograph equipped with dual flame ionization detection, interfaced to a 18850A GC Hewlett Packard terminal was used for permeant detection. The 5830A GC is a keyboard controlled instrument with a multifunctional digital processor. From the digital processor, printed output with a plot of the amount of material detected as a function of time, the area under this curve (expressed in area units) and retention time was obtained.

Before starting a permeation run, the lower cell chamber, the capillary tubing, stream selection valve, and automatic sampling valve were flushed of any residual vapor with a nitrogen source. The system was considered clean when the signal from the GC was less than 500 area units. The film sample was mounted between the two sections of the permeation cell and clamped securely to prohibit possible leaks. A constant stream of nitrogen was introduced through the vapor generator to provide a steady concentration of the vapor. For each vapor activity the settings on the rotameters were adjusted. Two separate rotameters provided a means of maintaining a constant stream of nitrogen through the low concentration cell chamber of the permeability cell. Two digital mass flowmeters provided a continuous monitor of this nitrogen stream.

Permeation studies were also utilized to determine both the diffusivity of the individual components through the test barrier, and to evaluate the effect of a co-permeant on the diffusivity of the penetrant studied. Diffusivity was determined by the method described by Smith et al., (1981). This method is described in Appendix D.

RESULTS AND DISCUSSION

The Effect of Ethyl Acetate Vapor Concentration on Penetrant Diffusion and Permeability

The results of permeability studies carried out with ethyl acetate vapor, are presented graphically in Figure 2, where the transmission rate ($\Delta Q/\Delta t$) is plotted as a function of time for ethyl acetate vapor activity levels of a = 0.12, 0.18, 0.30, and 0.48, respectively. The transmission rate profile curves as shown are illustrative of the effect of vapor concentration on both the permeability and penetrant lag time characteristics. A plot of the relative transmission rates (transmission rate at a given time/steady state transmission rate), as a function of time, for the same vapor activity levels further illustrates the penetrant lag time characteristics, which can be seen from Figure 3. The permeability and diffusion coefficients calculated from this data are summarized in Table 1, from which it becomes evident that at vapor activity levels below a = 0.2, the effect of penetrant concentration on the permeability constant (P) is minimized. However, at higher concentration levels (i.e.

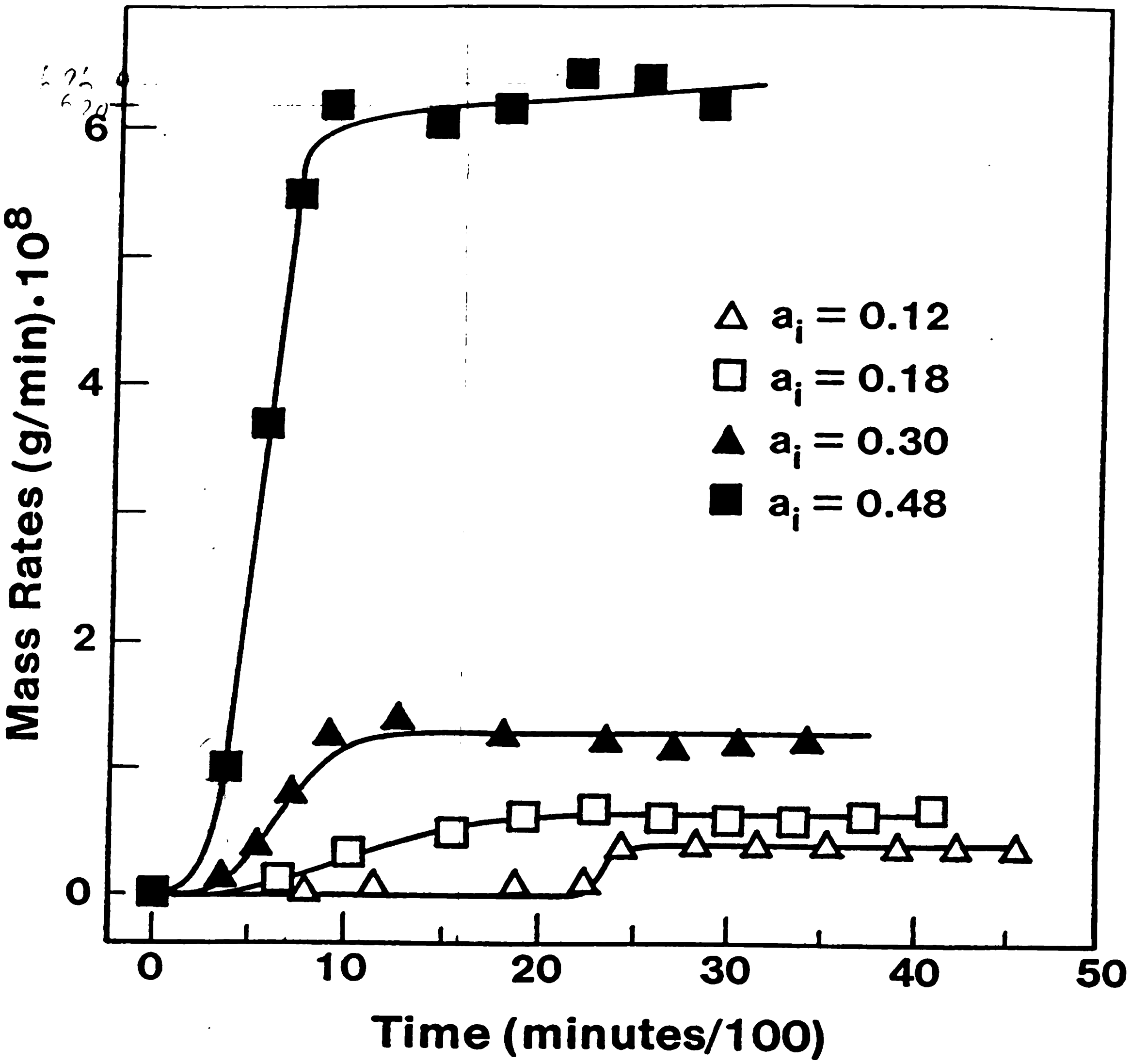

Figure 2. Transmission rate profile curves for ethyl acetate vapor permeability through oriented polypropylene (23°C)

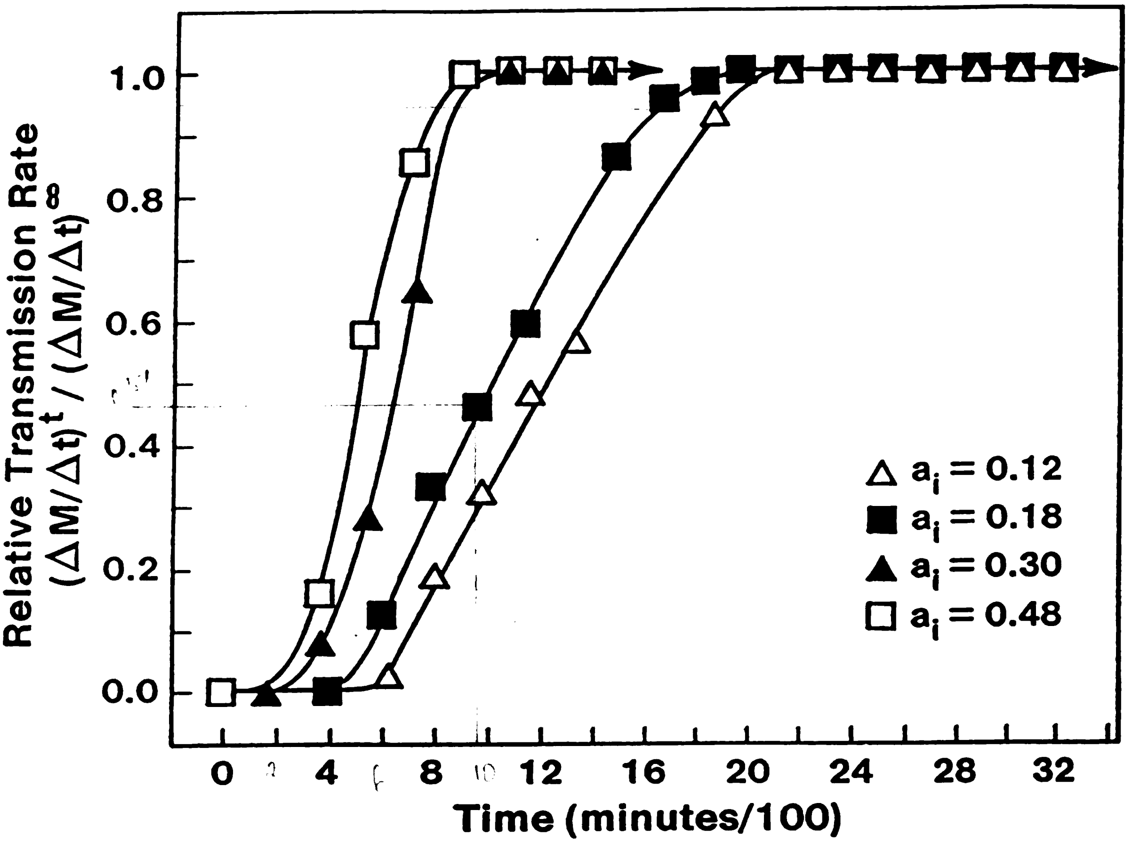

Figure 3. Plot of relative transmission rate curves for ethyl acetate (23°C)

Table 1

Permeability Parameters Calculated from Ethyl Acetate (23° C)

Vapor Activity a	P (a) Permeability Constant kg m/s m^2 pascal (x 10^8)	D (a)(b) Diffusion Coefficient m^2/sec (x 10^{14})
.052	4.2 +/-.5	4.5 +/-.44
.120	5.0 +/-.2	6.2 +/-.48
.179	5.8 +/-.3	6.3 +/-.22
.300	9.0 +/-.6	15.9 +/-.25
.480	29.1 +/-.2	21.0 +/-.18

(a) Average of Replicate Runs
(b) Diffusion Coefficient determined from method of Smith and Adams (1981)

above a = 0.2) the permeability coefficient is markedly dependent upon penetrant concentration, with P increasing exponentially with an increase in vapor activity. This is illustrated in Figure 4 where log P is plotted as a function of ethyl acetate vapor activity. The observed concentration dependency of the permeability coefficient suggests strong penetrant/polymer interaction, resulting in swelling of the polymer matrix by the sorbed ethyl acetate vapor, and a concomitant alteration of polymer chain conformations, leading to an increase in penetrant diffusivity, and therefore permeability. This phenomenon was visibly evident by the observed swelling of the membrane.

Diffusion coefficient values were determined from the permeability data based on the method of Smith et al., (1981). As shown in Table 1, there is a small increase in the diffusion coefficient with an increase in vapor activity for ethyl acetate levels, ranging from a = 0.052 to 0.18. However, above an ethyl acetate vapor activity of a = 0.2, the diffusion coefficient is highly affected by penetrant concentration. Figure 5 is illustrative of this trend.

