THE "LAMINATE FILM" METHOD FOR MEASURING THE
PERMEATION OF VOLATILE ORGANIC COMPOUNDS
THROUGH POLYMER FILMS

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ABSTRACT

The use of barrier polymers for packaging foods has created a need to test the transmission of organic penetrants, such as flavour and aroma compounds, that can be lost from the food to the polymer. Many studies have been carried out on organic penetrants but due to the large number of possible penetrant-polymer combinations and the interactions between these plus the factors that can affect these interactions, there are many conflicting results. In addition, the tests were generally carried out at high penetrant concentrations and the results were not applicable to the low concentrations found in food packages. Traditional methods for measuring permeation of organic compounds are slow and capital intensive, with no standard test method or test conditions existing. A simple, inexpensive method, known as the "laminate film" method was developed by Holland and Santangelo in 1988 in which the transmission of a penetrant is measured by the change in absorbance in a polymer film.

This "laminate film" method was used to measure the sorption of d-limonene and vanillin by low density polyethylene, nylon 6 and polyvinylidene chloride coated nylon 6 at 10, 25, and 40°C and in ethylene-vinyl alcohol films at 25°C and 90% relative humidity. Different thicknesses of the polymers were also tested. The sorption of d-limonene and vanillin was studied over long periods of time up to 8000 hours.

The amounts of vanillin sorbed and the rate of uptake of vanillin were lowest in low density polyethylene and polyvinylidene chloride coated nylon 6. Nylon 6 and moist ethylene-vinyl alcohol films rapidly picked up large amounts of vanillin. Increasing the temperature increased the rate and amount of vanillin sorbed.

Both orientation of the film and increasing the proportion of ethylene in the ethylene-vinyl alcohol films decreased the amount of vanillin sorbed, but increasing the relative humidity increased it.

Increasing the thickness of the films increased the amount of vanillin sorbed but did not affect the rate or method of uptake. Therefore, more layers can be used to

accurately estimate small diffusion coefficients without affecting the permeation of the penetrant.

The results became less reproducible with time due to effects such as oxidation of the penetrant, degradation of the polymer film and concentration effects.

Diffusion, partition (or solubility) and permeation coefficients were calculated for all films with vanillin. For low density polyethylene, these were of the order of $10^{-9}cm^2/s$, 10^{-3}, $10^{-12}cm^2/s$ respectively. For nylon 6, they were $10^{-12}cm^2/s$, 10^{-2}, $10^{-13}cm^2/s$; polyvinylidene chloride coated nylon 6 $10^{-14}cm^2/s$, 10^{-2}, $10^{-15}cm^2/s$ and ethylene-vinyl alcohol films $10^{-13}cm^2/s$, 10^{-2}, $10^{-13}cm^2/s$. The units used for the coefficients allow for the direct comparison of results for other penetrants as no conversion is necessary when comparing solid, liquid or gaseous penetrants.

D-Limonene was not an appropriate compound to be used with this method as it had a low extinction coefficient and the absorbance was not easily measured.

From this study, there are certain requirements that need to be met ,if this method is to be used as a standard test method. The compound to be tested needs a large extinction coefficient so that sorption of the penetrant can be accurately measured, and the polymer must be transparent. Temperature and relative humidity, (if the film is moisture sensitive), must be controlled as these factors can have dramatic effects on the permeation.

The "laminate film" method would be useful in industry, where a simple and inexpensive method is needed to measure transmission of flavours and aromas in polymer films in order to enable the best barrier film for a packaging application to be chosen.

<u>ACKNOWLEDGEMENTS</u>

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1.0 INTRODUCTION

The recent growth in the use of barrier polymers for packaging foods that were previously packaged in glass or metal containers has created a need to develop a better understanding of the transport of gases and low molecular weight compounds into and through polymer films. Barrier polymers are those materials that show a high resistance to the permeation of liquids or vapours through the polymer matrix.

Polymers are less inert than glass or metal and can interact with foods to alter their flavour or aroma in a number of ways. The three important methods of interaction are migration of compounds from the polymer to the food, and sorption and permeation of food components into and through the polymer. Components of the polymer, such as processing additives, may migrate into the food to cause off flavours and odours.

The mechanism of transmission of vapours through polymeric films is either by leakage or permeation. Leakage occurs if there is a discontinuity such as a pinhole, crack or faulty seam in the material. Permeation involves mass transfer across the film and this occurs in three steps (Gilbert et al., 1983). A penetrant molecule must first collide with the surface of the film and dissolve into it. The molecule must then diffuse through voids in the polymer network. Finally, the penetrant molecule must come out of solution and evaporate into the atmosphere on the opposite side of the film. Sorption involves the first two steps of this process, whereas permeation consists of all three (Gilbert et al., 1983; Anon., 1987).

The polymer may absorb or adsorb compounds thereby reducing the total volatile content of the food. Absorption involves matrix dissolution. It refers to the case of penetration by the molecules into the bulk structure of the polymer such that a mixture similar to that of a true solution is created. Adsorption refers to surface attraction and applies to cases where the molecules remain on the surface of the polymer. The packaging may also selectively absorb key compounds which contribute to the aroma of the food, and thus alter the characteristic odour of the food. As well, the package surface can act as a catalyst or co-reactant to chemically

change a component of the food.

Foreign odours from the environment may pass through the package wall to the food. Alternatively, flavour compounds may be lost by permeation through the plastic to the environment. Figure 1.1 shows some possible interactions between the polymer, the product and the environment.

<u>Figure 1.1 Possible Interactions Between the Polymer, the Product and the Environment</u>

FOOD	$<$------------------ ------------------$>$	POLYMER	$<$------------ ------------$>$	ENVIRONMENT
<u>FOOD CHANGE</u>				<u>FOOD CHANGE</u>
Discolouration, Nutrient Degradation	$<$-----	Light Penetration		
Flavour, Toxicity	Additives, Monomer $<$-----	Polymer Migration		
Oxidation	O_2 $<$-----	Gas Permeation	CO_2 -----$>$	Carbonation loss
Texture change, Microorganisms	H_2O $<$-----	Water Permeation	H_2O ----$>$	Drying
Undesirable Odours	Volatiles $<$-----	Odour Permeation	Volatiles ----$>$	Loss of Intensity
Loss of Intensity	Volatiles ----$>$	Aroma Sorption		

When dealing with the loss of compounds from food, the important mechanisms of interaction are both sorption and permeation as losses occur to both the polymer and the environment.

The transport of penetrants such as oxygen, carbon dioxide and water vapour through polymer structures has been the subject of numerous investigations and standard test methods are available for these penetrants. However, while the transport of organic penetrants through polymeric materials has been the subject of several studies, there is a lack of data available in this area. Permeation is more complex for organic compounds in contact with polymers because:

- the materials concerned are not simple gases;

- polymers are complex structures which are not homogeneous, particularly multilayer structures;

- major chemical and physical affinities exist of which the most important is tendency to solution (Briston and Katan, 1974b).

The organic penetrant/polymer interactions and the ways in which various factors affect these interactions is not fully understood. There are complications due to the large number of flavour compounds and the wide variety of available polymeric films. A vast number of combinations need to be investigated before these interactions are completely understood.

In the studies of organic penetrants, there are many conflicting observations and many different test methods, which makes comparison of the results difficult. In addition, a large proportion of the published work has involved the use of saturated vapours and it is generally not valid to use this data to estimate the permeation rates at the lower levels encountered in typical retailing situations. No standard methods for the measurement of odour permeation exist. Many of the test methods currently used are only suitable for use with high concentrations of vapours.

The need is therefore for a test method that can be used at the low concentrations found in food packages. Baner et al., 1986; Landois-Garza et al., 1988; Mohney et al., 1988 and Zobel, 1982, 1985; have carried out studies at low concentrations. Their work has found that permeation behaviour can be accurately predicted from theory at these levels.

Traditional methods for measuring the interaction of organic compounds with polymers could be time consuming and capital intensive. A novel, simple and

inexpensive method was developed by Holland and Santangelo, 1988; and is known as the "laminate film" method. The important difference is that a concentration gradient not a pressure gradient drives the penetrant through the film. In this method, the usual gas or liquid supply and collector systems are replaced by completely solid state systems. The procedure is quite general as it is independent of vapour pressure, and also applies to non-volatile diffusants. In food packages, flavour and aroma molecules are absorbed largely from the liquid or solid food rather than from the headspace so this method is more closely attuned to the practical situation.

This present research continues Holland's work. It also studies vanillin but includes another flavour compound, d-limonene. The polymers studied were low density polyethylene, nylon 6, polyvinylidene chloride coated nylon 6 and ethylene-vinyl alcohol copolymers. The polymers were chosen as typical examples of food packaging materials. D-Limonene and vanillin were used as examples of common food flavours. D-Limonene was also chosen as it has already been extensively studied using existing techniques. It is also an important flavour that is often lost to the packaging material.

The aim of this research was to determine if the "laminate film" method was a suitable method to use to test the permeation of flavour and aroma compounds and the applications and limitations of this method. This would be particularly useful in industry where a simple, cheap method is needed.

2.0 LITERATURE REVIEW

The general theory of permeability is discussed and the problems with using this theory to predict permeation of organic penetrants are outlined. Research on factors such as temperature, relative humidity, concentration of the penetrant and the nature of the polymer and the penetrant and their effects on diffusion, solubility and permeability coefficients are reviewed. Examples are given of experimental studies of polymer-penetrant interactions illustrating the many different observations that can be made depending on the relative influences of each of these factors.

The traditional methods of measuring the permeation of organic volatiles in polymer films are compared and the problems associated with these are discussed. Three methods of estimating permeability are also described. A new technique, the "laminate film" method, for measuring the permeation of volatile organic compounds is reviewed.

2.1 GENERAL TRANSMISSION OF VAPOURS THROUGH POLYMERIC FILMS

Briston and Katan, 1974b; DeLassus and Jenkins, 1986; DeLassus and Hilker, 1987; DeLassus, 1987; DeLassus et al., 1988a and Stepek et al., 1987; described the theory of permeability. Equations have been developed to describe the permeability of polymer films to gases and vapours. The basis of polymer permeation is a restatement of Fick's First Law of Diffusion (Briston and Katan, 1974b) :

$$\frac{1}{A}\frac{dM}{dt} = -D\frac{dc}{dx}$$

where   A = area of film

$\frac{dM}{dt}$ = transport rate of species M across the film in time dt

D = diffusion constant

$\frac{dc}{dx}$ = concentration gradient across thickness dx

For a film of thickness, x and a concentration gradient of (c_1-c_2):

$$\frac{dM}{dt} = \frac{D(c_1-c_2)A}{x}$$

where c_1, c_2 = concentration on either side of the film

However, for vapour diffusion through a film, vapour pressure is a more convenient parameter to measure than concentration. These parameters are related by Henry's Law:

$$c=Sp$$

where   S = solubility coefficient

p = partial pressure of penetrant

Therefore,

$$\frac{dM}{dt} = \frac{DS(p_1-p_2)A}{x} \qquad\qquad \text{Equation (2-1)}$$

This is an expanded version of Fick's Law. It allows analysis of the movement of molecules in polymers from knowledge of the gross geometry of the film, the allowable movement of molecules and the environmental conditions.

Equation (2-1) is sufficient for simple penetrant molecules such as oxygen and water vapour and also for more complicated penetrants provided the polymer film is thin and has a high permeability. It is not adequate for analysis of organic vapour permeation of barrier and rigid packaging. In these cases it is better to describe permeation in terms of its fundamental component parts, that is, diffusivity (D) and solubility (S) (DeLassus and Jenkins, 1986; DeLassus and Hilker, 1987; DeLassus, 1987).

$$P = DS$$
Equation (2-2)

where   P = permeability coefficient

The permeability coefficient, P, describes the transport rate at steady state. The solubility coefficient, S, describes the amount of penetrant that will be absorbed by the package wall and measures how many molecules are migrating into the film at steady state. The diffusion coefficient, D, describes how fast molecules are moving through the polymer and determines how much time will be required to reach steady state (DeLassus and Jenkins, 1986; DeLassus, 1987).

Equation (2-1) becomes :

$$\frac{dM}{dt} = \frac{P(p_1 - p_2)A}{x}$$
Equation (2-3)

Permeation is a multi-step process and study of the diffusion and solubility coefficients gives more insight into what is happening. Permeability can increase or decrease depending on the relative magnitudes of the rates of change of diffusion and solubility under different conditions.

If any two coefficients are determined experimentally, the third can be calculated by substitution in equation (2-2).

The diffusion coefficient, D, is usually obtained from the linear portion of a permeation curve. Figure 2.1 (DeLassus and Hilker, 1987) shows a typical curve generated during a permeation experiment.

At t = 0, a film free of penetrant is exposed to a constant concentration of penetrant. Initially, the permeation rate is zero as more penetrant dissolves in the film than evaporates from it. Solubility is the dominant parameter. Later, diffusion controls the process. After a time, break through occurs and penetrant molecules begin to come through the film at a measurable rate. The transport rate rises to a steady state.

Figure 2.1 Relative Transport Rate as a Function of Time
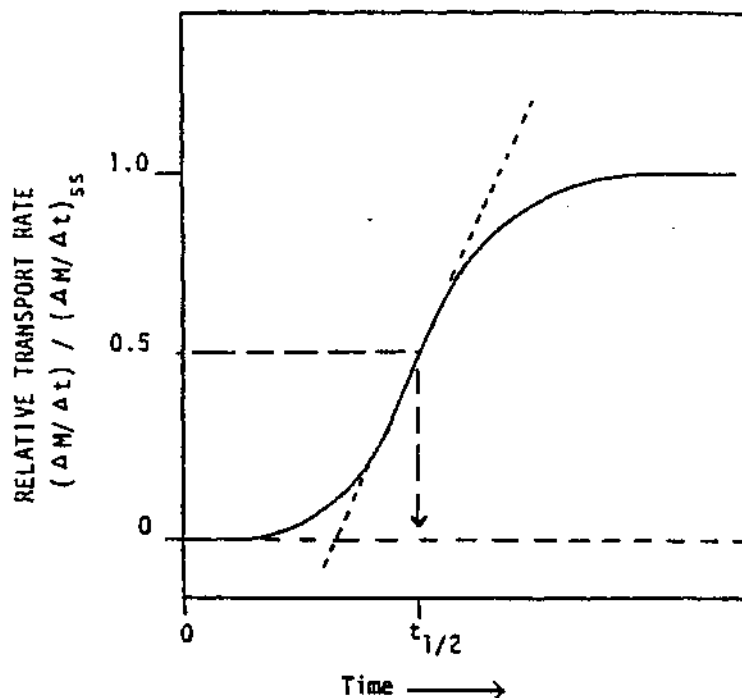
D can be calculated in two ways: (DeLassus and Jenkins, 1986; DeLassus, 1987; DeLassus et al., 1988a)

i) by using the slope of the transient portion of the curve and the response of the detector at steady state, R_{ss}.

$$D = \frac{0.176x^2(slope)}{R_{ss}}$$

or   ii) from the time, $t_{1/2}$, which is the time taken to reach a transport rate that is one half of the steady state rate;

$$D = \frac{x^2}{7.2t_{1/2}}$$

where x = thickness of the film

The permeability coefficient is determined by substituting values in equation (2-3). $\underline{dM}$ is measured at steady state. A and x are known and (p_1-p_2) is either measured
$\ \ dt$
or calculated separately (DeLassus et al., 1988a).