The free volume theory of Fujita (1961), has been proposed to describe the concentration dependency of the diffusion coefficient for an organic penetrant, where the relationship between the diffusion coefficient (D) and the equilibrium solubility (C_s) for a penetrant/polymer system is expressed by:

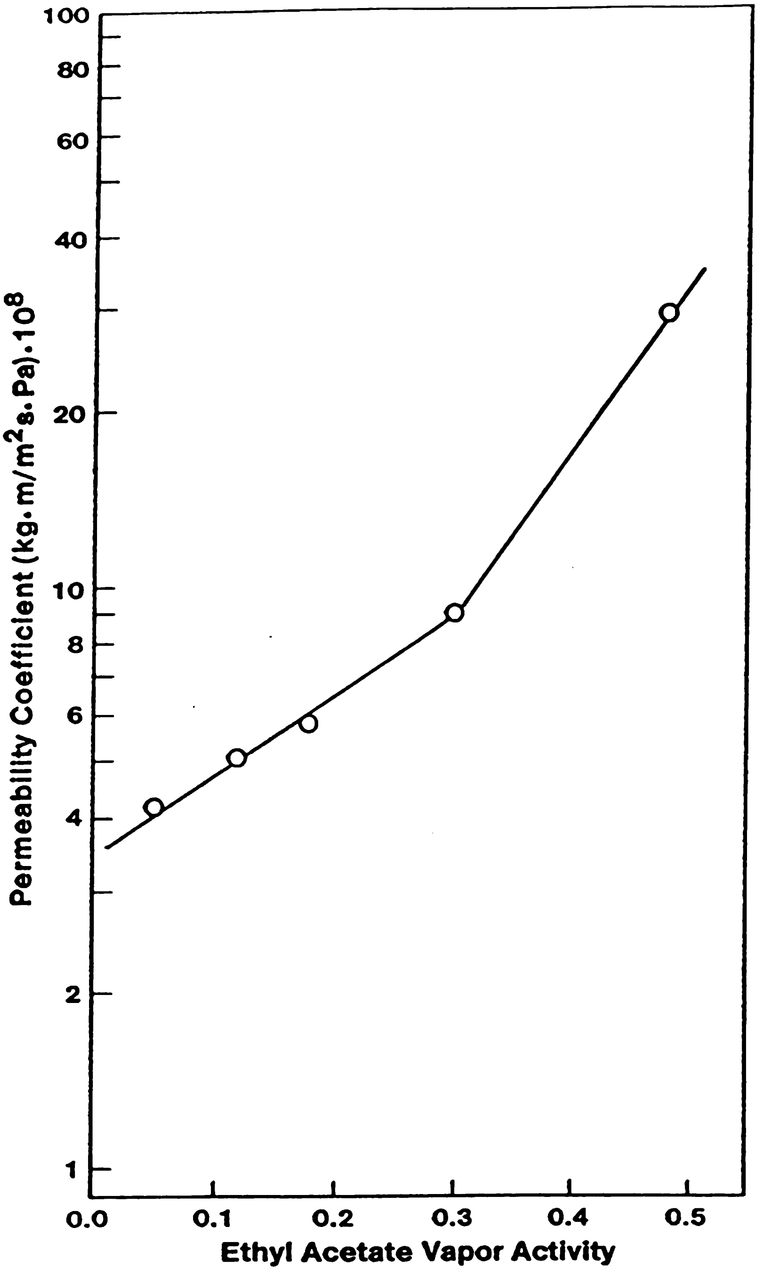

Figure 4. The effect of permeant vapor concentration on log P for ethyl acetate

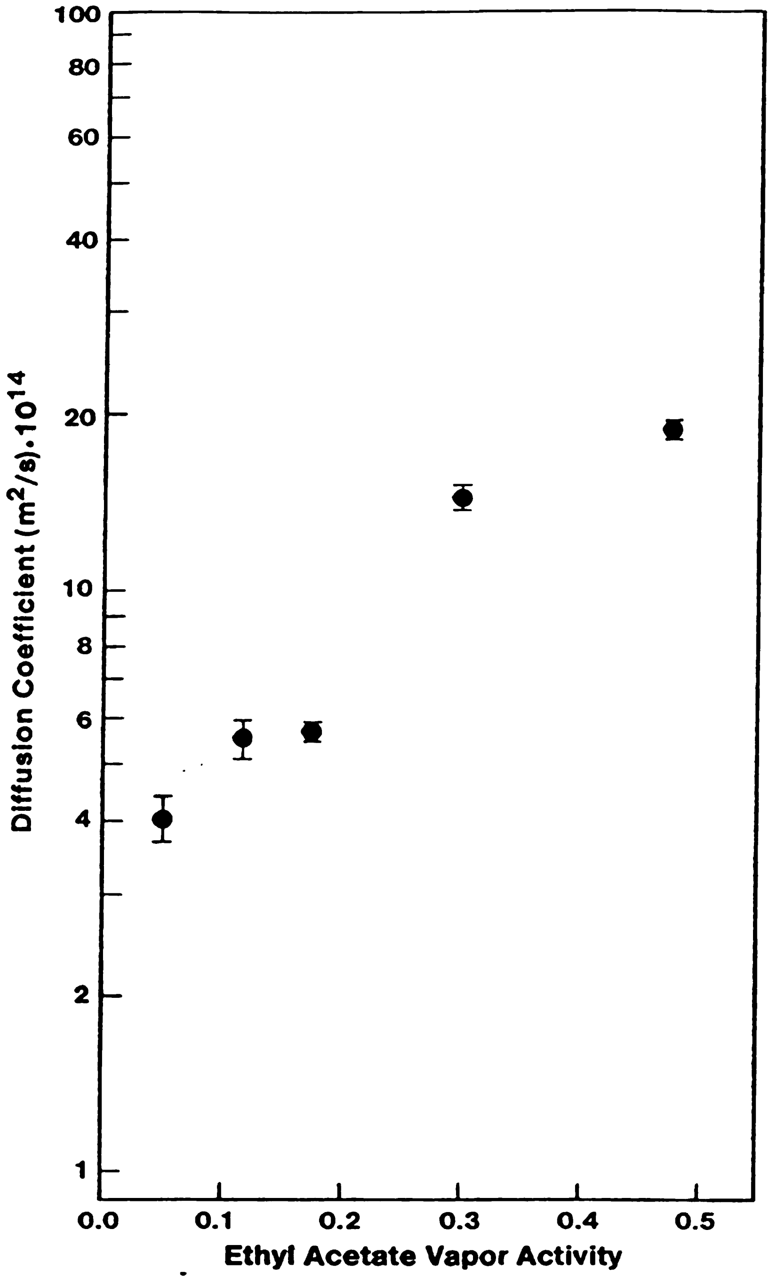

Figure 5. The effect of permeant vapor concentration on log D for ethyl acetate

$$D-D_o \mathrm{exp}\gamma C_s \qquad (36)$$

where D^o is a pre-exponential factor, sometimes referred to as the limiting diffusion coefficient, and γ is a proportionality factor, related to free volume parameters by:

$$\gamma-\frac{B\beta}{f_0^2} \qquad (37)$$

where f_0 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 γ denotes the effectiveness of the penetrant molecules for increasing the free volume of the polymer (Choy, et al., 1984). The diffusion coefficient values reported are calculated from the transient state region of the transmission rate profile curve and potentially may not be representative of the diffusion coefficient values at steady state, where penetrant/polymer interaction may lead in a gradual relaxation of the polymer structure, resulting in a change in the free volume parameter γ.

The Effect of Limonene Vapor Concentration on Penetrant Diffusion and Permeability

The results of the permeability studies carried out with limonene vapor are presented in Figure 6, where the transmission rate curves obtained for limonene vapor activities of a = 0.21, 0.29, 0.42, and 0.50 are plotted. As with the ethyl acetate permeability data, the superimposition of the transmission rate curves for the respective penetrant activity levels shows a concentration dependency of the mass transport process. A plot of the relative transmission rates further illustrates the diffusion characteristics, for the limonene/polypropylene, penetrant/polymer system (see Figure 7). The permeability parameters determined from these studies are summarized in Table 2. From Table 2, it can be seen that the permeability coefficient values obtained are highly concentration dependent for limonene vapor activity levels below a = 0.30. Above this limonene activity (a = 0.30) however, a further increase in vapor concentration did not significantly effect the permeability constant. The relationship between limonene vapor activity and the permeability coefficient P is shown graphically in Figure 8, where log P is plotted as a function of vapor activity. A similar trend was observed in an earlier study, where the permeability of limonene vapor through a co-extruded biaxially oriented polypropylene film was evaluated (Giacin et al., 1986). The diffusion coefficient values are also presented in Table 2. From this data it is evident that the diffusion coefficient (D) values were highly dependent upon vapor activity at the lower values of limonene concentration, but

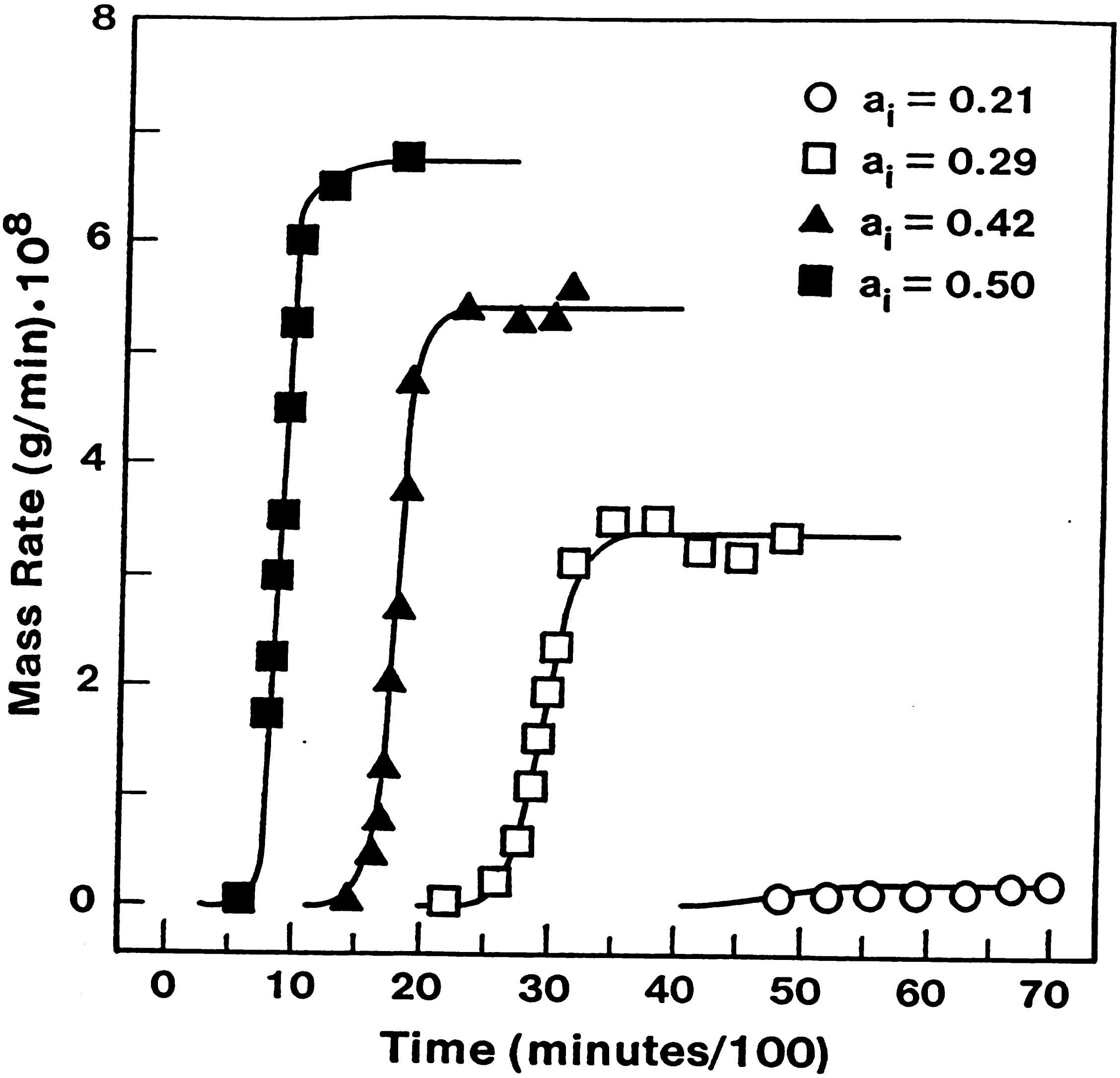

Figure 6. Transmission rate profile curves for limonene vapor permeation through oriented polypropylene (23°C)

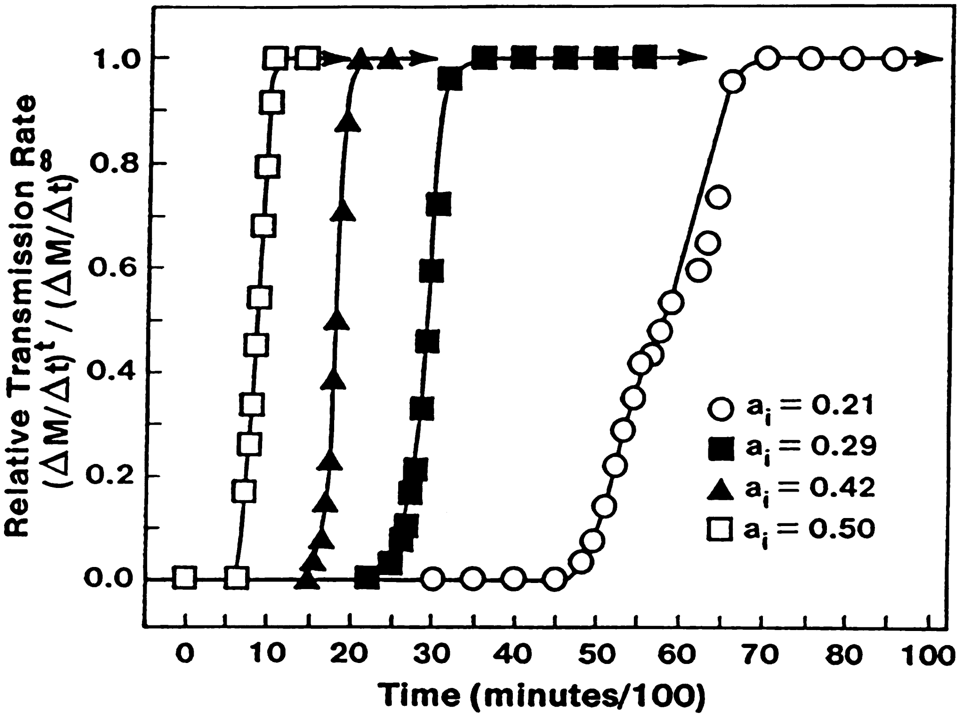

Figure 7. Plot of relative transmission rate curves for limonene (23°C)

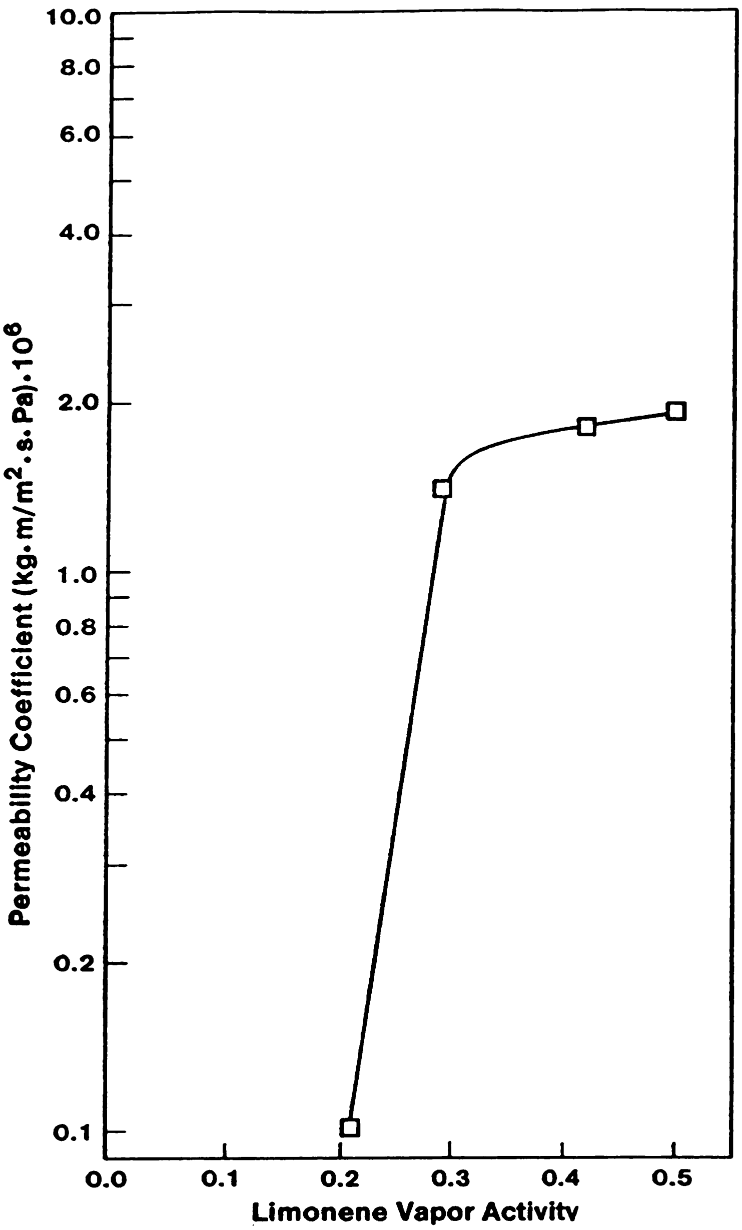

Figure 8. The effect of permeant vapor concentration on log P for limonene

Table 2

Permeability Parameters Calculated from Limonene (23° C)

Vapor Activity a	P (a) Permeability Constant kg m/s m^2 pascal (x 10^6)	D (a)(b) Diffusion Coefficient m^2/sec (x 10^{14})
.21	0.1 +/-.02	3.5 +/-.17
.29	1.4 +/-.2	11.1 +/-.26
.42	1.8 +/-.3	24.7 +/-.34
.50	1.9 +/-.4	23.3 +/-.47

(a) Average of Replicate Runs
(b) Diffusion Coefficient determined from method of Smith and Adams (1981)

approach a constant value above a limonene vapor activity concentration of a = 0.4. A plot of log D vs. vapor activity is shown in Figure 9 for better illustration.

The Effect of Binary Mixtures (Ethyl Acetate/Limonene) Composition on Co-Penetrant Permeability

Results of permeation studies for a series of binary mixtures are presented in Tables 3 and 4, respectively. Permeability values for the pure penetrants are also listed for comparison. With the lowest combination of vapor activities, (ethyl acetate a = 0.10 and limonene a = 0.18) limonene vapor had a marked effect on the transport properties of the ethyl acetate. A five fold (500%) increase in the permeability coefficient of ethyl acetate was obtained, when compared to ethyl acetate vapor permeability alone, at similar test conditions. Figure 10 graphically presents this data, where the transmission curves for ethyl acetate in the binary mixture, and for ethyl acetate vapor alone are shown. The transmission rate profile curve for limonene vapor in the binary mixutre is superimposed in Figure 10 to provide a complete description of the transmission characteristics of the mixed vapor system. At this concentration level, however, ethyl acetate did not appear to influence the permeation of the limonene vapor, with $P = 0.1 \times 10^8$ (kg m/m^2 s Pa) for limonene vapor (a = 0.18) in the binary mixture, and $P = 0.1 \times 10^8$ for limonene vapor (a = 0.21) alone. These results are

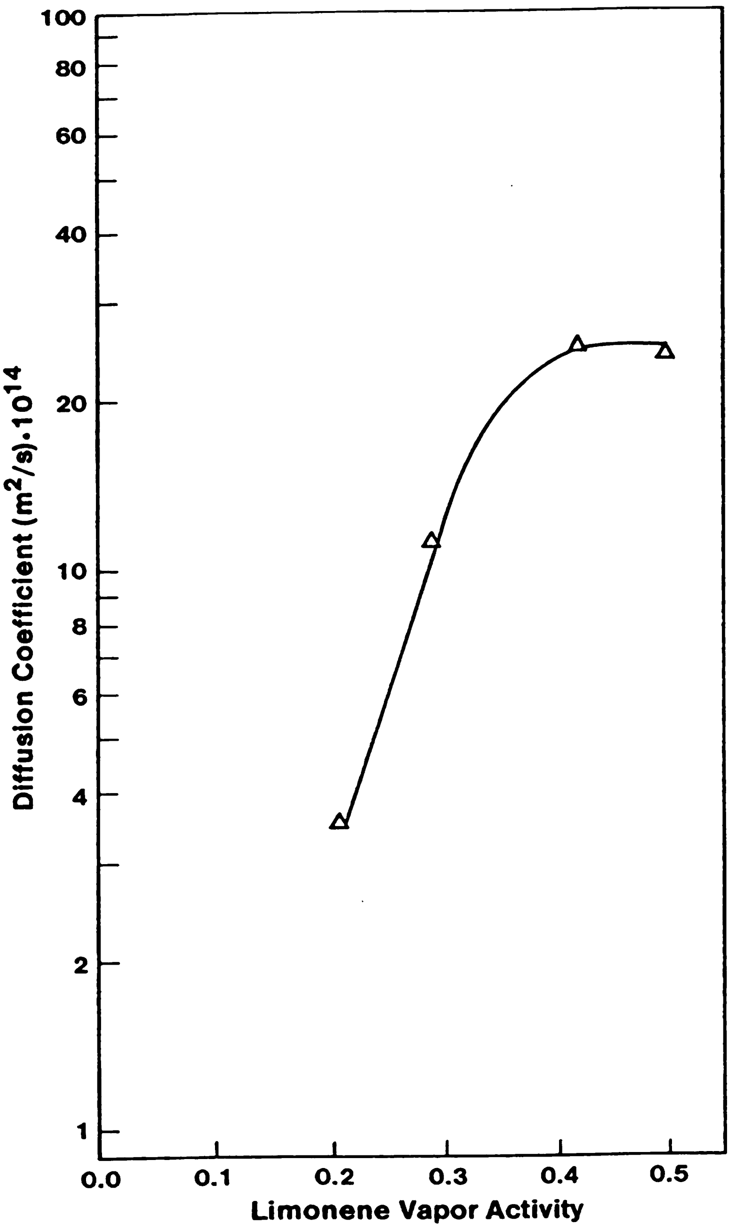

Figure 9. The effect of permeant vapor concentration on log D for limonene

Table 3

The Effect of Limonene Vapor on the Permeability of Ethyl Acetate in Binary Mixtures

Ethyl Acetate Vapor Activity	Pure Ethyl Acetate Permeability Constant (a)(b) x 10^8	Binary Mixtures	
		Limonene Activity	Ethyl Acetate Permeability Constant (a)(b) x 10^9
0.05	4.2	-	-
0.12	5.0	-	-
0.10	-	0.18	2.9
0.10	-	0.29	19.0
0.10	-	0.41	40.1
0.18	5.8	-	-
0.30	9.0	-	-
0.29	-	0.19	3.3
0.29	-	0.29	25.4
0.27	-	0.38	49.5
0.48	29.1	-	-
0.48	-	0.18	14.8
0.50	-	0.29	22.0
0.50	-	0.38	67.9

(a) Permeability Coefficient values expressed as kg m/m^2 s Pa.