The solubility coefficient, S, can be obtained by substitution of P and D in equation (2-2). Alternatively, S can be obtained by measuring the equilibrium amount of vapour absorbed by a known volume or weight of polymer using sorption apparatus (Stepek, 1987).

The equations in sections 2.1 and 2.1.1 have been developed to describe the transmission of gases across rubbery polymers and they may not always represent the behaviour of vapours permeating across glassy polymers. The equations are also not valid for organic vapours which can interact with the polymer. They should be used with care in these situations (Landois-Garza and Hotchkiss, 1988; Zobel, 1982).

2.2 FACTORS AFFECTING PENETRANT-POLYMER INTERACTIONS

To understand the mechanism of permeability, it is essential to know both the diffusion and solubility coefficients of the penetrant in the polymer and the dependencies of these parameters on temperature, structure of the polymer, size of the permeating molecule and concentration of the penetrant (Stepek, 1987). Equations have been developed to attempt to predict the changes in D, S and P due to the effects of these factors.

2.2.1 Temperature

D, S and P are strong functions of temperature (DeLassus and Hilker, 1987; DeLassus et al., 1988a).

$$P(T) = P_o \exp(-E_p/RT) \qquad \text{Equation (2-4)}$$

$$D(T) = D_o \exp(-E_d/RT) \qquad \text{Equation (2-5)}$$

$$S(T) = S_o \exp(-H_s/RT) \qquad \text{Equation (2-6)}$$

$$E_p = E_d + H_s \qquad \text{Equation (2-7)}$$

where P_o, D_o, S_o = constants

T = absolute temperature (°K)

R = gas constant

E_p = activation energy for permeation

E_d = activation energy for diffusion

H_s = heat of solution

Equations (2-4) to (2-7) were developed for use with rubbery polymers and should be used with care for glassy polymers and/or organic vapours that interact strongly with the film.

These equations are valid above and below the glass transition temperature of the polymer, Tg, but not at Tg. Straight line extrapolations cannot be made through Tg as the slope changes at Tg. Extrapolation is necessary to get values at lower temperatures as experiments are conducted at elevated temperatures to get measurable results in a reasonable time. A technique has been adopted to estimate P and D below Tg. This is shown graphically in Figure 2.2 (DeLassus et al., 1988a). First, a simple straight line extrapolation is made to room temperature. This yields values of P and D which are lower than the so-called "truth". An extrapolation is then made down to Tg followed by a horizontal translation. As E_p and E_d are positive quantities, this gives P and D values that are higher than the "truth". The geometric average of the two extrapolated values is used as an arbitrary estimate of the transport parameters below Tg (DeLassus et al., 1988a, 1988b).

Figure 2.2 Temperature Dependence of Permeability
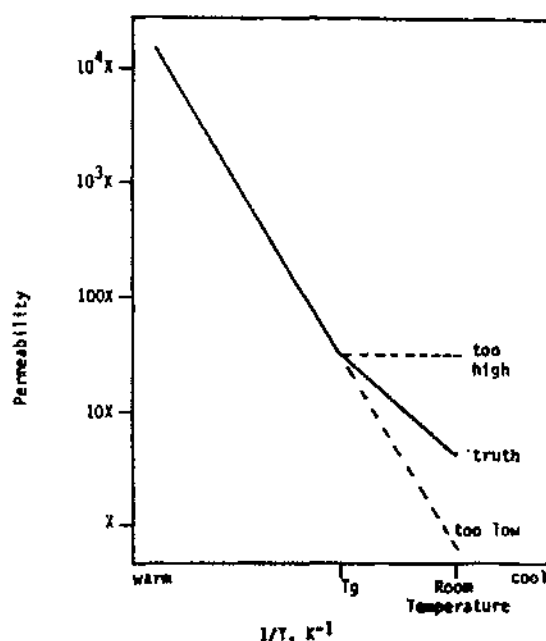
2.2.2 Concentration

D and S are dependent on concentration of the penetrant as shown by the following equations (Zobel, 1982):

$$D=D(O)\exp(k_1c)$$

$$S=S(O)\exp(k_2c)$$

where   D(0), S(0) are D and S at zero concentration

k_1, k_2 = constants

At low vapour concentrations, solubility approaches zero according to Henry's Law, that is $k_2=0$, so:

$$P=P(O)\exp(k_1c)$$

The solubility coefficient can be used to find the average concentration of penetrant, c(avg), in a polymer film when p(avg) is the average of the penetrant vapour pressures on either side of the polymer:

$$c(avg)=Sp(avg)$$

The quantity of penetrant that will be dissolved in the film, (or the sorptive loss), Q, is (DeLassus, 1987):

$$Q=c(avg)V=c(avg)Ax=Sp(avg)V$$

where   V = volume of film

A = area of film

x = thickness of film

2.2.3 Molecular Weight of the Penetrant

D is dependent on the molecular weight of the penetrant as it affects the ease with which molecules move through the film (Zobel, 1985).

Molecular volume, $V = \pi ab^2/6$

(assuming an ellipsoidal shape to give greater emphasis to shorter dimensions)

where   a = length

b = root mean square width

$$D = K_d V^{-n}$$

$$\log D = \log K_d - n \log V$$

where K_d = proportionality constant

V = volume occupied by molecules

A relationship between S and the boiling point of a gas (T) for low vapour concentrations and no interactions between the polymer and the vapour is given by the following equations. Polarity interactions will also affect S.

$$S = S_o \exp(K_s T)$$

$$\log S = \log S_o + K_s T$$

where S_o = proportionality constant

K_s = constant

As P = DS, then :

$$\log P = \log K_d - n \log V + \log S_o + K_s T \qquad \text{Equation (2-8)}$$

Equation (2-8) allows the relationship between the permeability coefficient, P and penetrant molecular structure to be examined.

2.2.4 Multilayer Polymer Structures

For equation (2-3), $\underline{dM}$ will be the same for each layer at steady state as the
$\qquad\quad\ dt$

penetrant concentration in the wall layers will remain constant, but the total pressure drop of the penetrant will be the sum of the pressure drop across each layer (DeLassus and Hilker, 1987):

$$(p_1 - p_2)_{total} = \frac{dM}{dt\,A}[\frac{x_1}{P_1} + \frac{x_2}{P_2} + \frac{x_3}{P_3} + ...]$$

2.3 PERMEABILITY UNITS

There are many different methods of measuring permeability and therefore there are a variety of units used to report permeability data. To make comparisons easier and to ensure that equation (2-3) is valid, SI units should be used. This gives permeability the dimensions of quantity of (gas-thickness) / (area-time-pressure), that is, kg m/m^2 s Pa. As this results in very large and cumbersome numbers, a more convenient unit known as the Modified Zobel Unit has been developed (DeLassus et al., 1988a, 1988b).
1 MZU = 10^{-2} kg m/m^2 s Pa which gives the diffusion coefficient units of m^2/s and the solubility coefficient units of kg/m^3 Pa.

Permeability constants can also be expressed by the units of cm^2/s, which are identical to the units of the diffusion coefficient (Yasuda, 1975).
The advantages of using these units for the permeability coefficient are:

- the numerical value can be directly compared with permeability coefficients of other penetrants (non gaseous) in the same membrane;

- the solubility coefficient is the partition coefficient, which may provide a numerical expression of the significance of the membrane phase for transport;

- the numerical value itself, without any further conversion, can be used to detect the deviation of the transport mechanism from the diffusive type permeation;

- calculation of the permeability coefficient in cm^2/s from gas phase experimental data is simpler than using other units.

2.4 EXPERIMENTAL STUDIES OF PENETRANT-POLYMER INTERACTIONS

No simple, widely applicable relationship exists for the behaviour of penetrants permeating through polymers as permeation is a complex process and there are a wide variety of types of polymers and penetrants. From the relationships described previously, it can be seen that the size, shape and nature of the penetrant molecule affects D, S and P as does the structure of the polymer. Investigations of flavour-polymer interactions have to consider the effect of these factors and variables such as temperature, humidity, concentration of penetrant and interaction between components of the flavour. Many different observations of the interactions between flavours and polymers can be made from similar studies depending on the relative influence of each of these factors in the experiment. The effects of these factors are described here.

2.4.1 Temperature

As temperature increases, the rate of diffusion should increase as the movement of the chains will be increased as activation energy for diffusion, E_d, is always positive (Murray, 1987; Salame, 1990; Salame and Steingiser, 1977). Activated diffusion occurs as a result of segmental motion of the polymer chains to create temporary voids.

Sorption is also higher at elevated temperatures due to the increased free volume of the polymer and the increased ease of hole formation (Anon., 1987).
The heat of solution, H_s, can be positive or negative and large or small in magnitude. Therefore, solubility can increase, decrease or remain constant as temperature increases (DeLassus, 1987).
Depending on the relative magnitudes of change of D and S, permeability can either increase or decrease with increased temperature. For ethylene-vinyl alcohol (EVOH) and vinyl chloride / vinylidene chloride (VC/VDC) copolymers and apple aromas, it was found that small changes in temperature caused large changes in the performance of the films. Permeability increased as D increased more than S decreased (DeLassus et al., 1988a).

2.4.2 Relative Humidity

Hatzidimitriu, 1987; showed that for some combinations of films and penetrants, permeation increased at high relative humidities, while for others the opposite occurred. Water can act as a plasticiser in some films and increase D. When a hydrophilic film is dry, there is little permeation through the amorphous regions as interchain hydrogen bonds restrict chain mobility and reduce diffusion of the penetrant; addition of water decreases the cohesive forces between the polymer chains and increases the polymer chain mobility, resulting in an increase in diffusion of the penetrant. High relative humidities can also cause a change from glassy to rubbery states in a polymer by lowering Tg (Liu et al., 1988). For glassy polymers, increasing the relative humidity can lower the solubility coefficient as water can occupy some solution sites and exclude the penetrant molecules.

When S is lowered more than D is increased by the plasticisation effect, permeability can decrease (DeLassus, 1987; DeLassus et al., 1988b).

DeLassus and Hilker, 1987 and DeLassus et al., 1988a, 1988b; studied the effect of relative humidity on permeation of apple aromas in EVOH copolymers and VC/VDC copolymers. The permeabilities of EVOH films increased as the humidity increased as EVOH is a hydrophilic polymer. Above Tg, EVOH was plasticised and D increased while S remained constant; below Tg, D increased and S decreased. For VC/VDC copolymers, increases in relative humidity had no effect on permeability.

The permeability of VC/VDC copolymer coated oriented polypropylene to toluene was also increased by increasing the humidity. Water acted as a copermeant, plasticising the polymer membrane and enhancing the transport of the organic penetrant through the polymer (Baner et al., 1986).

However, for the permeation of ethyl esters through polyvinyl alcohol (PVOH) films, permeation decreased as humidity increased. D remained constant and S decreased. This was the reverse of what was expected as PVOH is a hydrophilic film. Water was more polar than the penetrant and competed better for the sorption sites. The length of the path for diffusion through the film of the penetrant was increased. The increase in resistance to diffusion was greater than the relaxation of the polymer due to plasticisation (Landois-Garza et al., 1988).

Hydrophobic structures, polymers with low polarity and polymers whose barrier properties are dependent on dipole interaction are not adversely affected by water absorption. Some polymers, such as polyesters and some aromatic polyamides, show slightly lower gas permeability when wet as free volume voids fill up and are inaccessible to diffusion by gas. Permeation will decrease by approximately 10% if water absorption is not sufficient to plasticise the polymer (Salame and Steingiser, 1977; Brody, 1989; Salame, 1990).

2.4.3 Concentration of the Penetrant

The concentration of penetrant in a polymer is not a simple straight line relationship with penetrant partial pressure as suggested by Henry's Law; some curvature occurs at high partial pressures (DeLassus, 1987).

It has been found that at low concentrations, (below 10% of the penetrant's saturated vapour pressure), the permeability coefficient is linear and changes little. Fickian behaviour is followed. At higher concentrations, the permeability coefficient increases nonlinearly (Zobel, 1982, 1985; Baner et al., 1986; Mohney et al., 1988).

Diffusivity is a function of penetrant concentration. If the penetrant concentration is high enough, the film may be plasticised and D will increase as E_d will decrease. In glassy polymers there are two mechanisms of diffusion and as the concentration of the vapour changes so does the contribution from each mechanism (DeLassus, 1987). Above Tg, solubility increases with increasing penetrant concentration. Below Tg, solubility varies in a more complicated way as there is dual mode sorption and the contribution from each mechanism changes as the concentration of the penetrant changes. Dual mode sorption is a combination of Henry's Law and Langmuir type sorption. It is observed during the sorption of gases in glassy polymers. Sorption in the amorphous phase of the polymer follows Henry's Law and that in the microvoids, ("holes"), obeys a Langmuir isotherm (Felder and Huvard, 1980; Naylor, 1989).

Earlier research showed little difference in the flavour/odour barrier properties of acrylic and polyvinylidene (PVDC) coated versus uncoated oriented polypropylene

(OPP) films but these studies were carried out at high concentrations. In more recent investigations, using toluene, limonene and ethyl acetate as penetrants, coated OPP films provided better barriers to flavours and odours than coextruded films for a longer period, at real life levels of concentration, such as those encountered during normal distribution and display. The aroma barrier was concentration dependent unlike oxygen and water barriers (Johnson, 1989; Tarkenton, 1989).

Permeation of d-limonene was also studied in oriented polypropylene, PVDC copolymer coated OPP, acrylic (heat seal) coated biaxially oriented polypropylene (PP) and one side PVDC copolymer coated, one side acrylic coated OPP as a function of penetrant concentration. As expected, the permeability constant P, was concentration dependent and increased as concentration increased due to the interaction between the polymer and the penetrant. This resulted in configuration changes and alteration of polymer chain conformational mobility.
Coating led to an increase in barrier properties of OPP at low limonene concentrations compared to uncoated OPP but at concentrations greater than 4ppm, the advantage of the barrier properties was diminished (Giacin and Hernandez, 1987). This agreed with earlier studies (Kail, 1984).