(b) Average of replicate runs,. with a confidence limitof 10% (maximum).

Table 4

The Effect of Ethyl Acetate on the Permeability of Limonene in Binary Mixtures

Limonene Vapor Activity	Pure Limonene Vapor Permeability Constant (a)(b) x 10^8	Binary Mixtures Ethyl Acetate Vapor Activity	Binary Mixtures Limonene Permeability Constant (a)(b) x 10^8
0.21	0.1	-	-
0.18	-	0.10	0.1
0.19	-	0.29	0.1
0.18	-	0.48	1.4
0.29	1.4	-	-
0.29	-	0.1	0.9
0.29	-	0.29	1.0
0.29	-	0.50	1.2
0.42	1.8	-	-
0.41	-	0.10	1.2
0.38	-	0.27	1.3
0.38	-	0.50	1.6
0.50	1.9	-	-

(a) Permeability coefficient values expressed as Kg m/m^2 s Pa.

(b) Average of replicate runs, with a confidence limit of 10% (maximum).

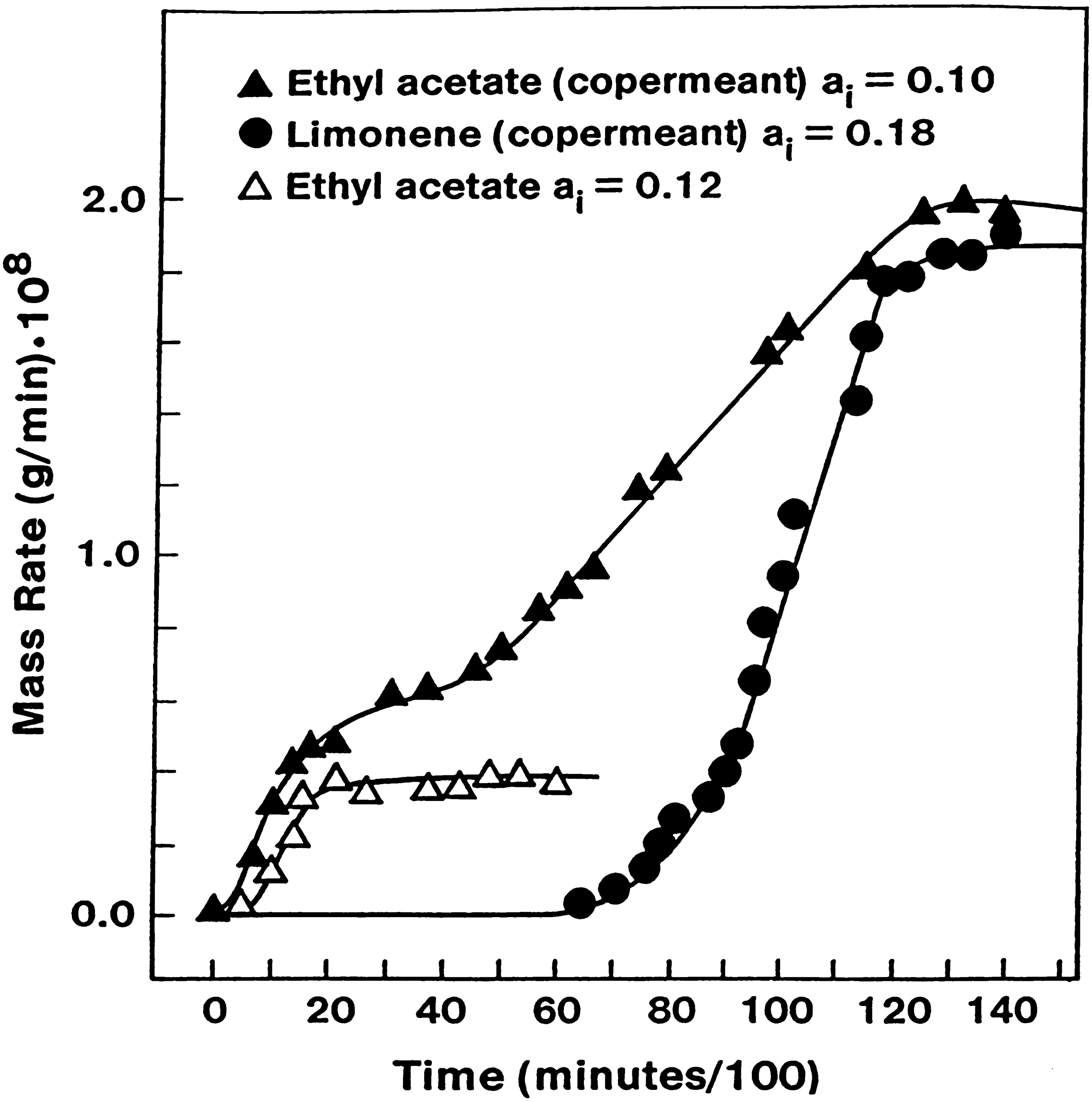

Figure 10. Comparison of the transmission profile of the binary mixture, ethyl acetate a=0.1/limonene a=0.18, with the transmission profile ethyl acetate (a=0.12)

shown in Figure 11.

Results of the ethyl acetate vapor (a = 0.29)/limonene vapor (a = 0.19) mixture were very similar to those obtained with the above mixture. At steady state, the permeability coefficient of ethyl acetate in the given binary mixture was approximately 3.7 times greater than the transmission rate of ethyl acetate alone, at an equivalent concentration. Figure 12 illustrates the effect of limonene on the transport characteristics of ethyl acetate. The transmission curves for ethyl acetate in the binary mixture, and for ethyl acetate vapor alone are shown, with the transmission rate profile curve for limonene vapor in the binary mixture superimposed. The permeability coefficient of limonene again was not influenced by the co-permeant, with $P = 0.1 \times 10^8$ (kg m/m^2 s Pa) for limonene vapor (a = 0.19) in the mixture, and $P = 0.1 \times 10^8$ (kg m/m^2 s Pa) for limonene vapor (a = 0.21) alone.

Similar results were obtained from the ethyl acetate vapor (a = 0.10)/limonene vapor (a = 0.29) mixture, where the ethyl acetate permeation rate is 40 times greater than the transmission rate of pure ethyl acetate vapor of an equivalent concentration, (see Table 3). This is illustrated graphically in Figure 13, where the transmission profile plot of the binary mixture is presented, and compared to the transmission rate profile curve for pure ethyl acetate vapor. At this ethyl acetate concentration level, the permeability coefficient of limonene in the binary mixture was slightly

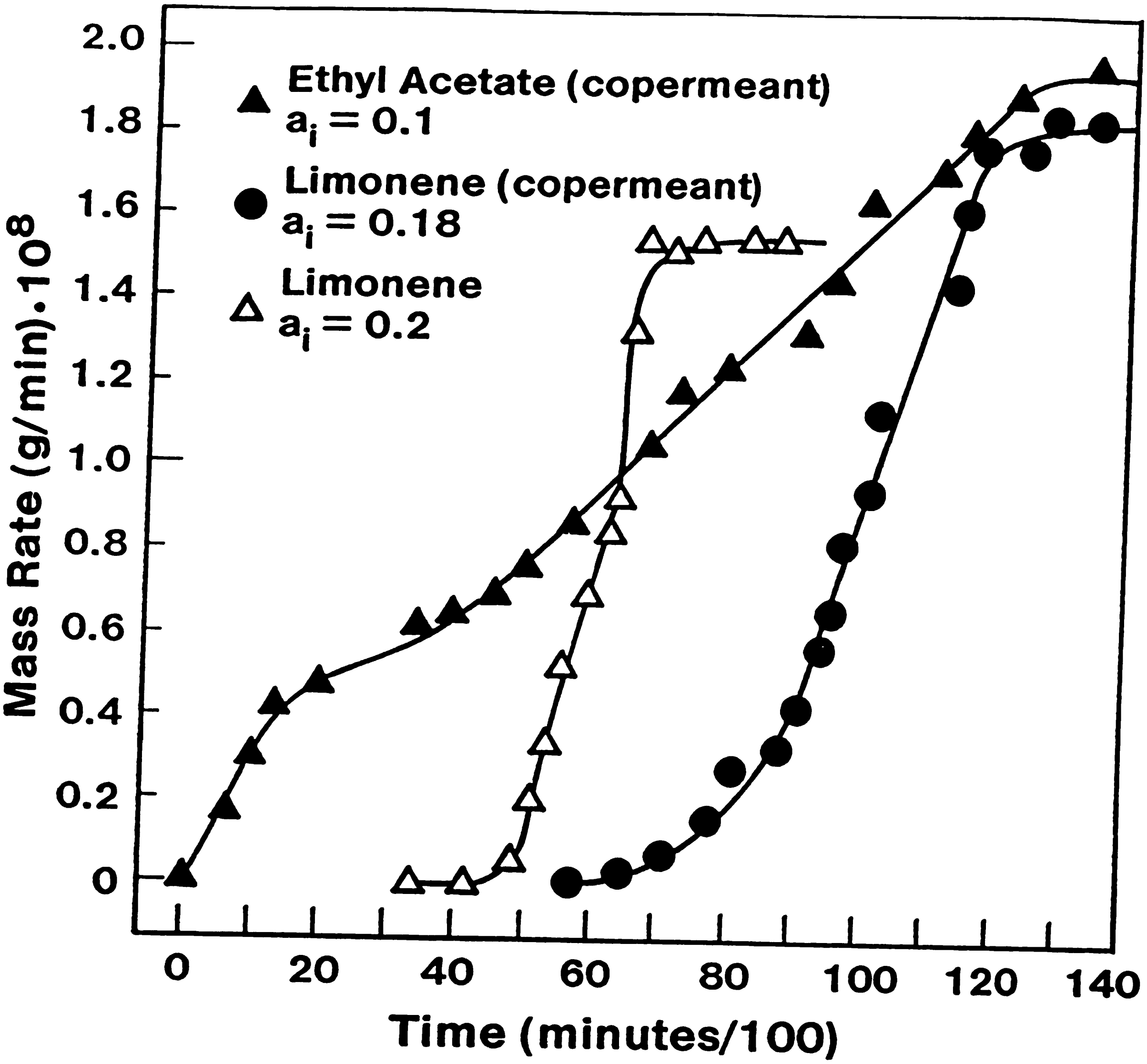

Figure 11. Comparison of the transmission profile of the binary mixture, ethyl acetate a=0.1/limonene a=0.18, with the transmission profile limonene (a=0.21)

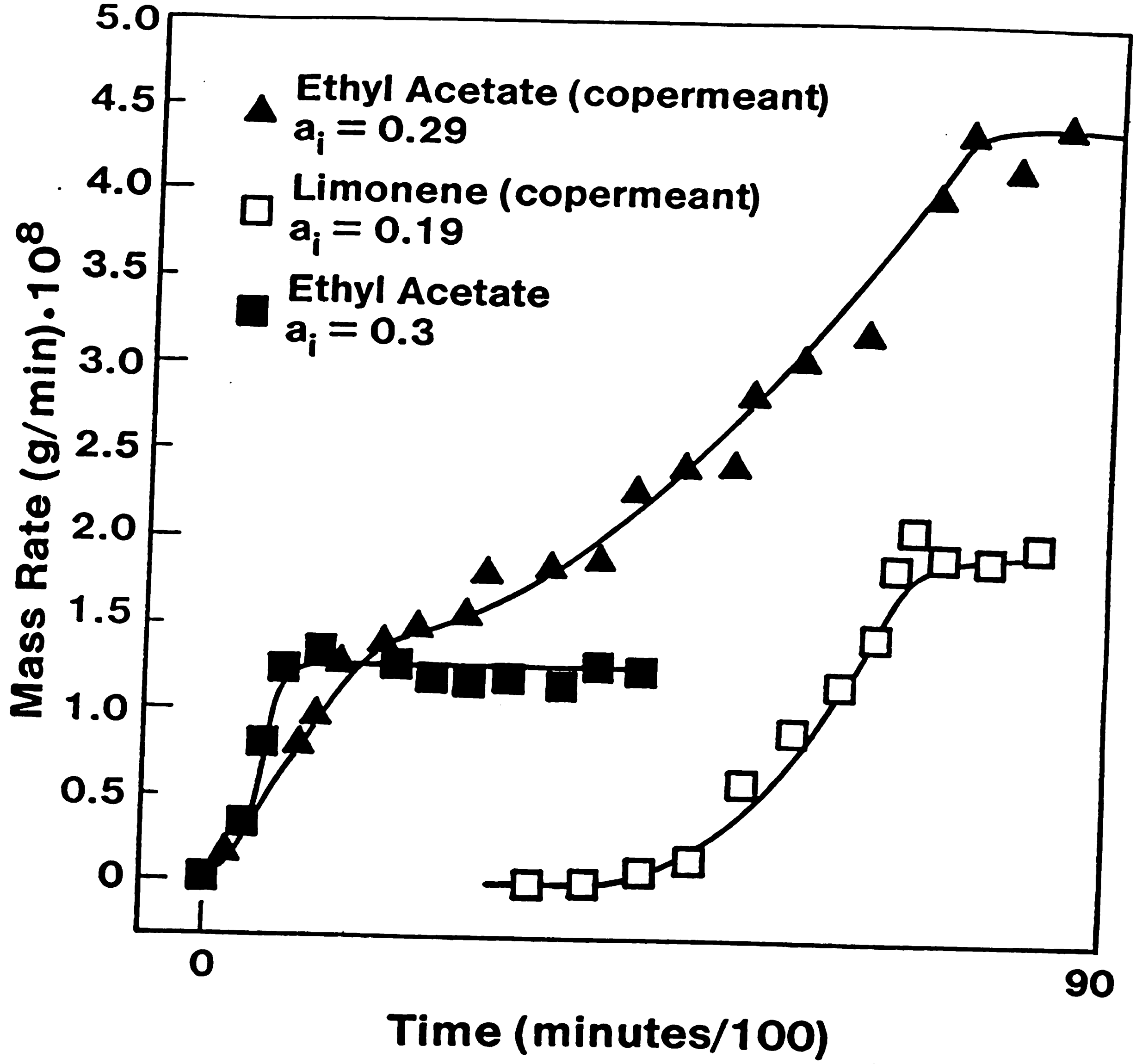

Figure 12. Comparison of the transmission profile of the binary mixture, ethyl acetate a=0.29/limonene a=0.19, with the transmission profile ethyl acetate (a=0.30)

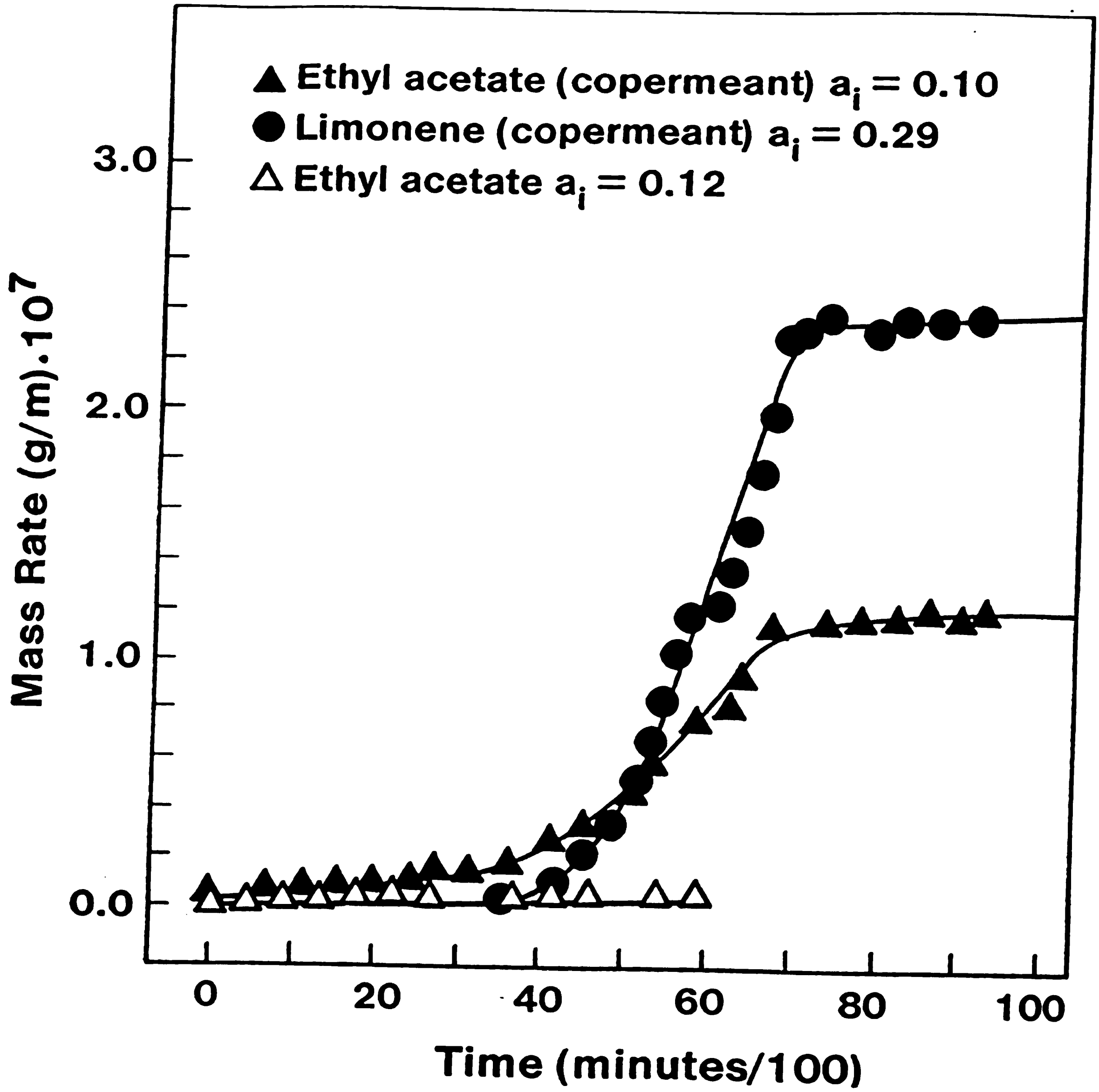

Figure 13. Comparison of the transmission profile of the binary mixture, ethyl acetate a=0.1/limonene a=0.29, with the transmission profile ethyl acetate (a=0.12)

lower than for pure limonene vapor, at an equivalent concentration, with $P = 1.4 \times 10^8$ (kg m/m^2 s Pa) for limonene vapor ($a = 0.29$) alone, and $P = 0.9 \times 10^8$ (kg m/m^2 s Pa) for limonene vapor ($a = 0.29$) in the binary mixture. Similar results were obtained for the ethyl acetate/limonene binary mixtures of the following concentrations: (i) ethyl acetate vapor ($a = 0.3$)/limonene vapor ($a = 0.3$), (ii) ethyl acetate vapor ($a = 0.1$)/limonene vapor ($a = 0.4$), and (iii) ethyl acetate vapor ($a = 0.3$)/limonene vapor ($a = 0.4$), where a decrease of 28 to 36% in the permeability coefficient of limonene was observed (see Table 4).

While statistical analysis showed a significant difference, at a confidence level of 95%, between the permeability of pure limonene and for limonene in the binary mixtures described above (see Appendix C), the effect of the co-permeant (i.e. ethyl acetate) was minimal when compared to the synergistic effect which limonene vapor was found to have on ethyl acetate permeability.

For studies carried out with a mixture of a higher ethyl acetate vapor activity ($a = 0.48$), and a limonene vapor activity of $a = 0.18$, results showed the individual components of the mixture to have a significant effect on the permeation rates of the respective co-penetrant. As shown in Tables 3 and 4, the permeability of both ethyl acetate and limonene through the oriented polypropylene film increased by an order of magnitude when compared to the permeability of the individual components of the mixture, at equivalent concentration levels. Although the effect was only observed at the higher activity levels, ethyl acetate as a co-permeant was still found to act in a synergistic manner. Typical results are presented in Figure 14 where the transmission profile plot of the binary mixture is shown, and compared to the transmission rate profile curve for ethyl acetate vapor alone, and in Figure 15 where the transmission profile plot of the binary mixture is presented, and compared to the transmission rate profile for pure limonene vapor, at an equivalent concentration.