Another study measured the permeation of d-limonene vapour through polyester and OPP at very low concentrations (Apostolopoulos and Winters, 1991). Polyester was an excellent barrier as no permeation was observed after 30 days at the highest concentration tested. Experiments with OPP showed that Fickian behaviour was followed. These experiments also demonstrated that the permeability, diffusion and solubility constants were influenced considerably by the concentration of the penetrant. This demonstrated, again, that permeation studies must be carried out at low concentrations similar to those found in food so that the data obtained actually reflects the true behaviour of the packaging material.

Two common cereal pack liners, a high density polyethylene (HDPE)/sealant laminate structure and a glassine structure, (wax/polyvinyl alcohol/glassine/ polyvinyl alcohol/wax), were tested to find the relationship between mass transport parameters and solubility of d-limonene. Once again an increase in permeation was

observed with an increased concentration. The permeability constant was lower in glassine than in HDPE so permeation losses would be reduced by packaging in the glassine based structure. Sorption studies showed d-limonene was less soluble in glassine. The solubility coefficient was concentration dependent and therefore would need to be determined at the concentrations of interest (Giacin and Hernandez, 1987).

Concentrations of 20-150ppm of toluene, B-pinene, ethyl acetate, limonene and menthol were used in a study of the permeation coefficients of coextruded OPP, acrylic and PVDC coated OPP films and a HDPE/ethylene-vinyl acetate (EVA) film (Hagenbaugh, 1987). The permeation coefficients were concentration dependent and so was the diffusion lag time. Differences between coated and uncoated films particularly at low concentrations were observed. Coated films were better barriers at low concentrations. Lag times were longer than those for coextruded films. The enhanced barrier protection was not observed for coated films at higher concentrations.

When the solubility becomes high enough, large concentrations of penetrant can dissolve in the polymer. The penetrant can act as a solvent, weakening bonds and allowing the polymer to swell. Runaway permeation can occur. The swollen polymer allows more penetrant through the film and this can solvate and destroy the normally impervious crystalline regions (DeLassus, 1987; DeLassus et al., 1988a; Marcus et al., 1978).

Useful permeation data can only be gathered at low concentrations where there is little interaction between the polymer and the penetrant. High concentrations of penetrant are not applicable to real packaging situations. Concentrations in packs will be in the linear region and permeation behaviour can be predicted from theory provided other factors are not affecting the permeation of the vapour. Materials reported as unsuitable from tests using saturated vapours may offer sufficient protection at realistic concentrations (Landois-Garza et al., 1988).

2.4.4 Multiple Component Permeation

Interactions between components of a flavour and their effects on permeation are also important.

One component may assist or retard the permeation of another. This may happen by enhancing the solubility of the copermeant by altering the structure or morphology of the polymer, or by excluding the penetrant from sorption sites (DeLassus and Hilker, 1987).

For example, a solution of d-limonene was found to increase the oxygen permeability of films (Hirose et al., 1988). If the concentration of all volatiles is low enough to eliminate interactions, then the permeation rates of the components of mixed vapours should be independent and additive (Zobel, 1988). One study found that the components of orange oil were not sorbed equally (Kwapong and Hotchkiss, 1987). Another study of the permeation of apple aromas in low density polyethylene film also demonstrated how a flavour imbalance could develop. One aroma may permeate faster than others. While the concentrations of all components decreased on storage, the relative concentration of one component decreased more rapidly. The residual aroma will be weaker in one component and this may be unacceptable even if the total aroma loss is within acceptable bounds (DeLassus et al., 1988a).

2.4.5 Molecular Weight of the Penetrant

It has been found that the equations in section 2.2.3 can be used to relate the permeation of a penetrant to its molecular weight and boiling point (Zobel, 1985; Landois-Garza and Hotchkiss, 1988).

D decreased as the molecular volume of the penetrant increased since it required the co-operative motion of larger sections of the polymer chain to open holes through which the penetrant could diffuse. A higher activation energy was required and the probability of a molecule achieving this energy was lower. The average speed with which the molecule moved through the polymer was decreased. Solubility increased as molecular weight increased. That is, even though the molecule moved more slowly there was a larger number of molecules moving and

more emerged at the other side of the film.

Permeability can increase or decrease depending on the relative magnitudes of the changes in D and S.

Permeation decreased with increasing molecular size for compounds with a molecular weight below 60. Above 60, the effect of solubility outweighed diffusion, and permeation increased as molecular weight increased (Zobel, 1985; Landois-Garza and Hotchkiss, 1988).

If higher molecular weight molecules are more soluble, the polymers may absorb and transport these flavour compounds more than others and a flavour imbalance could result.

2.4.6 Multilayer Polymer Structures

The location of the barrier film in a multilayer structure is very important in retaining flavour in packages. As the pressure drop of the penetrant is proportional to the (thickness of the film)/(permeability), the pressure drop will occur predominantly across the barrier film. The thickness may only vary slightly among the layers but the permeability can vary greatly. Most of the pressure drop occurs across the layer with the lowest permeability. Different sorption and concentration profiles can therefore be obtained by altering the order of the layers.

The effect of the barrier layer on sorption is shown in Figure 2.3 (DeLassus and Jenkins, 1986). If the barrier layer is located on the outside of the package, the transmission rate at steady state is reduced. Short time sorption is not changed as film A is still in contact with the product. If the barrier layer is placed on the inside, sorption will be reduced as the barrier layer has a lower D, and if S is not high, the time for significant sorption to occur can be extended beyond the shelf life of the product.

Therefore, to prevent the loss of flavour and aroma the barrier layer should be on the inside of the package.

Figure 2.3 Pressure Drop of a Penetrant in a Multilayer Polymer Structure.

"PRESSURE" OF PERMEANT

A   B

INSIDE PACKAGE   FILM EDGE   FILM EDGE   OUTSIDE PACKAGE

$\longleftarrow$ LOCATION $\longrightarrow$

"PRESSURE" OF PERMEANT

B   A

INSIDE PACKAGE   FILM EDGE   FILM EDGE   OUTSIDE PACKAGE

A= STRUCTURAL LAYER,
   HIGH PERMEABILITY

B= BARRIER LAYER,
   LOW PERMEABILITY

"PRESSURE" OF PERMEANT

A   B   A

INSIDE PACKAGE   FILM EDGE   FILM EDGE   OUTSIDE PACKAGE
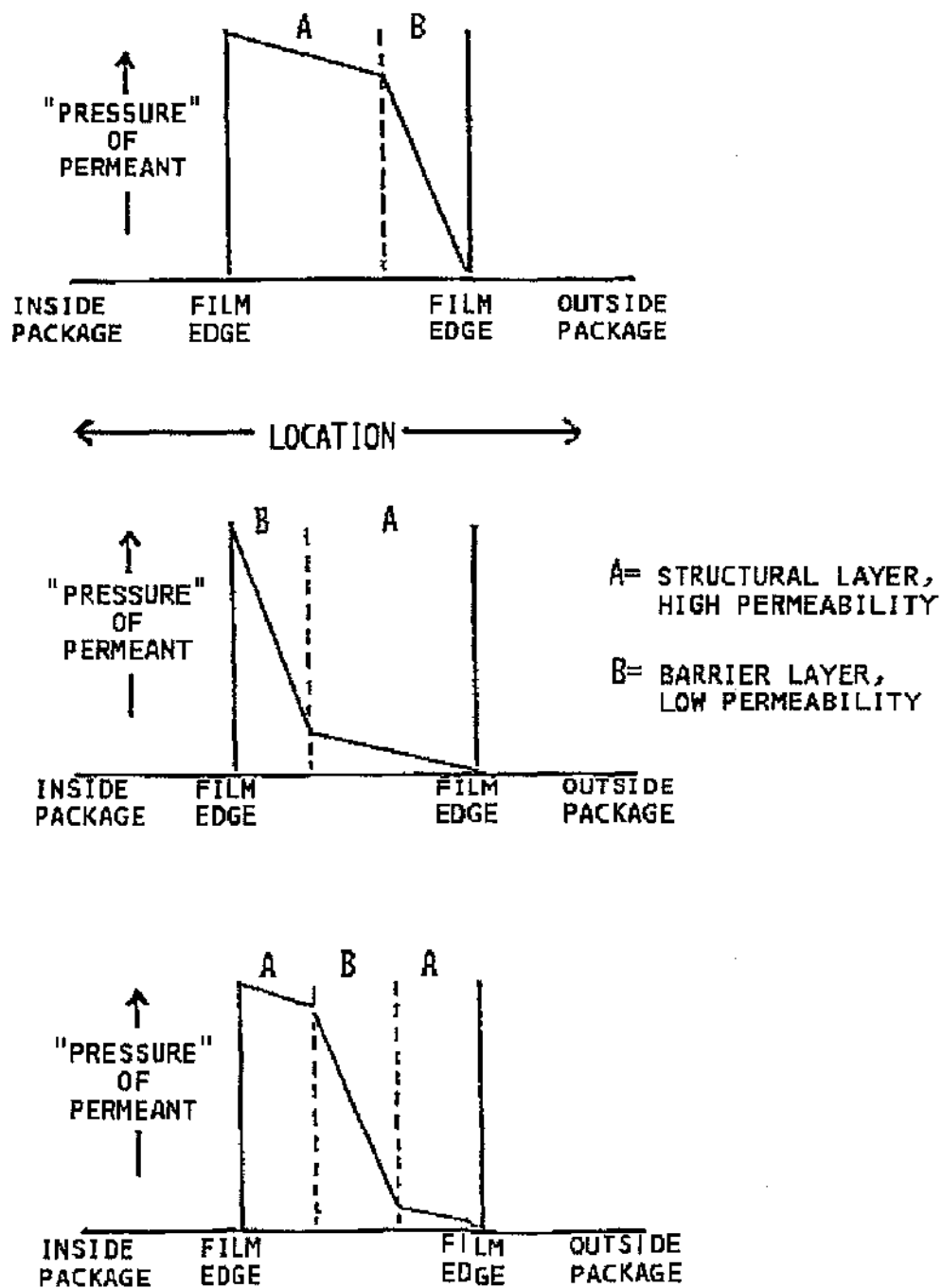
To prevent the ingress of molecules from the polymer, the barrier layer should also be on the inside. To stop molecules from the environment entering the pack, the barrier layer may be placed anywhere.

This presents a problem for moisture sensitive barrier films as they are normally placed between layers of protective polymers and may lose their barrier properties if placed on the inside of the package (DeLassus, 1987; DeLassus and Hilker, 1987).

2.4.7 Structure of the Polymer and the Nature of the Penetrant

Organic vapours show non-ideal diffusion, solubility and permeability properties as they are able to swell the polymer matrix and change the configuration of the polymer chain (Baner et al., 1986).

Compounds whose structure is similar to the functional group of the polymer or whose polarity is similar will be strongly absorbed by it, that is, like dissolves like (Salame, 1977; Brody, 1989).

Smaller molecules are absorbed more rapidly than larger molecules as they can pass through the small temporary voids in a polymer more quickly than a bulkier molecule. As the penetrant molecule becomes larger and bulkier, transmission rates are reduced and D decreases. Very large molecules plasticise the polymer and increase solubility due to newly available sorption sites.

The volatility of a compound affects its maximum concentration (Salame, 1977; Murray, 1987; Brody, 1989).

Components of the food which have an affinity for the polymer will compete for sorption sites and reduce the amount of other components sorbed, compared to the amount sorbed if that component were present in isolation.

The chemical nature of the penetrant will determine if it will act as a swelling agent, plasticiser or solvent in certain polymers to give a higher concentration-dependent permeation rate. Comparison of the solubility parameters of the polymer and penetrant will help to predict this. Similar solubilities indicate possible swelling or

solvency on contact (Anon., 1987; Murray, 1987; Zobel, 1988; Shimoda et al., 1988; Brody, 1989).

Plastics whose structures allow them to form closely packed networks are less sorptive (Murray, 1987; Brody, 1989). Below Tg, plastics do not form holes easily and absorb less flavour. The highest permeabilities are found with elastic polymers and the lowest with rigid polymers which have strong intermolecular attractions or chemical crosslinks. Strong intermolecular forces prevent chains rotating and decrease segmental motion of chains. The forces can be reduced and permeation increased in the presence of plasticisers which promote chain mobility.

Free volume is the molecular "void" volume that is trapped in the solid state. The permeating molecule finds an easy path in these voids. A polymer with poor symmetry or bulky side chains has high free volume and high permeability (Salame, 1990).

The cohesive energy density of a polymer is a measure of the amount of energy forcing the chains together. The higher it is, the greater the forces holding the polymer together and the lower the gas permeability, as a gas molecule depends on chains to "open" in order to pass through (Murray, 1987; Brody, 1989; Salame, 1990).

Fifteen different compounds, in solutions of 1000ppm of compound in a water or water/alcohol mixture, were placed in containers made from LDPE, polyvinyl chloride (PVC), polyethylene terephthalate (PET) and polyacrylonitrile (PAN) copolymer to test absorption of flavours. The results were reported as the percentage loss of the compound from the solution. As expected, the better the barrier properties of the film, the lower the absorption of the organic compound (Salame, 1987).

The permeation of 13 odours in polyolefins and PVC were compared. The diffusion coefficient was lower for PVC while polyolefins had lower solubility coefficients. As permeability is the product of diffusion and solubility, PVC had only a small barrier advantage over polypropylene when the two coefficients were multiplied together (Koszinowski and Piringer, 1987).

Permeation of some flavouring substances in a methanolic solvent through LDPE, HDPE, PP copolymer, PP homopolymer and PVC was examined. PVC had the largest solubility constant for flavour compounds. The polyolefins were more sensitive to the size and shape of the diffusing molecule. PVC had a low permeability constant but PVC and PP are poorer barriers than HDPE due to swelling effects (Koszinowski and Piringer, 1986).

EVOH is a good barrier to odours but it is moisture sensitive. Approximate times for a variety of odours to permeate this material and other plastics have been recorded (Ikari et al., 1987). The permeability of structures with and without a layer of EVOH to vanillin, menthol, piperonal and camphor showed that including a layer of EVOH in the structure greatly increased the barrier properties of the films (Foster, 1986).

Permeation studies were carried out for nylon 6 in combination with 2-propanol, 1-hexanol, ethyl acetate, 2-heptanone and toluene. Some penetrants exhibited Fickian behaviour. Previous results for glassy semicrystalline polymers were confirmed. Anomalous permeation curves with high initial permeation rates which decreased with time to a final steady value can occur. The high initial rate was due to microcracks, internal pores and regions of low density in the polymer. Imperfections were eliminated as sorption proceeded by swelling and rearrangement of the polymer structure. High adsorption coefficients were due to hydrogen bond formation with the amide groups of nylon 6 and the hydroxyl groups in 1-hexanol and 2-propanol. 2-heptanone had a side reaction with nylon 6 (indicated by yellowing of the film), and therefore gave lower results than expected (Hatzidimitriu et al., 1988).