The effect of limonene on the permeability of ethyl acetate through the biaxially oriented film is illustrated in Figure 16, where the permeability coefficients of ethyl acetate are plotted as a function of limonene (co-permeant) activity, for ethyl acetate activity levels of a = 0.12, 0.3, and 0.48, respectively. Figure 17 illustrates the effect of ethyl acetate on limonene permeability values, where the limonene permeability coefficients are plotted as a function of ethyl acetate activity, for limonene activity levels of a = 0.2, 0.3, and 0.4, respectively. As shown, for mixtures with the highest ethyl acetate activity level (a = 0.48), the limonene permeability values are very similar, irrespective of limonene vapor activity. It should be noted that for each binary mixture investigated, the collective permeation rate for the mixture was significantly higher than the transmission

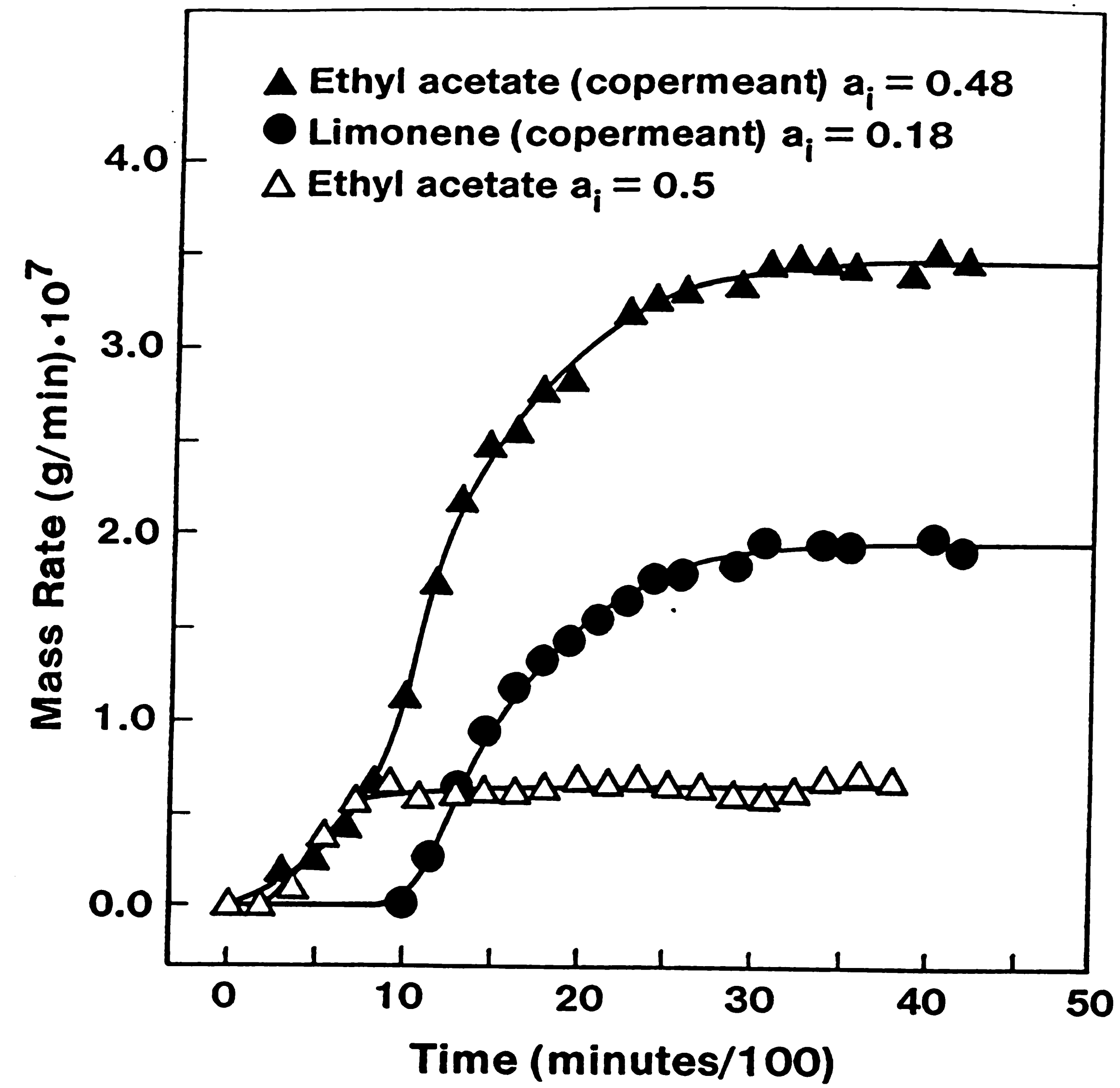

Figure 14. Comparison of the transmission profile of the binary mixture, ethyl acetate a=0.48/limonene a=0.18, with the transmission profile ethyl acetate (a=0.5)

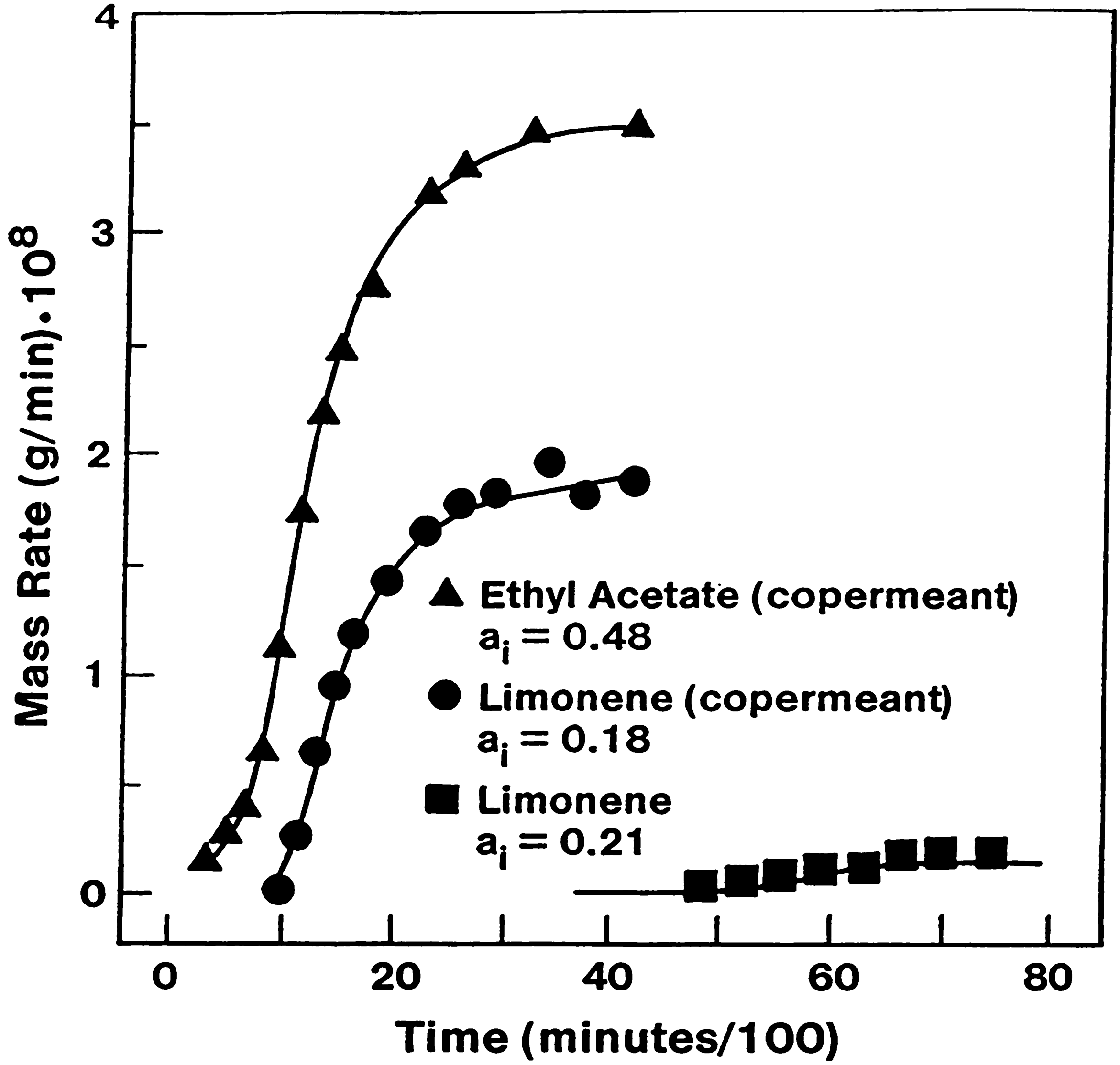

Figure 15. Comparison of the transmission profile of the binary mixture, ethyl acetate a=0.48/limonene a=0.18, with the transmission profile limonene (a=0.21)

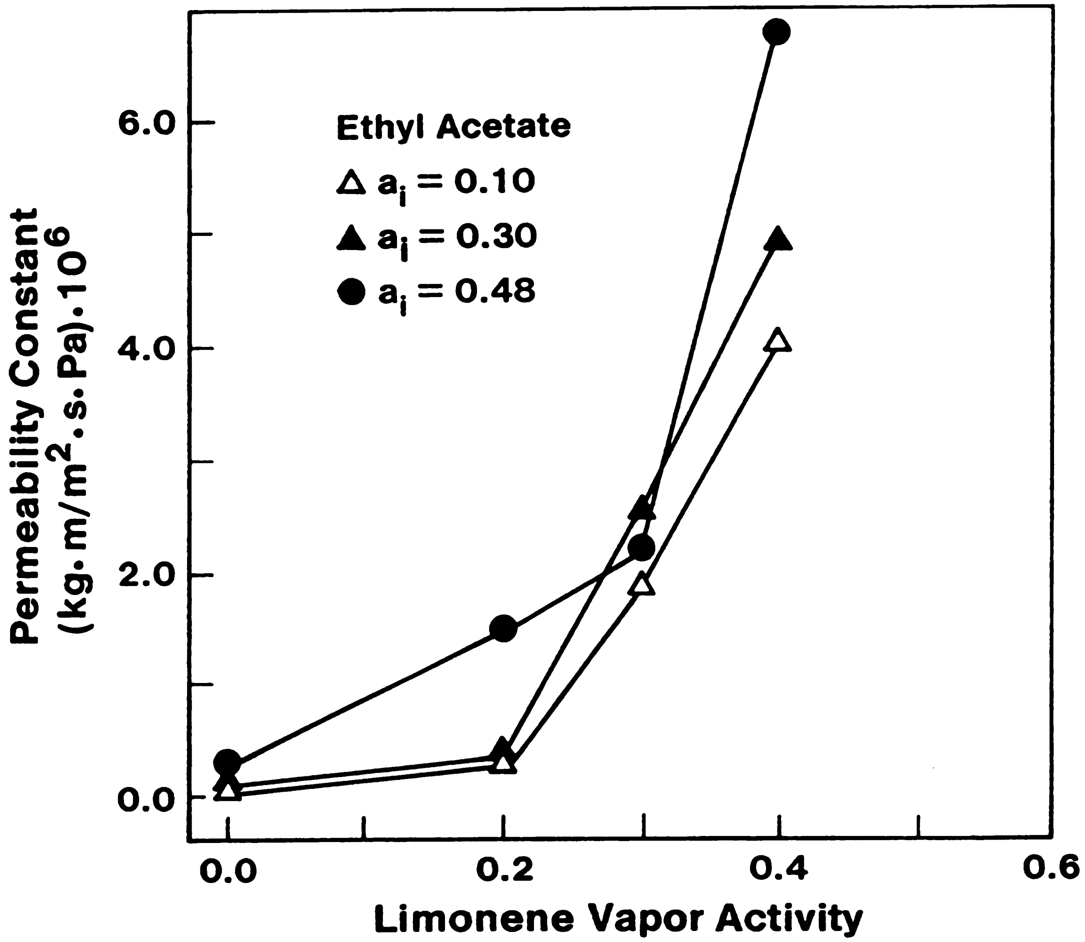

Figure 16. The effect of limonene vapor (co-permeant) on ethyl acetate permeability at ethyl acetate a = 0.1, 0.3, and 0.48

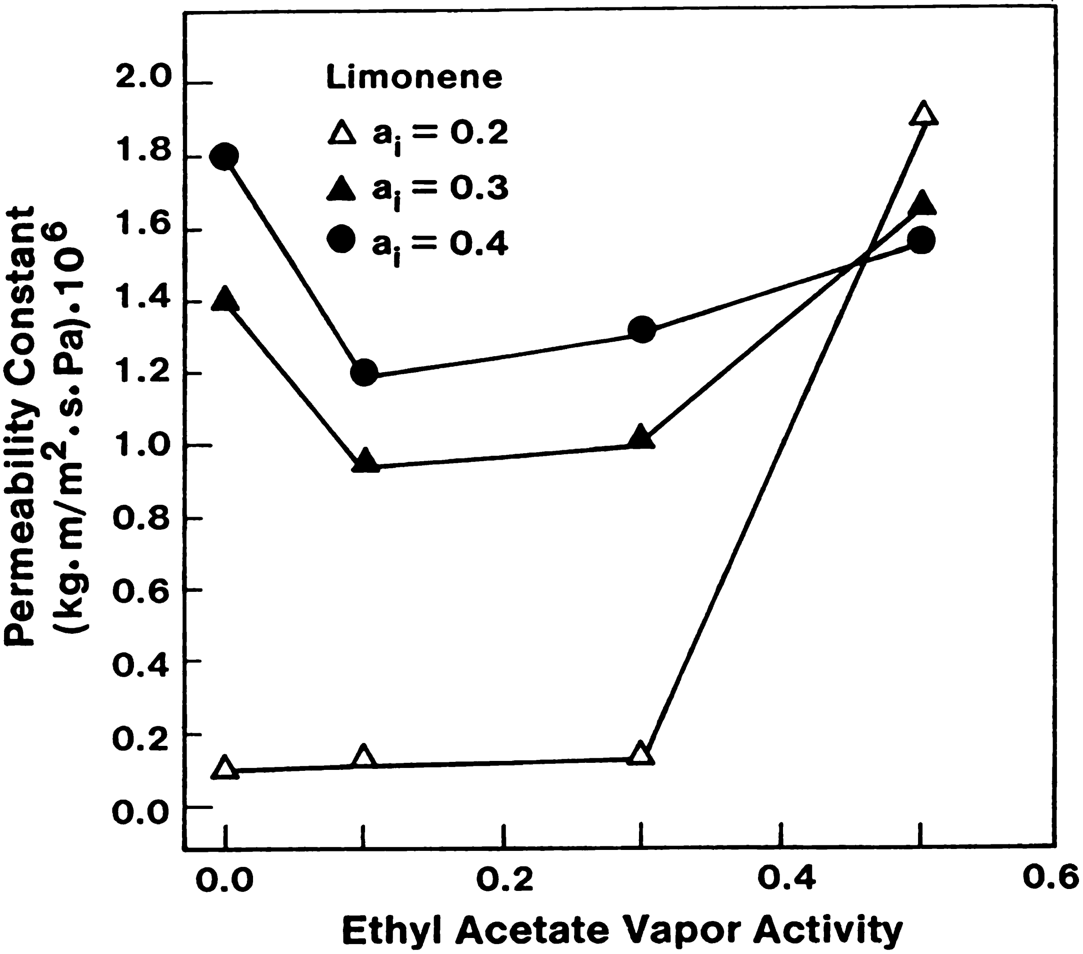

Figure 17. The effect of ethyl acetate vapor (co-permeant) on limonene permeability at limonene a = 0.2, 0.3, and 0.4

rates for the pure components of the mixture.

This study was designed to determine the effect of varying concentrations of organic vapors alone, and in binary mixtures on the barrier properties of an oriented polypropylene film. The results presented indicate that ethyl acetate and limonene vapor both show concentration dependency for the mass transport parameters P and D, within a selected activity range. When combined in a binary mixture, the constituents were also shown to be capable of altering the transport properties of the co-penetrant. This capacity of altering the transport properties of the co-penetrant can be attributed to the fact that in addition to the plasticization of the polymer by the sorbed penetrant, there may be changes in the polymer morphology due to swelling and distortion incurred during sorption, as well as actual chemical attack on the polymer (Rogers, 1964). With respect to chemical attack, the solvent (in this case, the organic vapors) may disrupt 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; Gedraitte et al., 1989). It has also been shown by Rogers (1964), that in most polymer-penetrant systems, the permeability generally increases with chemical similarities between the components. The permeation rate through non polar polyolefins, such as polyethylene, is lowest for strongly polar penetrant molecules, and highest with volatile organic molecules in the following order of increasing permeability: alcohols, acids, nitro-derivatives, aldehydes and ketones, esters, and ethers (Rogers, 1964). This phenomenon was observed with the penetrant/polymer system studied. The more polar penetrant, ethyl acetate, had lower permeation rates through the non-polar polypropylene than the more hydrophilic limonene.

The solubility parameters of the polymer and penetrants should also provide insight with respect to penetrant solubility. By comparing permeability and diffusivity data it appears that the solubility coefficient of limonene is much higher (10-100 times) than that of ethyl acetate, which is supported by the numerical values of the solubility parameters of the components of the system; polypropylene = 8.1 $(cal/cm^3)^{1/2}$, ethyl acetate = 9.1 $(cal/cm^3)^{1/2}$, and limonene = 7.8 $(cal/cm^3)^{1/2}$). The difference between the solubility parameter values of limonene and polypropylene is less than 0.5, while the difference between ethyl acetate and polypropylene is 1.0. Accordingly, from solubility theory it is expected that the value of solubility for limonene in polypropylene should be higher than for ethyl acetate. This may explain the fact that only at the highest ethyl acetate vapor activities studied is the permeability of limonene affected. The proposed penetrant induced swelling of the polymer matrix by sorbed ethyl acetate at the higher concentration levels ($a > 0.3$) results in alteration of polymer chain conformational mobility, which can account in part for this finding. This should be of major consideration, since other types of interactions, such as hydrogen bonding, are not expected.

The free volume theory has been proposed to explain the concentration dependency of the permeability of organic penetrants. It has been shown by Meares (1958) and by Fujita et al., (1960) that the free-volume approach provides a fairly reasonable explanation of the principal features of the concentration and temperature dependence of the diffusion coefficient (D), characteristic of organic vapors in (amorphous) polymers above Tg. The basic hypothesis of these investigators is that the mobilities of both the polymer segments and the diffusant molecules in a polymer/penetrant mixture are primarily determined by the amount of free volume present in the system. According to the free volume theory, the observed concentration dependency of the diffusion coefficients for polymer/organic vapor systems can be attributed to the extreme sensitivity of the mobility of diffusant molecules and polymer chain segments to a slight change in the average free volume in the system.

The free volume theory could also be applied to the theory of competition for sorption centers or units of stable free volume present in the polymer, between components of the mixture. For example, in the binary mixtures where the limonene permeation values were found to decrease from those of the limonene alone, it can be proposed that both ethyl acetate and limonene compete for active sites within the polymer bulk phase, and there is a decrease in the number of active sites for limonene with an increase in the level of ethyl acetate sorbed. Pye (1976) proposed a similar interpretation, where the permeability of a membrane to component A may be reduced due to the sorption of a second component B in the polymer which "... effectively reduces the microvoid content of the film and the available diffusion paths for the non reactive gases." In the present study, the sorption of ethyl acetate by polypropylene reduced the permeability of the second component limonene, by as much as 36 % for the case of the binary mixture, ethyl acetate vapor activity $a_i = 0.10$/limonene vapor activity $a_i = 0.29$.

The observed concentration dependency of P for the respective penetrants is related to the interaction of the penetrant with the polymer phase, resulting in a gradual relaxation of the structure. This permits additional penetrant sorption, which results in a significant increase in the mobility of the penetrant within the polymer bulk phase, and a concomitant increase in penetrant diffusivity, and therefore permeability. 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). 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 accessibility to accommodate more penetrant molecules (Berens, 1978). The diffusion coefficient values may therefore also be related to the change in the free volume of the polymer matrix. 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.

For permeation of polymer films under a zero total pressure differential, the rate of attainment of a constant concentration of permeant in the upstream surface, and hence of a steady state permeation rate, will be controlled by the rate of stress relaxation in the lower regions of the film (Blackadder and Keniry, 1973). Reported studies on stress relaxation in polyethylene indicated that an imposed stress does not decay to zero in an experimentally accessible time (Blackadder and Keniry, 1973). Stresses induced in the downstream side of the membrane by solvent sorption at the upstream surface during the nonsteady state period have been shown to lead to underestimation of D (Blackadder and Keniry, 1973). Diffusion coefficient values calculated in the usual way from apparent steady-state permeation rates may also be grossly underestimated (Blackadder and Keniry 1973). This phenomenon could possibly be occurring in the polypropylene film studied, where visible distortion of the sample could be seen, as a result of the penetrant swelling the film to a greater degree at the upstream surface.

Statistical Interpretation

Statistical analysis, utilizing the Dunnett's t test, was performed to compare the permeability coefficient values of the pure penetrant with the penetrant in a binary mixture to determine if there were any interactions, and if so, which ones were significant, at a confidence level of 95%. In all cases, the addition of limonene to ethyl acetate resulted in increased ethyl acetate permeation values, and the resultant increase was significant with a confidence level of 95%, with the exception of the following two binary mixtures: (i) ethyl acetate vapor (a = 0.1)/limonene vapor (a = 0.2); and (ii) ethyl acetate vapor (a = 0.3)/limonene vapor (a = 0.2).

With respect to the effect of ethyl acetate vapor on the permeability of limonene, in only one case did the presence of ethyl acetate result in a statistically significant increase in limonene permeation value. This was observed with the ethyl acetate vapor (a = 0.48)/limonene vapor (a = 0.2) binary mixture. However, in four cases, the addition of ethyl acetate resulted in a significant decrease in the limonene permeation value. This occurred with the ethyl acetate vapor (a = 0.1)/limonene vapor (a = 0.3), ethyl acetate vapor (a = 0.3)/limonene vapor (a = 0.3), ethyl acetate vapor (a = 0.1)/limonene vapor (a = 0.4), ethyl acetate vapor (a = 0.3)/limonene vapor (a = 0.4) mixtures. Refer to Appendix C for further details of the statistical analysis utilized.