Brody, 1989, gave times for the permeation of flavours and aromas in various packaging materials. This showed the permeability of different materials to flavours and aromas varied greatly between specific flavour systems.

More flavour was lost in a thick walled container than in a thin film pouch (Anon., 1987; Murray, 1987; Stepek et al., 1987). Loss of flavour can be minimized by choosing a suitable barrier film as the crystalline nature of barrier materials ensure

the solubility of the penetrant is low. As the amount of crystallinity increased, solubility decreased as crystallites were impervious to the penetrant (Shimoda et al., 1988; Zobel, 1988). Orientation only reduces permeability significantly if the polymer has some crystallinity. Orientation "lines up" crystallites and the permeating molecule is forced to take a more tortuous path (Salame, 1977, 1990; Giacin, 1987).

Another study of EVOH copolymers with a variety of compounds demonstrated the effects of ethylene content, biaxial orientation and film thickness on sorption (Ikegami et al.,1991). The amount of penetrant that was sorbed depended on the functional groups of the penetrant and polymer. For example, more d-limonene (a non-polar hydrocarbon), was sorbed when there was a higher ethylene content in the polymer than when there was a high vinyl alcohol content. The reverse was true when alcohols were used. Biaxial orientation of the EVOH polymer decreased sorption considerably.

A good barrier film requires some polarity, high chain stiffness, inertness, close packing, bonding or attraction between chains and a high Tg (Salame, 1977).

The method of manufacture of the polymer also affects flavour-polymer interactions. Oxidised (i.e. corona treated) polyethylene contact surfaces produced off-flavours in orange juice (Mannheim et al., 1988).

Hermetic seal integrity of packs is important because the diffusion of molecules in air is much faster than for diffusion through a polymer. In a polymer, molecules can only diffuse when it is energetically favourable for them to do so. Molecules will escape more quickly through seal leaks than by permeation through the film (Zobel, 1988).

2.4.8 Mechanical Properties of the Polymer

Sorption and permeation of compounds can affect the mechanical properties of a polymer. The degree of change in the properties depends on the type of polymer. Environmental stress cracking of polyethylene is enhanced by polar organic

materials (Briston and Katan, 1974a).

One study found the modulus of elasticity was decreased as the absorption of d-limonene increased. The penetrant decreased the stiffness of the film. Tensile strength was also decreased. The amount of elongation was increased in some films as the penetrant acted as a plasticiser and allowed the chains to move past each other. Films with strong interchain bonds were not affected.
The seal strengths of the films were decreased. Impact resistance was increased (Hirose et al., 1988).

Absorption of compounds can weaken the package and cause it to fail during distribution. Pinholing, flex cracking and leakage can occur (Mannheim et al., 1988).

Abuse during converting, packaging and transportation can result in deterioration of barrier properties. One study found that flexing decreased the barrier properties of acrylic coated oriented polypropylene but did not affect PVDC-coated oriented polypropylene film (Kail, 1984).

2.4.9 Sorption of Organic Vapours

These results are useful for deciding the proper compensations for changes in flavour profiles and illustrate the importance of learning the nature of flavour-polymer interactions between food and packaging materials.

Mixtures of seven characteristic flavour solutes commonly found in orange juice were studied for interaction with low density polyethylene (LDPE) at 20°C (Kwapong and Hotchkiss, 1987; Halek and Meyers, 1989). Selective sorption occurred with hydrocarbons being preferentially absorbed.
In 25 days, hydrocarbon monoterpenes such as d-limonene, myrcene and alpha-pinene showed 30-40% sorption by LDPE; the oxygenated monoterpenes, l-carvone, citral a+b and d-linalool showed 10% sorption. Ethyl butyrate showed no interaction with LDPE as did the straight chain aldehyde, decanal, and ethanol. There was a rapid initial decrease in the levels of both types of compounds. For

oxygenated terpenes no further change occurred but sorption of hydrocarbons continued at a slower rate. This biphasic rate of decreasing solute concentration suggests adsorption followed by absorption.

D-limonene showed both adsorption and absorption while l-carvone showed predominantly adsorption.

When d-limonene and carvone were sorbed individually the sorption of d-limonene alone exceeded that of the sorption in the mixture.

Carvone had a slower sorption rate than d-limonene in the polymer.

Hotchkiss, 1987; exposed aqueous solutions of citrus essential oils to LDPE and ionomer at concentrations of 49-121 mg/l. These were similar concentrations to those expected in beverages. Sensory analysis showed that the aroma changed both in intensity and character, (suggesting that the polymers selectively sorbed some compounds) and gas chromatography confirmed that limonene was more than 95% sorbed while linalool was less than 5% sorbed. An increase in temperature increased the amount of limonene sorbed indicating that absorption rather than adsorption onto the surface was occurring.

LDPE, ethylene-vinyl alcohol copolymer (EVOH) and copolyester (CoPET) were evaluated for the sorption of organic volatiles from orange juice. The probe compounds chosen were d-limonene, neral and geranial. Gas chromatography was used to identify the penetrants. LDPE sorbed d-limonene and geranial. The d-limonene was readily sorbed as it has an affinity for hydrocarbons. EVOH slowly absorbed d-limonene. The copolyester did not absorb any compounds (Imai et al., 1990).

Orange juice was packaged in polyethylene lined cardboard containers and glass. Loss of d-limonene in the polyethylene layer was initially rapid and then proceeded at a slower rate. Increasing the storage temperature also increased the loss (Durr et al., 1981; Mannheim et al., 1987).

Permeation was also studied in systems of LDPE/dishwashing agent, (taken as an example of a complex system of flavouring substances) and LDPE/methanol, which contained the same flavours in a methanolic solvent.

The dishwashing agent/LDPE system had larger permeation constants. This was

due to polar compounds being highly soluble in aqueous and alcoholic phases and therefore they had low vapour pressures over the solution and low permeation constants. A non-polar substance is sparingly soluble in methanol and water so large partial pressures occurred over the solution and give rise to large permeation constants. Solvents affect the permeation process.

The solubility constants were more influenced by the structure of the penetrant than the diffusion coefficients (Koszinowski and Piringer, 1986).

Desorption studies were carried out to examine the permeation of aromatic substances which are hard to volatilize.

LDPE dosed with alkanes by absorption were desorbed into air and alcohol. Desorption was the rate determining step for higher alkanes. Fast absorption or desorption was possible without inhibiting diffusion for compounds with molecular weights up to 200 (Koszinowski and Piringer, 1987).

2.4.10 Diffusion of Organic Penetrants in Polymeric Films

Size, shape and interactions of the molecules with nylon 6 gave high diffusion coefficients for toluene and 2-propanol and low coefficients for 2-heptanone due to its larger size and the elongated shape of the molecule (Hatzidimitriu et al., 1988).

The effect of water vapour on diffusion in polymers was demonstrated using cellulose acetate, polyvinyl acetate and polystyrene (PS), and acetone, carbon tetrachloride or benzene. Diffusion into plasticised films was faster than in an unplasticised polymer. Water diffused rapidly into the polymer, acted as a plasticiser and led to a higher diffusion coefficient for the organic vapour than that calculated for the dry film. Water is a small molecule and diffuses quickly so other small molecules could have the same effect (Long and Thompson, 1954).

2.5 PERMEATION MEASUREMENT

There are a number of experimental methods that can be used in order to determine the relative barrier properties of plastic films with respect to an organic vapour.

Sensory panels are used to detect changes in aroma intensity and character due to permeation. The product is packaged in the film, stored and given to the panel for evaluation (Kail ,1984; Allison, 1985; Hotchkiss, 1987).

Another method commonly used is to place strips of the packaging material in flavour solutions in sealed containers. The solution or headspace gas can be analysed for changes in concentration of the components (Hotchkiss, 1987; Salame, 1987).

New methodology is only now developing. Methods used in the past were adequate for low barrier requirements but today the device to hold the specimen and penetrant has specific requirements.

2.5.1 Types of Permeation Cells

Permeation cells generally fall into one of the following categories (Murray, 1985, 1987):
- Single chamber
- Evacuated chamber
- Two-part
- Pouches

A single chamber cell exposes one side of the membrane to the atmosphere containing the vapour. Permeability is calculated from the weight gain or loss of the cell depending on the direction of permeation. The difficulty is that often the change in weight is very small or is the sum of two or more transport processes.

Evacuated chamber cells have a high vacuum on one side of the membrane and penetrant on the other. As permeation proceeds the pressure or volume change is

noted and mathematically translated to a permeability. While the method is sound, calibration is rigorous, the cells are prone to leakage and the penetrant volatility may be too low. The method may also not be specific to the penetrant tested if impurities are present. A gas chromatograph or mass spectrometer can also be used to quantify the permeating vapours.

A two-part cell consists of two sealed chambers at atmospheric pressure separated by the test film. The penetrant is loaded on one side of the cell while the other side contains penetrant free air. The cell is closed and the concentration of the penetrant in the low concentration side of the membrane is monitored by a gas chromatograph over a period of time.

The pouch technique utilizes a heat sealed pouch containing the penetrant placed in a closed container fitted with a septum. The air surrounding the pouch is sampled periodically and analysed for the penetrant level. This technique is useful but depends on good seal integrity and interlay or adhesion in the case of multicomponent films.

Pouch and two-part cells have contained compressible seals and a septum for sampling. These rubbery materials can absorb permeating vapours often to the extent that a permeation rate cannot be measured as the penetrant level is diminished by sorption. The effect is negligible if permeation is rapid but when permeation is slow, sorption by cell materials will bias the measurement of permeation rate. These problems have been overcome by designing a two-part cell which isolates rubbery polymers from the penetrant vapour on the low penetrant concentration side of the membrane. An ethylene-propylene "O" ring face seal on the high penetrant concentration side of the test film compresses the film against a stainless steel face. This apparatus was used to determine "relative permeation rates" of organic vapours. The method was limited to determining the transmission rate and permeability constant values for the saturated vapour pressure of the liquid penetrant at a given temperature as vapour was not continuously swept away as is the case in other studies.

2.5.2 Procedures for Measuring Permeation

There are two types of procedures available for permeation studies of organic vapours through polymer membranes.

2.5.2.1 Quasi-Isostatic Method

The quasi-isostatic method, or accumulation technique, determines the total amount of penetrant that has passed through the film and accumulated as a function of time.

Figure 2.4 (Giacin, 1987) shows a generalized transmission rate profile curve for this method.

Figure 2.4 Typical Transmission Rate Profile Curve for the Quasi-Isostatic Method
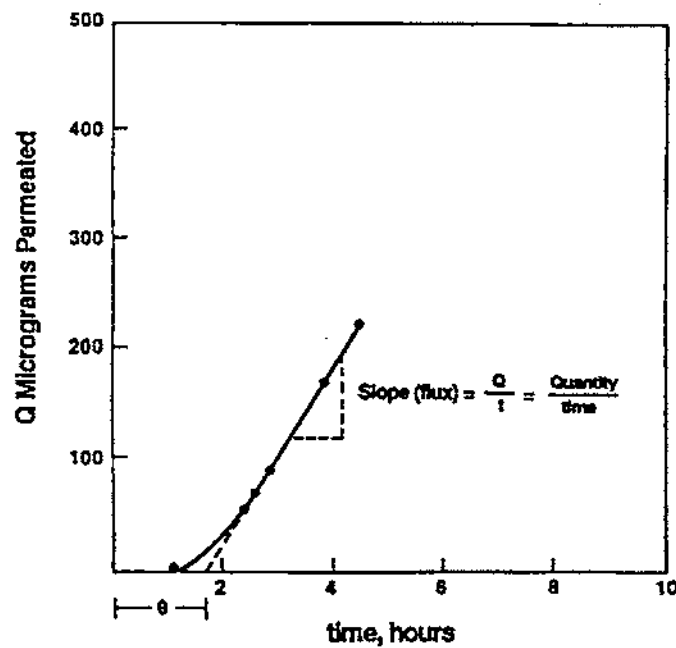
The diffusion coefficient is obtained from:

$$D = \frac{x^2}{6\theta}$$

where θ = is the intersection of the steady state portion of the transmission curve and is called the lag time.

The permeability coefficient is determined from:

$$P = \frac{yx}{Ab}$$

where y = the slope of the straight line portion of the transmission rate curve, (Q/t), (mass/time)

x = thickness of the film

A = area of the film exposed to the penetrant in the permeability cell

b = driving force given by the concentration or partial pressure gradient, that is, (c_1-c_2) or (p_1-p_2)

(Baner et al., 1986; Giacin, 1987; Hernandez et al., 1990)

2.5.2.2 Isostatic Method

This is any method in which the total pressures on both sides of the membrane are kept approximately equal (Felder and Huvard, 1980). In the isostatic technique, a constant low concentration stream of penetrant flows through the upper chamber of the permeability cell as a stream of carrier gas simultaneously passes through the lower chamber of the cell, conveying the penetrant away to a gas chromatograph for analysis (Baner et al., 1986; Giacin, 1987; Hernandez et al., 1990).

At selected time intervals, the concentration of the penetrant in the low concentration side of the cell is determined and the transmission rate is monitored until steady state conditions are reached.

For each transport rate value, a value of $\frac{x^2}{4Dt}$ can be calculated. By plotting these values as a function of time a straight line is obtained. From the slope of this graph D is calculated from :

$$D = \frac{slope * x^2}{4}$$

The permeability coefficient, P, is obtained from:

$$P = \frac{a \; G \; f \; x}{A \; b}$$

where a = calibration factor to convert detector response to units of mass of penetrant/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)

x = film thickness (thickness units)

A = area of the film exposed to penetrant in the permeability cell (area units)

b = driving force given by the concentration or partial pressure gradient, that is, (c_1-c_2) or (p_1-p_2), (pressure or concentration units)

(Giacin, 1987; Hernandez et al., 1990)

2.5.2.3 Sorption Measurements

Sorption measurements should also be made as a compound may not permeate through the polymer matrix but may be sorbed by the polymer and be lost from the product just as much as if direct permeation had occurred.

Sorption measurements are usually carried out by the continuous flow method (Long and Thompson, 1954; Giacin and Hernandez, 1987) using a Cahn Electrobalance. The film sample is suspended from the balance and a constant concentration of penetrant vapour is flowed through the sample tube so that the sample is totally surrounded. The gain in weight of the sample is monitored until the system attains steady state. Diffusion and solubility coefficients can be calculated from the results (Hernandez et al., 1990).

Figure 2.5 shows a plot of the ratio of the amount of penetrant vapour (M_t) absorbed at any time, t, and the equilibrium sorption level (M_∞) versus time.