SUMMARY AND CONCLUSIONS

Independently, the organic vapors showed concentration dependency for both permeation and diffusion characteristics. This can be seen from the increase in the permeability and diffusion coefficient values with an increase in vapor activity, for both permeants. With the permeant ethyl acetate, the effect of vapor activity is minimal below a = 0.2, but at higher vapor activities (above a = 0.2), the permeability coefficient is markedly dependent upon penetrant concentration, with P increasing in an exponential manner with an increase in vapor activity. The diffusion coefficient values followed similar trends, with a minimal increase of the diffusion coefficient between the vapor activities a = 0.052 to 0.18, followed by a marked increase above an ethyl acetate vapor activity of a = 0.2. For the permeant limonene, however, significant concentration dependency was observed at the lower vapor activity levels studied. Permeability coefficient values obtained showed concentration dependency at vapor activities below a = 0.3, while above this level, an increase in concentration did not result in a significant increase in permeability coefficient values. The diffusion coefficient values obtained for limonene were also highly dependent upon vapor activities below a = 0.4, but approach a constant level above this vapor activity.

With the binary mixtures studied, the collective permeation rate for the mixture was significantly higher than the transmission rates for the pure components, for every mixture investigated. For the binary mixtures studied at the lower activity levels, the presence of limonene vapor resulted in a significant increase in the permeation rate of the co-permeant, ethyl acetate. However, only at the highest vapor activity (a = 0.48) did ethyl acetate significantly increase the transport properties of limonene, as compared to the permeability of pure limonene at similar activity levels.

PROPOSAL FOR FUTURE RESEARCH

A number of studies can be proposed for future investigation which could lead to an increased understanding of the mass transport properties of binary mixtures of organic vapors. For example, solubility values were not determined in the present study, and could only be estimated from the relationship $P = SD$. Sorption studies involving both varying concentrations of the individual penetrants, and binary mixture combinations could provide data leading to a better understanding of the concentration dependency of the mass transport process involving organic penetrants, and are proposed. Also, it is known that the flavor and aroma profile of products can contain numerous organic constituents. The present study considered two organic penetrants with one packaging system (i.e. polypropylene film), which is representative of only a small portion of the volatiles found in a product. A more detailed study involving the determination of the permeability of various organic constituents characteristic of a product system could be made, to determine which vapors have the greatest effect on the gain or loss of flavor or aroma moieties of the packaged product.

Differing binary mixtures of the more reactive constituents combined with lesser reactive constituents would lead to a more practical understanding of what the capabilities of different mixtures are in a given product. Further studies could also include various packaging systems.

APPENDIX

Appendix A

Gas Chromatograph Calibration Procedure

Equipment

- (6) 10 ml volumetric flasks with stoppers
- (2) 100 ml volumetric flasks with stoppers
- (4) 10 ml liquid sampling syringe
- (4) 10 ml pipets with automatic pipet fixtures

Materials

Limonene
Ethyl Acetate
Dichloromethane - solvent for Limonene
Dichlorobenzene - solvent for Ethyl Acetate

Concentrations of 10, 20, 40, and 100 ppm (wt/v) or (v/v) of permeant in solvent were utilized to create the calibration curves.

Procedure

In all cases, a standard curve of response vs. penetrant concentration was constructed from standard solutions of known concentration. Calibration solutions were prepared by dissolution of known quantities of ethyl acetate in dichlorobenzene and limonene in dichloromethane. The following procedure was followed:

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) to the 100 ml volumetric flask partially fill with solvent.
    b) add 10 μl of permeant.
    c) stopper and slightly swirl to mix.
    d) fill flask to volumetric line with solvent.
    e) mix flask's contents.

This provides the 100 ppm stock solution. From this solution, the other concentrations can be obtained. For example:

a) to a 10 ml volumetric flask partially fill with solvent, using a pipet.
b) swirl stock solution to ensure proper mixing.
c) add 1 ml of the stock solution to the 10 ml flask.

f) mix flask's contents.

This provides the 10 ppm concentration. The other concentrations are obtained similarly.

4. Set Gas Chromatograph Conditions:

Column: 10% Carbowax, 20 M on 80/100 Supelcoport
(Supelco, Inc., Bellefonte, PA)
1/8" o.d. x 6 ft. SS column

Analysis Conditions:

He carrier gas	33 ml/min
col. temp.	165°C
FID temp.	350°C
Injection Port	175°C
Oven Max	225°C

5. A 1 ml sample was injected directly into the gas chromatograph and the area response recorded.

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.

Appendix B

Saturated Vapor Concentration Versus Temperature

Vapor activity was calculated by dividing the experimentally determined vapor pressure (p_i) by the saturated vapor pressure (p_o).

Procedure

To determine the saturated vapor concentration at different temperatures, add 2 ml of liquid permeant to three vials (10 ml) and seal with septum and aluminum crimp caps. Allow to equilibrate at 2°C (refrigerator), 22°C (room temperature) and 40°C (oven). Inject 1 μl of one vial head space into GC to obtain area response. Do ten repetitions of each vial, making sure to allow equilibrium at each temperature before the next injection. The area response can be converted to concentration by the following equation: (area resp.)(calibration factor)(1/qty injection) = concentration.

The saturation vapor concentration was then converted to its corresponding saturation vapor pressure using the ideal gas law:

$$PV = nRT$$

By knowing the saturation vapor, settings for the vapor activities of 0.1, 0.2, 0.3, 0.4, and 0.5 were determined on the rotameters, regulated by Nupro "M" series needle valves solving for p in the vapor activity equation:

$$a = p/p_0$$

The following vapor activities were studied:

<u>Individual Penetrants:</u>

ethyl acetate a = 0.05, 0.1, 0.2, 0.3, 0.5

limonene a = 0.1, 0.2, 0.3, 0.4

<u>Binary Mixtures:</u>

The penetrants were combined in nine variations with the following combinations:

limonene		ethyl acetate	
	0.1	0.3	0.5
0.2			
0.3			
0.4			

A plot of concentration vs. temperature results in a linear relationship (refer to attached Figures). These values correlate quite well with interpolation from values published in Perry's Handbook as shown:

Source	Penetrant	Vapor Pressure (mmHg)
Perry	Ethyl Acetate	.1092
Hensley	Ethyl Acetate	.1100
Perry	Limonene	2.60
Hensley	Limonene	2.10

Appendix C

Statistical Analysis

Statistical analysis was performed based on the Dunnett's t test utilizing the following equation:

$$t_D=\frac{y_1-y_0}{\sqrt{meansquare}}$$

where:

y_i = average P value from a given a_i in the mixture
y_0 = average P value from the corresponding a_i alone

The mean square was determined from a one way analysis of variance (ANOVA) performed on the MSTAT statistical program.

The Dunnett's t test will tell if there is a significant difference in P from that obtained from the penetrant alone to that obtained from the same vapor activity in different mixtures. Refer to the following Table for the ANOVA values used for the analysis.

Table 5

ANOVA for Pure Ethyl Acetate Permeability Values vs. Ethyl Acetate Permeability Values in Binary Mixtures with Limonene

	Sum of Squares	d.f.	Mean Square	f-test
Between	97.991	15	6.53	2.37
Within	1.909	16	0.119	

Comparison Mean Difference

Pure Ethyl Acetate Vapor Activity	Comparable Ethyl Acetate Activity with This Limonene v.a.	t_D	F-test
0.12	0.18	0.61	
0.12	0.29	4.65	*
0.12	0.41	9.90	*
0.30	0.19	0.65	
0.30	0.29	6.14	*
0.30	0.38	12.23	*
0.48	0.18	3.20	*
0.48	0.29	4.65	*
0.48	0.38	16.39	*

* Significant at 95%

Table 6

ANOVA for Pure Limonene Permeability Values vs. Limonene Permeability Values in Binary Mixtures with Ethyl Acetate

	Sum of Squares	d.f.	Mean Square	f-test
Between	24.502	15	1.633	2.37
Within	0.531	16	0.033	

Comparison Mean Difference

Pure Limonene Vapor Activity	Comparable Limonene Activity with This Ethyl Acetate v.a.	t_D	F-test
0.21	0.10	0.14	
0.21	0.29	0.25	
0.21	0.48	9.45	*
0.29	0.10	3.57	*
0.29	0.29	3.02	*
0.29	0.50	1.37	
0.42	0.10	4.12	*
0.42	0.27	3.30	*
0.42	0.50	1.37	

* Significant at 95%

Appendix D

Model for the continuous-flow calculation of D

The permeation flux F through the membrane of thickness l is given by:

$$F(x) = -D \frac{\partial c}{\partial x}$$

where c is the concentration of the permeant in the membrane at a position x. In order to solve approximately our system, it is assumed that the diffusion coefficient is not a function of concentration, that the surface concentration is proportional to the pressure of the permeant, and that swelling of the membrane is negligible. According to the geometry of the system only flux is of interest. The concentration of the permeant was kept constant during the permeation process.

The following boundary conditions complete the description of the system:

$c = c_0$ at $x = 0$ $t = 0$
$c = c_1 = 0$ at $x = l$ $t > 0$
$c = c_2\ 1-x/l$ at $0<x<l$ $t = \infty$

where c_0 is the concentration at $l = x$ in equilibrium with the permeant flow. These boundary conditions represent the change from one steady-state, $t = 0$ and $c_1 = 0$, to the final c_2 at $t = \infty$, with the pressure of permeant on the downstream side of the membrane always kept at zero, since pure nitrogen is continuously flowed.

Solution for the given equations is already given in the literature, Pasternak et al (1970):

$$F = \frac{Dc_1}{l} + \frac{D(c_2-c_1)}{l} \quad \frac{4}{\sqrt{\pi}}^{1/2} \infty\Sigma n \exp \frac{-n^2\ l^2}{4Dt}$$

Since the second term contributes less than 2% to the sum, it is reasonable to retain only the first term. This condition is satisfied for $\Delta F/\Delta F\infty < 0.97$ where ΔF represents the change in flux at time t and $\Delta F\infty$ at $t = \infty$.

The first order approximation of the previous equation is:

$$\frac{\Delta F}{\Delta F\infty} = \frac{4}{\sqrt{\pi}} \quad \frac{l^2}{4Dt}^{1/2} \exp \frac{-l^2}{4Dt}$$

that can be written in the following form:

$$\frac{\delta F}{\delta F\infty} = \frac{4}{\sqrt{\pi}}\ x^{1/2} \exp(-x)$$

where $x = l^2/4Dt$

For each value of $\Delta F/\Delta F\infty$ an x can be calculated, and plotting x^{-2} versus t a straight line is obtained. The slope of this line equals $4D/l^2$.

To solve the previous equation for each value of $\Delta F/\Delta\infty$ a Newton-Rawson method was employed:

If
$G = x^{1/2}\ e^{-x} - A$
where $A = \sqrt{\pi}/4\ \Delta F/\Delta F\infty$

$$x^{k+1} = x^k - \frac{x^{k1/2}\ e^{-x^k} - A}{\exp{-x^k}\ 1/2x^{k^{\frac{1}{2}}} - x^{k1/2}}$$

where $x^{(k+1)}$ is the k+1 interaction for x value.

From the graph of x vs. t, determination of slope can be made, which can be used in the following equation to determine D:

$$D - \frac{slope\ x\ l^2}{4\ x\ 3600}$$

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