Figure 2.5 Generalized Sorption Plot.
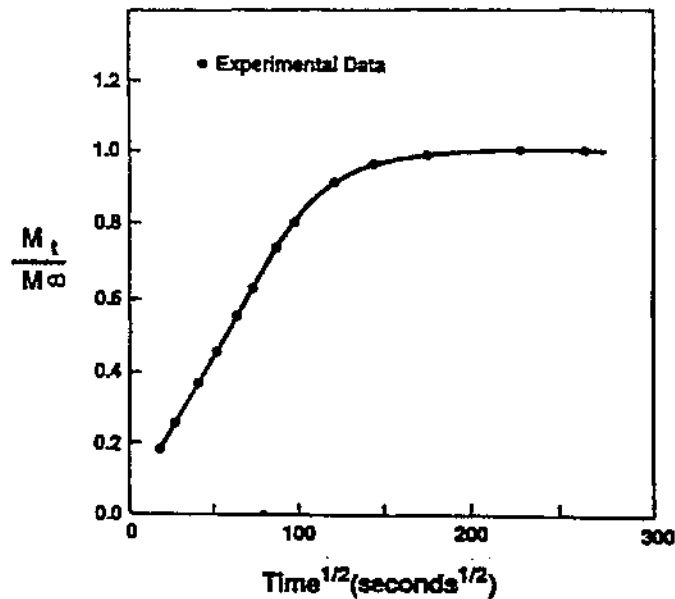
The sorption diffusion coefficient is:

$$D = \frac{0.049x^2}{t_{1/2}}$$

where $t_{1/2}$ = the "half sorption time"

i.e. the time when $\dfrac{M_t}{M_\infty} = 0.5$

The solubility coefficient is expressed as:

$$S = \frac{M_\infty}{wb}$$

where M_∞ = total mass of vapour sorbed at equilibrium by the polymer at a given temperature.

w = weight of the polymer sample under test

b = value of the penetrant driving force in units of concentration or pressure, that is, $(c_1 - c_2)$ or $(p_1 - p_2)$

(Giacin, 1987; Hernandez et al., 1990)

A procedure has been developed to measure the adsorption of organic compounds using an oxygen electrode (Sadler and Braddock, 1990). Adsorption of limonene by LDPE was measured using this method. The polymer was mounted on an oxygen electrode. Limonene absorption produced an increase in oxygen permeability directly proportional to the limonene concentration sorbed. The diffusion coefficients calculated were similar to those from weight change experiments.

Organic vapours often solvate host polymers. Plasticised membranes usually exhibit increased permeability to oxygen and other gases so oxygen permeability may give information on volatile scalping. Absorption of volatiles increases oxygen permeability so desorption of volatiles would reduce oxygen permeability.

An absorption influenced oxygen permeation electrode provides insight into solvation processes which might occur during absorption of volatiles.

2.5.3 Problems with Existing Methods

Many studies have been carried out based on these methods using the types of cells described. There are, however, problems with these methods.

The techniques, in particular the quasi-isostatic type, require mechanical support for the membrane and vacuum tight seals. The entire amount of vapour permeated or sorbed from the beginning of the experiment is accumulated and measured as a function of time. Measuring precision is not sufficient for detailed analysis of the data in terms of transient permeation rates and slow drifts caused by time dependent changes in membrane properties (Pasternak et al., 1970).

The collection medium could dilute the concentration of penetrant and it may have inadequate capacity for the penetrant particularly if the penetrant has a very low vapour pressure. Agitation in the cells is needed as high concentrations of penetrant at the interface interferes with permeation. Agitation is also essential if the solution is a multicomponent one (Schwope et al., 1988).

A standard test method should be developed or alternatively, permeation test methods and conditions need to be more specifically reported to allow comparison of results. The same permeation rates can produce a lower penetrant concentration

in the stream with the higher flowrate for two tests performed with the same analytical instrument and detection limits but different flowrates of the collection medium (Schwope et al., 1988).

2.5.4 The "Laminate Film" Method

Holland and Santangelo has developed a simple method, (the "laminate film" method), of measuring vapour transmission through polymers (Holland et al., 1981; Holland and Santangelo, 1984; Holland and Santangelo, 1988).

In the "laminate" method, the usual gas or liquid supply and collector systems are replaced by solid state systems. A supply film containing the penetrant is used as a source and a trilayer "laminate" system assembled. Two variations of the basic structure permit either transmission or sorption measurements to be made. Concentration changes in any layer of the "laminate" may be monitored by UV spectroscopy or microgravimetry. The procedure is quite general, being independent of vapour pressure, and also applies to non-volatile diffusants.

With solid polymer solvent systems any effects of a liquid solvent plasticising the test film can be avoided. However, at high penetrant levels concentration effects on the diffusion coefficient can be expected and these effects can be measured by varying the supply concentration.

Permeation equations are usually expressed in terms of pressure differences across test films as pressure is conveniently measured. In the "laminate" method, concentration provides the driving force. This is compatible with practical situations where ingredients diffuse in or out of a packaging material at liquid or solid food contact points rather than through the headspace.

This method does not require expensive instruments, specialised cells or sophisticated gas measuring techniques. It requires small samples and the technique has greater sensitivity than weighing. The disadvantages are that this method requires specific detectors for each class of penetrant and the test film ideally needs to be translucent.

2.6 ESTIMATION OF PERMEATION

2.6.1 Partition Coefficients

The partition coefficient (K_e) describes the equilibrium partition of a compound between the polymer and the aqueous phase. This coefficient is very useful in indicating if a compound will be sorbed by a polymer.

K_e is independent of concentration in most cases, but above 300 mg/l of limonene, K_e decreased. Absorption of large amounts of limonene affects the physical properties of the polymer, diminishing its capacity to absorb more limonene. The presence of other components in orange oil decreased the affinity of limonene for the polymer (Hotchkiss, 1987).

An onion/garlic flavoured sour cream product packaged in high impact polystyrene (HIPS) was studied for permeation of the probe compounds dipropyl disulphide and dimethyl disulphide. No permeation was detected but examination of the partition coefficient favoured association of the compounds with the HIPS. There was no flavour loss through the package but the compounds were highly soluble in HIPS. The potential amounts of the compounds that could be sorbed by the container far exceeded the amounts present in the product (Toebe et al., 1990).

Partition coefficients were calculated for d-limonene when orange juice was packed in LDPE, EVOH and CoPET. CoPET had the lowest K_e and little affinity for d-limonene. Experimental results verified that d-limonene was not sorbed by CoPET.
Order of K_e : LDPE > EVOH > CoPET (Imai et al., 1990).

Partition coefficients for penetrants in nylon 6 were calculated and again they corresponded well with the observed results (Hatzidimitriu et al., 1988).

2.6.2 Permachor Values

A method of correlating polymer structure and morphology with gas barrier properties has been developed; the correlation coefficients can be used to predict permeability (Salame and Steingiser, 1977; Salame, 1961, 1986, 1990). Using the free volume and cohesive energy density attributes of the polymer, a correlating parameter called the "Permachor" has been developed. When the value is used in the Permachor equation, the gas permeation of known or theoretical structures can be predicted.

Chemical segments of a polymer chain are broken down into discrete segments and assigned a numerical value. The total of the numerical values is the Permachor (π) value. The higher the value, the stronger the forces holding the chains together and the better the barrier properties.

$$\pi = (\Sigma \frac{\pi_i}{n})$$

where π = polymer permachor

π_i = individual segmental values of the backbone and side groups

n = number of individual units in the backbone repeat unit

The π value calculated using tables of values is for amorphous and non-oriented polymers. To correct for crystallinity, π_c can be calculated for the crystalline polymer as:

$$\pi_c = \pi - \ln a$$

a = volume fraction of amorphous content in the polymer

The π value is additive from the structure. The equation for relating gas permeation to Permachor values is :

$$P = Ae^{-s\pi}$$

where   P = permeability at any given temperature

A,s = constants for any given gas at any given temperature

π = permachor of the polymer

Orientation decreases permeability for crystalline polymers due to an increase in tortuosity caused by the lining up of crystallites.

To estimate the reduction in P from orientation:

$$P = (A/T_o)e^{-s\pi}$$

T_o = tortuosity caused by orientation of the crystallites

At about 200-300% orientation:

$$T_o = 1.13/\sqrt{a}$$

The method is most reliable at low temperatures because at high temperatures molecules are in more excited states of motion and give unpredictable results. Some melting of crystallites could occur, giving more amorphous content and increasing permeation.

Work has been carried out with oxygen, nitrogen and carbon dioxide and good agreement with experimental results was obtained. The method can be extended to other gases and vapours if there is no specific interaction or swelling between the penetrant and the polymer so water and organic liquid and vapour permeation could possibly be studied in the same way.

2.6.3 Solubility Parameter (δ)

Free energy is a composite quantity made up of an enthalpy term and an entropy term. One approach to predicting polymer solubility assumes that the enthalpic term is dominant (Hall, 1981).

A solubility parameter δ is defined for both solvent and polymer. δ is a measure of the strength of the intermolecular cohesion in the pure solvent or in the pure polymer.

For the solvent, δ is calculated from the energy of vapourisation and for the polymer it is obtained indirectly and may be estimated from the primary structure

of the chain.

The significance of δ is that polymers are only soluble in solvents of similar δ. This only holds if strong polymer-solvent interactions are absent. As permeation depends on solubility a method such as this for predicting solubility could be useful for flavour compounds.

There are limits to the amount of polymer a solvent will dissolve and the amount of solvent the polymer can absorb. Crosslinked polymers cannot dissolve but show extensive swelling when they come into contact with compatible solvents.

A simple predictive method cannot provide for the whole range of solubility behaviour.

Permeability depends on the interplay of diffusion and solubility parameters. Vapours of organic substances with values similar to the polymer have relatively high solubilities but diffuse more slowly due to larger molecular sizes and often strong interactions with polymer chains.

2.7 APPLICATION OF THE "LAMINATE FILM" METHOD

The use of polymers as barrier films in food packaging applications has led to problems with flavours and aromas being lost from the food inside the package. Traditional methods for measuring the interaction of organic compounds with polymers can involve the use of gas chromatographs and vacuum electrobalances and therefore can be very expensive. Static methods also tend to be time consuming because vapour equilibration is slow. In addition, the sensitivity of these methods decreases with low penetrant vapour pressures.

The measurement of penetrant transmission by absorbance change in a polymer film is as accurate as and usually much faster than common dynamic methods (Holland et al., 1981; Holland and Santangelo, 1984). New ways of measuring permeation of higher molecular weight diffusants such as flavours and aromas may prove successful because of their simplicity.

One example of these new techniques is the "laminate film" method (Holland and Santangelo, 1988). This method has been used by Holland and Santangelo, 1988; to measure the transmission of vanillin in LDPE and nylon 11 films. The present research extended Holland's work and measured permeation of vanillin not only in LDPE, but also in other types of polymers and also used another penetrant, d-limonene.

Permeation was measured at different temperatures, humidities and with varying film thicknesses, to determine the factors affecting the method and the limitations of the technique.

3.0 MATERIALS AND METHODS

In the "laminate" method, the penetrant source (supply film) is applied to one face of a test film. The other face is in intimate contact with a "collector" film. The permeation of a penetrant leads to a change in the UV absorbance of the collector film with time, proportional to the amount of penetrant which has diffused through the test film. This absorbance change is measured directly by a spectrophotometer, using the double film "laminate" if the test film is transparent, or otherwise on the separated collector film. The "laminate" can be assembled and disassembled with little loss of penetrant and simple layering of the films under tension or pressure is sufficient for sealing.

The above technique is an example of the transmission (or permeation) method of measuring diffusion where the usual gas or liquid supply and collector systems are replaced by a completely solid state system. Another possibility for measuring parameters for permeability calculations is the sorption technique. This is the method used in this research. Here, the supply film is applied to both faces of the test film which is also the collector film. Penetrant uptake is measured as before. Solubility is measured at the equilibrium point where the test film absorbs no more penetrant. The structure for the sorption method is therefore, supply film/test film/supply film and for the transmission method it is supply film/test film/collector film.

The supply and collector films must be highly permeable and good solvents for the penetrants to eliminate concentration gradients in the films which would distort the ideal concentrations across the faces. Ethyl cellulose is very permeable to common gases and was used. The supply film can be prepared by conditioning a suitable highly permeable polymer over a penetrant until the desired concentration is reached. Alternatively, the film can be cast with the penetrant and polymer dissolved in a solvent. The latter method is preferred especially if the saturated vapour pressure of the penetrant is low. Casting the film with the penetrant allows saturated films to be made. The supply films used in this research were made by casting. When measuring the permeability it is desirable to have a constant supply concentration so a thick, highly permeable, high concentration film is required.

3.1 MATERIALS

3.1.1 FILMS

Three film samples were obtained from Wrightcel Packaging NZ Ltd, Feilding, New Zealand. These were:

Low Density Polyethylene	44 μm thick
Nylon 6	16 μm thick
Nylon 6 coated with polyvinylidene chloride on one side	17 μm thick

Three samples of ethylene-vinyl alcohol copolymer films, with different ratios of ethylene, were obtained from the Kuraray Co., Ltd., Japan. These samples were:

EF-XL (XL15, biaxially oriented)	15 μm thick
EF-F (F15, 32 mol % ethylene)	15 μm thick
EF-E (E20, 44 mol % ethylene)	20 μm thick

3.1.2 Organic Compounds

The two flavour compounds used were:

D-limonene (MW = 136.2) (Sigma Chemical Company, St. Louis, U.S.A.)

Vanillin (MW = 152.15), laboratory grade (BDH Chemicals, Poole, England)

3.1.3 Other Chemicals

The other chemicals listed here were used in the preparation of the supply film. These were:

Ethyl cellulose, GPR (BDH Chemicals, Poole, England)

Ethyl acetate, laboratory grade (Ajax Chemicals, Auckland, New Zealand)

Chloroform, AR grade (Ajax Chemicals, Auckland, New Zealand)

3.2 METHODS

3.2.1 Preparation of 1 Molar Supply Films

The required amount of the test compound (d-limonene or vanillin) to give a 1M concentration in the film was weighed out. These weights were 0.356g for vanillin and 0.319g for d-limonene. These weights were calculated as shown in Appendices 3.1 and 3.2.

In the case of vanillin, sufficient chloroform was added to just dissolve the crystals. Ethyl acetate was then added to the d-limonene or vanillin solution to make the volume up to 20 ml. 2.7g of ethyl cellulose was added and the mixture was allowed to stand until this softened and a uniform polymer solution was obtained. Glass plates were covered with polyester film (oven bags) and clamped into a thin layer chromatography plate spreader. A 0.025mm film of the ethyl cellulose polymer containing the d-limonene or vanillin was cast. The film was dried overnight on the glass plates at 30°C. When dry, the film was peeled off the polyester.

3.2.2 Film Thickness

The thickness of the films were determined using a Mitutoyo Digimatic Indicator, (Model IDC - 112E, Tokyo, Japan).

3.2.3 Preparation of the Test Film

The test films were stored in desiccators over silica gel to prevent moisture uptake until they were required. The films were cut to size (3 cm x 3.5 cm). The film was then placed between the two layers of the supply film in the "laminate", as shown in Figure 3.1.

3.2.4 Film Arrangement and Testing for the Sorption Method

Two pieces of the supply film containing vanillin or d-limonene and the required number of pieces of test film were cut. The number of pieces of test film required

depends on whether one, two or four thicknesses were to be tested. One piece of the supply film was laid on top of the test film which was in turn laid on top of the second piece of supply film. A reactive collector was not required as vanillin absorbs strongly in the UV region. If the test compound does not have a suitable spectrum, the collector film can be weighed on a microbalance at intervals or a suitable reactive system can be devised.

The "laminate" films were taped to a beaker and aluminium foil was used to seal the "laminate" and prevent losses. The arrangement of films is shown in Figure 3.1, i.e. aluminium foil/supply film/test film/supply film.

Figure 3.1 Film Arrangement for Permeability Measurements.
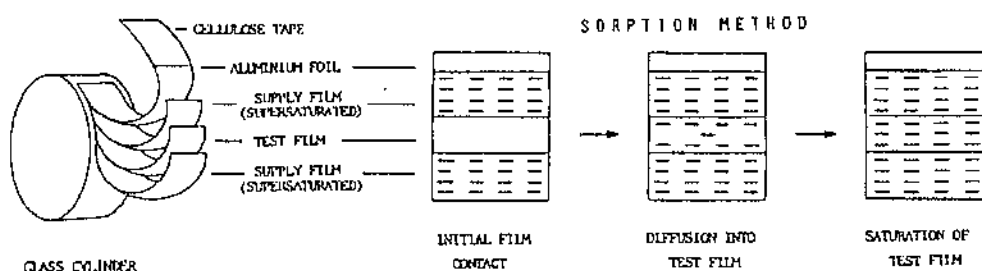
For volatiles, contact is not essential but large air gaps should be avoided as the diffusion coefficient in air is 1000 times larger than in liquids or polymers. Inefficient contact, however, does not necessarily lead to a marked reduction in transfer between films.

The film to be measured was removed and slotted back at regular intervals. Each film was tested in triplicate.

3.2.5 Test Conditions

The "laminate" systems were placed in incubators at 10°C, 25°C and 40°C. Ethylene-vinyl alcohol copolymers were also tested at 90% relative humidity, RH, by storing the "laminates" in desiccators over saturated potassium nitrate solution at 25°C.

3.2.6 Test Times

The time intervals at which the absorbance of the film was measured varied for each flavour/polymer combination tested. The initial measurements were made at intervals of between 6 minutes to one hour and when the permeation rate slowed down as equilibrium was reached, the measurements were made once a day.

3.2.7 Test Method

A UV/visible spectrophotometer, Pharmacia LKB Ultrospec II (Model 80-2091-73), was used to measure the change in absorbance in the test film. For vanillin, the wavelength used was 275 nm and measurements were made at 215 nm for d-limonene. The spectrophotometer was zeroed using a new piece of the test film. The test film was removed from its position in the "laminate" system at the required time intervals. It was clipped to the brass cell holder, shown in Figure 3.2. The cell holder was placed on the base plate in the spectrophotometer and the film's absorbance was measured.

Figure 3.2 Cell Holder and Base Plate
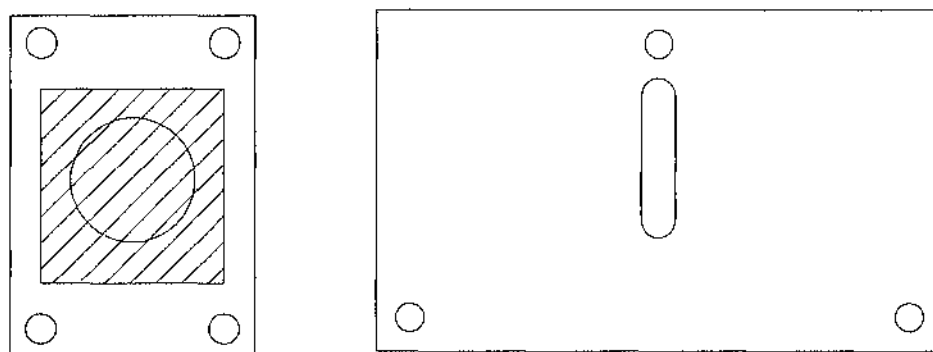
Cell Holder and Test Film   Base Plate

3.3 ANALYSIS OF RESULTS

Plots of the changes in absorbance with time for the polymer-penetrant combinations tested were constructed. From these graphs the equilibrium absorbance value and $t_{1/2}$, the time to reach half this maximum value were obtained.

The maximum absorbance value that could be measured with the spectrophotometer was three absorbance units. For experiments which exceeded this value before steady state was reached, the method described by Hayakawa, 1974; for predicting equilibrium values was used to estimate the equilibrium absorbance. This value was required to enable sorption plots to be constructed for further analysis of the data.

Sorption plots were constructed by plotting the $\frac{\text{absorbance at time } t}{\text{absorbance at steady state}}$

against $\frac{\text{time}^{1/2}}{\text{film thickness}}$.

The diffusion coefficient, D, was then calculated using the half time and initial slope methods. For the half time method :

$$D = 0.04919 / t_{1/2} / x^2$$

where $t_{1/2}$ = time taken to reach an absorbance value that is one half of the steady state value (s)

x = thickness of the film (cm)

D = diffusion coefficient

For calculation of the diffusion coefficient by the initial slope method :

$$\frac{\text{Abs}_t}{\text{Abs}_\infty} = 2.257 \, (Dt)^{1/2} / x$$

where Abs_t = absorbance at time t

Abs_∞ = absorbance at steady state

D = diffusion coefficient

t = time (s)

x = film thickness (cm)

Slope of sorption plot = $\frac{\text{Abs}_t}{\text{Abs}_\infty} / (t^{1/2} / x)$

$$\therefore \quad D = (\text{slope})^2 \times 0.1963$$

The saturation solubility, partition coefficients, permeability coefficient and flux were also calculated. Sample calculations are shown in Appendix 4.1.

4.0 RESULTS AND DISCUSSION

The absorbances were plotted against time for all films, temperatures and penetrants as shown in Figure 4.1. In all cases, the lines plotted were the mean values of three replicate measurements. The error bars represented ± one standard deviation, (SD_{n-1}).

The most important section of the plots of changes in absorbance with time were the initial linearly increasing region. Sorption plots were constructed from this data. Linear regression was used to find the lines of best fit. Again, the lines plotted were mean values of three replicate readings with error bars of ± one standard deviation, (SD_{n-1}). The slopes of the lines and the absorbance values at steady state for all films and vanillin are shown in Appendices 4.2 to 4.5.

Diffusion coefficients were calculated from the slopes of the sorption plots. Saturation solubilities, partition and permeability coefficients and fluxes were also calculated as described by Holland and Santangelo, 1988.

4.1 COMPARISON OF FILMS WITH VANILLIN

The comparison of changes in absorbance with time for two layers of low density polyethylene, nylon 6, polyvinylidene chloride coated nylon 6 and ethylene-vinyl alcohol films with vanillin at 25 and 40°C are shown in Figure 4.1. This shows the absorbances up to 8000 hours, but as the initial absorbance values were the most important, the first 300 hours for each film and temperature were replotted in Figure 4.2. As the nylon 6 was coated on one side, only two layers of coated nylon 6 were used. This ensured that the polyvinylidene chloride coating and not the nylon 6 was in contact with the vanillin.

4.1.1 Comparison of Rates of Uptake

The general trends in Figures 4.1 and 4.2 show that low density polyethylene (LDPE) and polyvinylidene chloride (PVDC) coated nylon 6 had the lowest rates of sorption of vanillin and they sorbed the least vanillin of all the films. Nylon 6 and ethylene-vinyl alcohol (EVOH) films rapidly picked up large amounts of vanillin. It can also be seen that increasing the temperature, increased the rate of uptake of vanillin and the amount sorbed, particularly for LDPE and PVDC coated nylon 6. Temperature had less effect with nylon 6.

It can be seen that low density polyethylene rapidly picked up vanillin and equilibrium was reached very quickly. LDPE reached steady state before any of the other films. It can also be seen that even at 40°C, LDPE sorbed the lowest quantity of vanillin for all the films tested.

Nylon 6 rapidly picked up vanillin and sorbed very large amounts of vanillin. The quantity of vanillin sorbed by nylon 6 became unmeasurable after only 300 hours.

Coating the nylon 6 film with polyvinylidene chloride slowed down the rate of sorption and decreased the amount of vanillin sorbed. At 25°C, there was a long time period where there was little change in absorbance as not much vanillin was picked up. After 5000 hours, (approximately 30 weeks), the absorbance began to increase rapidly. This was possibly due to vanillin breaking through the coating

Figure 4.1 Changes in Absorbance with Time for Two Layers of Polymer Films with Vanillin At 25 And 40°C for 8000 Hours
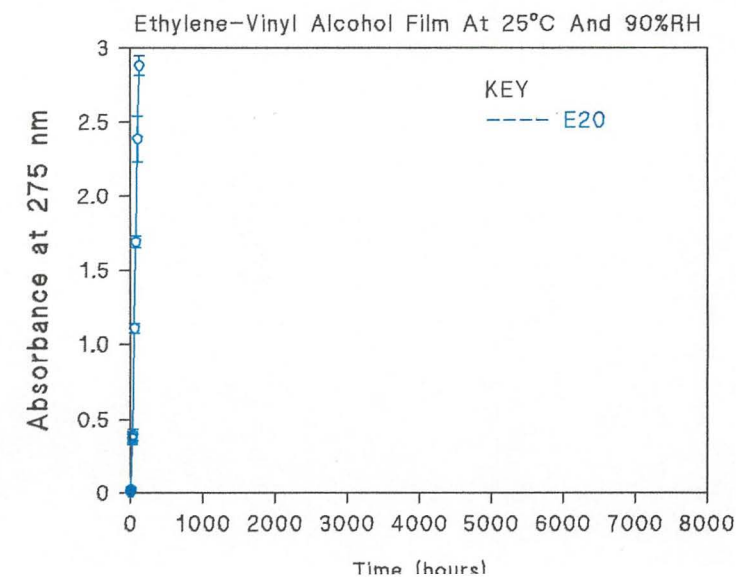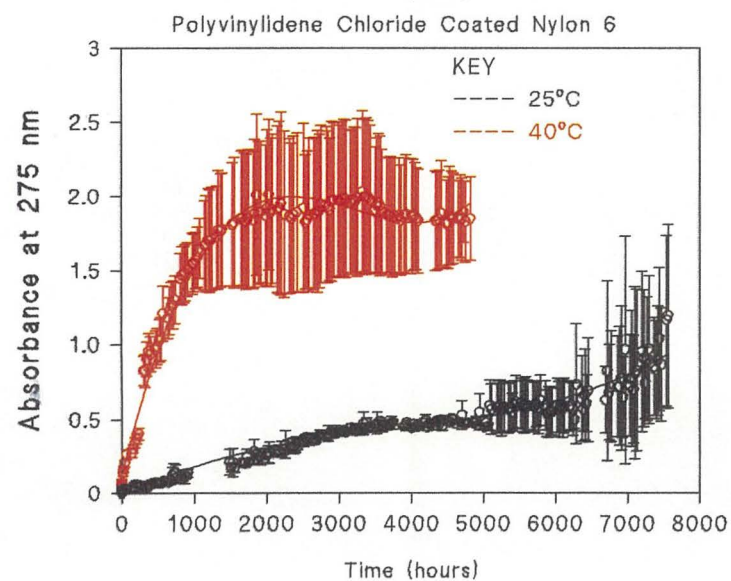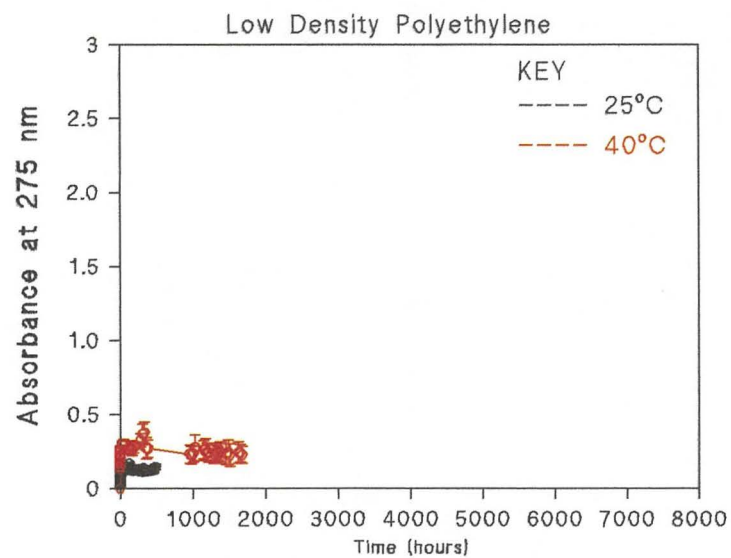
Figure 4.2 Changes in Absorbance with Time for Polymer Films With Vanillin for 300 Hours

Low Density Polyethylene, Two Layers At 10, 25 And 40°C
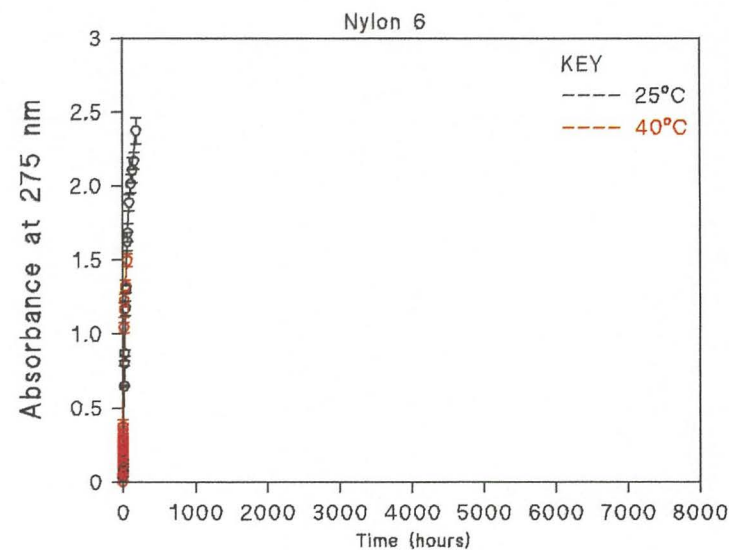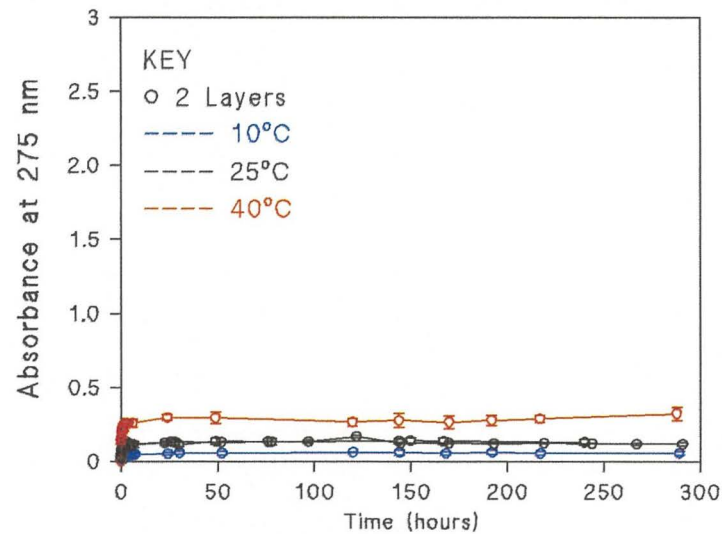
Nylon 6, One, Two And Four Layers At 25 And 40°C
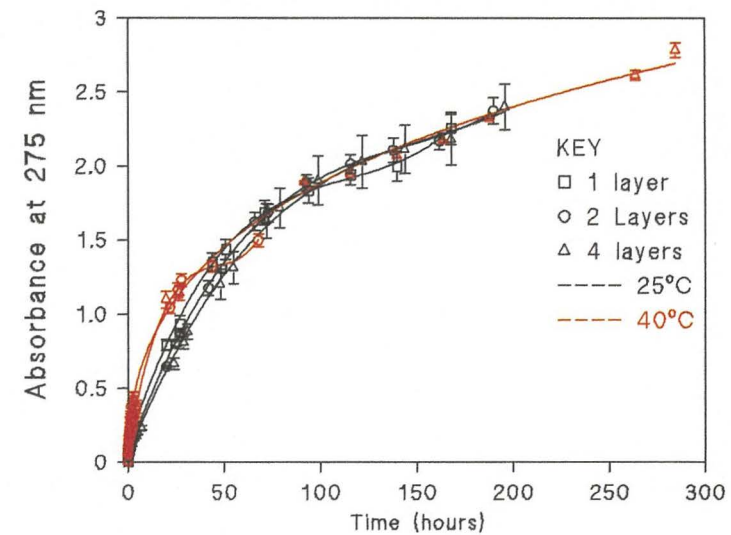
Polyvinylidene Chloride Coated Nylon 6, Two Layers At 25 And 40°C
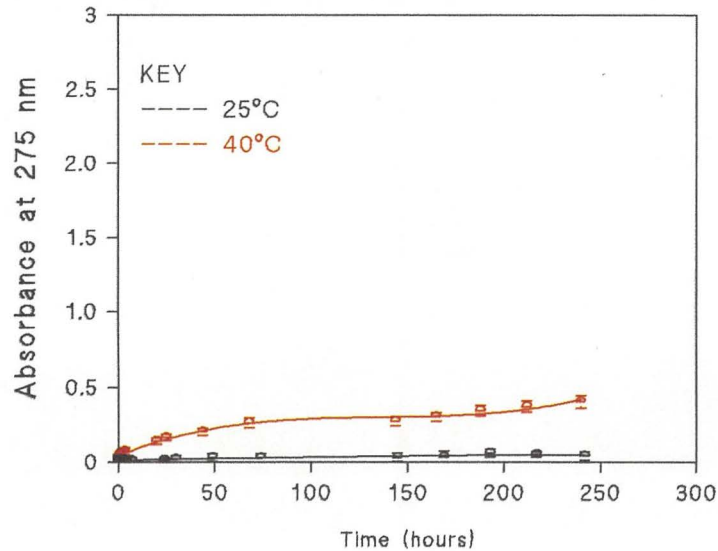
Ethylene-Vinyl Alcohol Films, One And Two Layers At 25°C And 90% RH

54
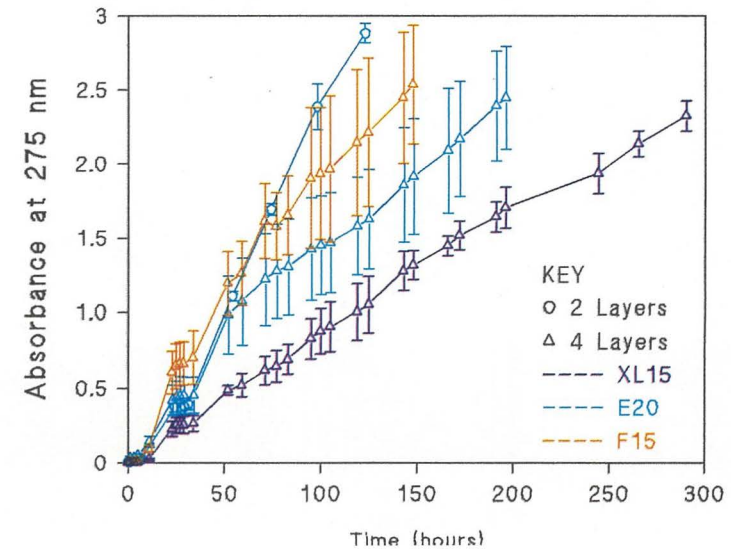
and beginning to be sorbed by the nylon 6. Figure 4.2 shows that initially the PVDC coated nylon 6 behaved in a similar manner to LDPE, that is, it sorbed very little vanillin.

The ethylene-vinyl alcohol films showed similar behaviour to the nylon 6 film. EVOH is a good barrier to odours including vanillin (Foster, 1986) but it is moisture sensitive. As these experiments were conducted at 90% RH, EVOH would not be expected to exhibit good barrier properties. As with nylon 6, all experiments became unmeasurable after 300 hours, before steady state was reached. The biaxially oriented film, XL15, sorbed the least vanillin of all the EVOH films. Orientation of a film reduces permeability by lining up the crystallites and forcing the permeating molecule to take a more tortuous path through the polymer (Salame, 1977, 1990; Giacin, 1987).

The ethylene-vinyl alcohol film, F15, contains 32 mole % ethylene. E20 contains 44 mole % ethylene. As the ethylene content increased, the amount of vanillin sorbed decreased as the polymer no longer had the same affinity for sorbing vanillin. Ikegami et al., 1991; found the same results for ethylene content and orientation with EVOH films and alcohols.

The trends observed confirmed previous research results. According to Salame, 1977 and Brody, 1989; compounds that have a structure similar to the functional group of the polymer or whose polarity is similar will be strongly absorbed by the polymer; that is, like dissolves like.

By examining the structures of the polymers and vanillin, (Figure 4.3), it was expected that LDPE and PVDC which are less polar than nylon 6 and EVOH would sorb less vanillin.

In a practical situation, PVDC would be a better barrier to vanillin than EVOH or nylon 6. While some vanillin would still be lost from the food to the PVDC much smaller quantities would be lost during the food's shelf life than if it were packaged in EVOH or nylon 6.

Figure 4.3 Structures of the Polymers and Vanillin

CHO

[Vanillin structure: benzene ring with CHO, OCH$_3$, OH substituents]

OH

Vanillin

$$-(- CH_2 --- CH_2 -)_n$$ Low Density Polyethylene

$$-(- CH --- CH -)_n$$ Polyvinylidene Chloride
with Cl substituents

$$-(- N --- (CH_2)_5 --- C -)_n$$ Nylon 6
with H and O

$$-(- CH_2 --- CH_2 -)_m -(- CH_2 --- CH -)_n$$
with OH substituent
Ethylene-Vinyl Alcohol
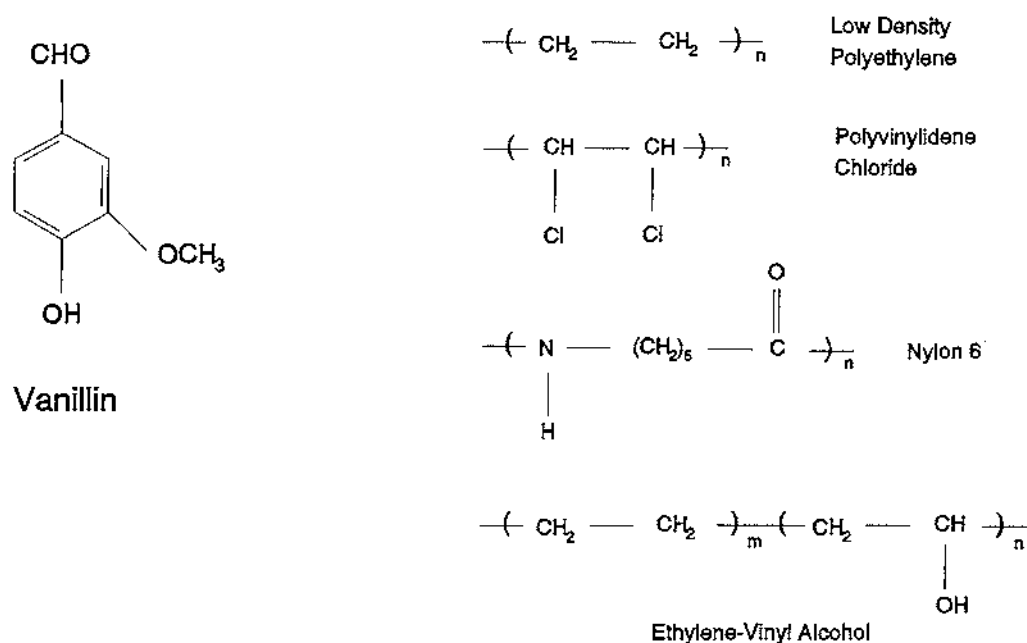
4.1.2 Long Term Effects

Over long periods of time, the results were less reproducible. This can be seen in Figure 4.1 for PVDC coated nylon 6. It is shown more clearly in Figure 4.4 for LDPE. The effect was more pronounced at 40°C.

There were a number of reasons for this. Firstly, as time progressed the concentration of vanillin in the film increased. Permeation behaviour can be concentration dependent and authors such as DeLassus, 1987; Zobel, 1982, 1985; Baner et al., 1986 and Mohney et al., 1988; have found that at high concentrations, deviations occur from ideal, theoretical behaviour due to effects such as plasticisation of the film.

Oxidation of vanillin could also have occurred, particularly at higher temperatures and this would cause variation in absorbance readings.

Figure 4.4 Changes in Absorbance with Time for Low Density Polyethylene with
Vanillin At 10, 25 And 40°C for 2500 Hours
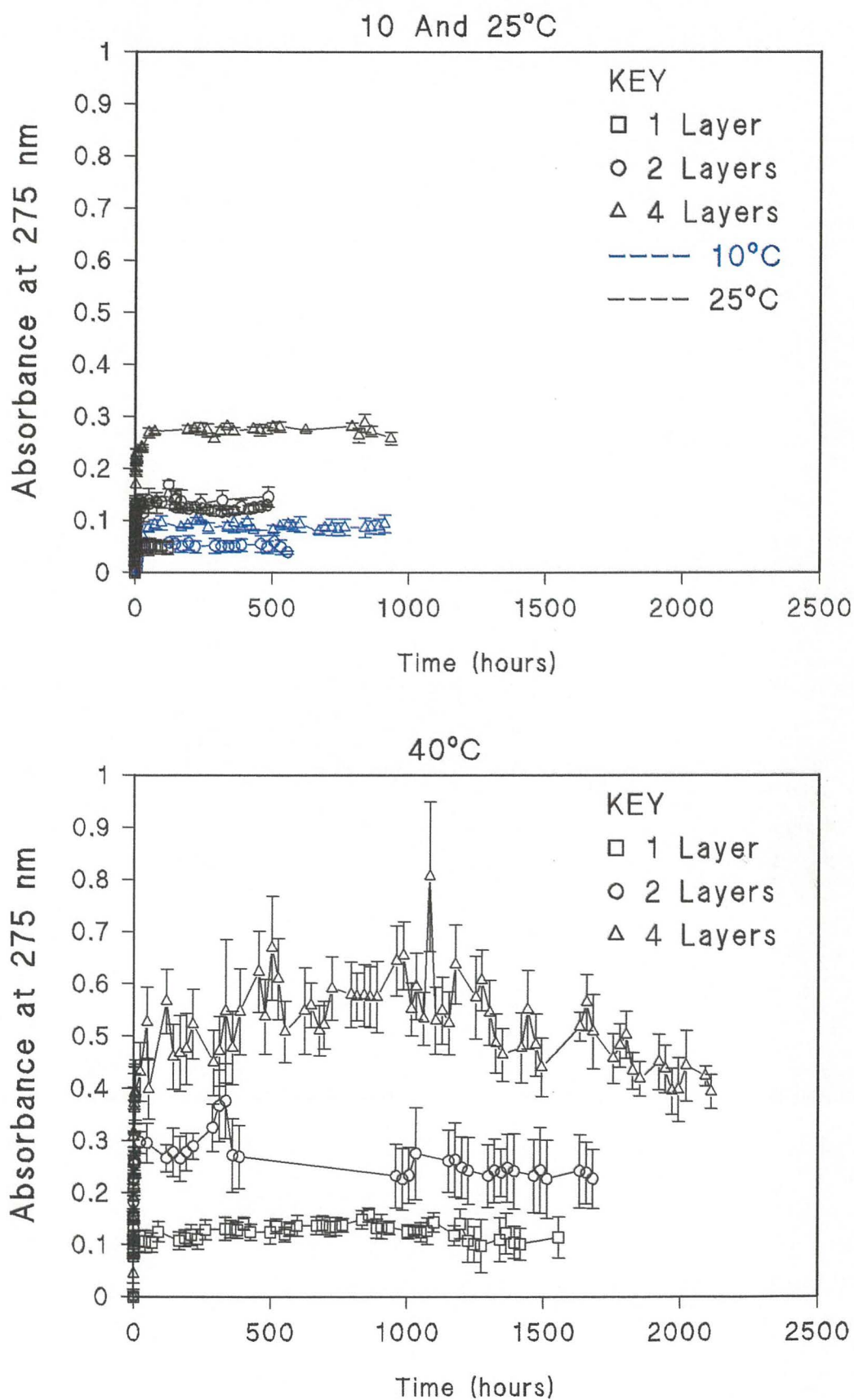
Nylon 6 film was found to turn yellow as the experiments progressed. This would also affect the absorbance readings. Hatzidimitriu et al., 1988; also reported yellowing of nylon 6 film which was thought to indicate a side reaction between 2-heptanone and nylon 6.

Another long term effect was demonstrated by the PVDC coated nylon 6. After 5000 hours, it appeared that vanillin broke through the coating and began to be absorbed by the nylon 6.

Johnson, 1989; Tarkenton, 1989; Giacin and Hernandez, 1987; Kail, 1984 and Hagenbaugh, 1987; all found that coated films provided good barriers at low concentrations for long periods of time but this enhanced barrier protection was diminished at high penetrant concentrations.

4.1.3 General Effect of Layers

The number of layers of polymer films did not affect the permeation behaviour. This can be seen in Figures 4.2 and 4.4. Increasing the number of layers did not affect the rate of uptake of vanillin or the way in which the film sorbed vanillin. The only difference was in the amount of vanillin sorbed at steady state. Therefore, more layers can safely be used to allow more accurate measurement of initial rates and enable diffusion coefficients to be measured accurately.

For LDPE, the more layers used, the more vanillin was finally sorbed. Stepek et al., 1987; Anon, 1987 and Murray, 1987; also found that more flavour was lost in a thick walled container than in a thin one.

4.1.4 General Effect of Temperature

As temperatures increased from 10°C to 40°C, sorption of vanillin was faster and more vanillin was sorbed (Figures 4.1 and 4.2). DeLassus et al., 1988a; Hotchkiss, 1987; Durr et al., 1981 and Mannheim et al., 1987; all found that increasing the temperature increased, sorption of compounds and that permeation increased as temperature increased. Therefore, temperature control is very important in these

experiments to get accurate information about permeation. Temperature fluctuations may have been another reason for the large error in experiments at 40°C. Absorbance readings were taken at room temperature (15-20°C). Samples at 40°C would change in temperature more quickly than those at 10 or 25°C as the temperature gradient is larger. Temperature fluctuations would therefore affect the readings at 40°C more than those at lower temperatures and hence errors may have been larger. The "laminate film" method should be conducted in temperature controlled rooms if possible to eliminate these effects. As temperature has a large effect on permeation, there is a danger in extrapolating data to higher or lower temperatures as permeability coefficients may not follow a linear relationship.

4.1.5 Reproducibility of the Method

The results of two separate experiments of three replicates each for two layers of LDPE and vanillin at 25°C are plotted in Figure 4.5. The method was very reproducible. This was shown by the good agreement of replicates, demonstrated by the small error bars obtained.

Errors became larger after long periods of time when effects such as oxidation of vanillin began to interfere. As the most important data is gathered over the first few hours or several days at the most, then these errors have little effect on further analysis of results.
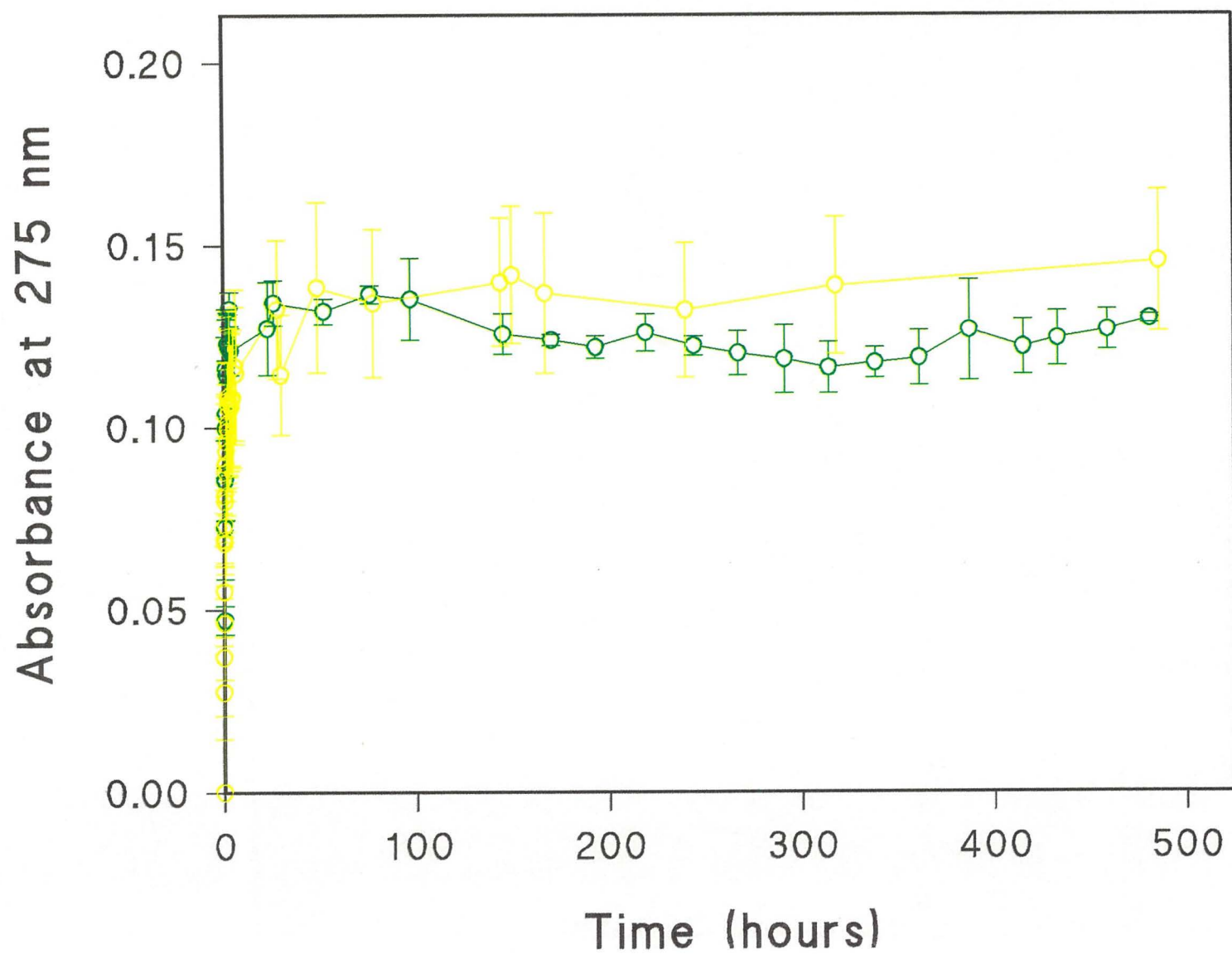
4.2 SORPTION PLOTS FOR VANILLIN

Sorption plots were constructed for all films and temperatures with vanillin. These allowed a more detailed examination of the data, rather than just the general trends that were observed from the changes in absorbance with time graphs.

4.2.1 Low Density Polyethylene

The first 6 hours of the changes in absorbance with time for LDPE is shown in Figure 4.6. After two hours all experiments began to level off as steady state was reached. The most important region of the absorbance versus time graph was the initial straight line region as calculations of diffusion, solubility and permeability constants were carried out on this data. The sorption plots for LDPE were therefore constructed on the data for the first two hours.

Three sorption graphs at 10, 25 and 40°C demonstrating the effect of layers are shown in Figure 4.7. As expected from the absorbance graphs, layers of polymers had little effect on sorption. The slopes of the lines for one, two and four layers were very similar.

Three sorption graphs of one, two and four layers of LDPE to show the effect of temperature are plotted in Figure 4.8. In this case the effect of temperature was very noticeable. Sorption increased as temperature increased. There was a large difference between 10 and 25°C. There did not appear to be much difference between 25 and 40°C.

4.2.2 Nylon 6 and Polyvinylidene Chloride Coated Nylon 6

The sorption graph for 1000 hours for nylon 6 and PVDC coated nylon 6 is shown in Figure 4.9.

As demonstrated by the absorbance graphs PVDC coated nylon 6 sorbed less vanillin and sorbed it more slowly than nylon 6 and LDPE.

Figure 4.6 Changes in Absorbance with Time for Low Density Polyethylene with Vanillin at 10, 25 And 40°C for 6 Hours
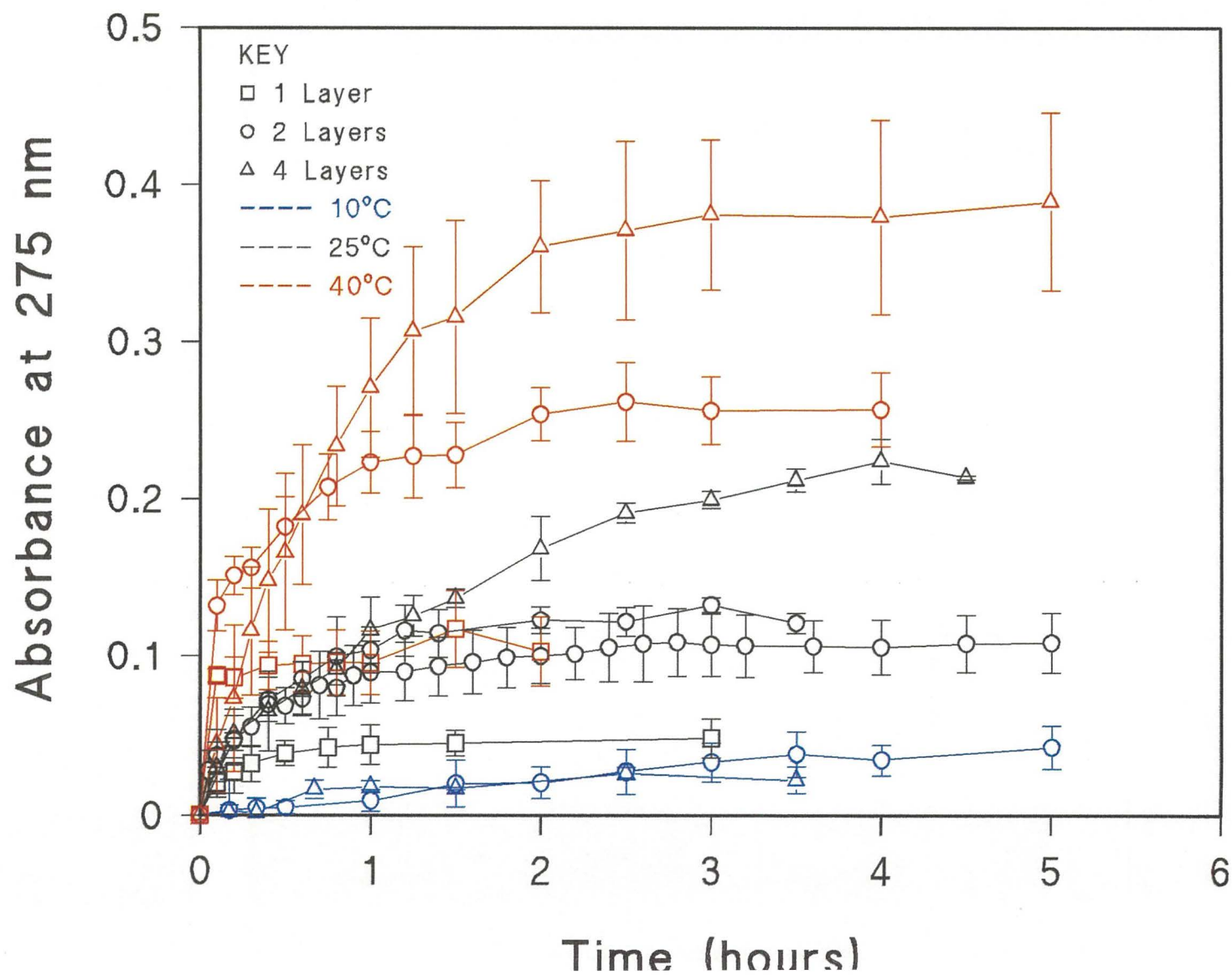
Figure 4.7 Sorption Plots for Low Density Polyethylene with Vanillin at 10, 25 And 40°C
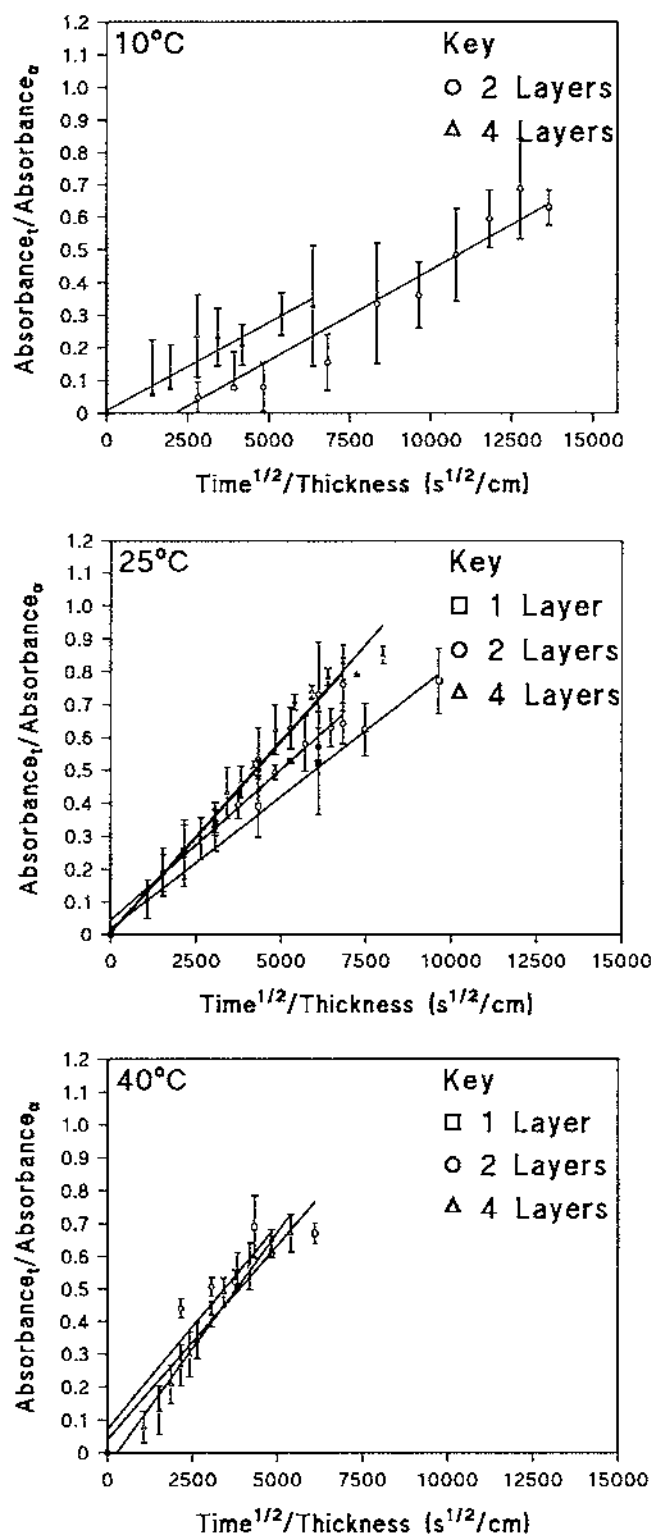
Figure 4.8 Sorption Plots for One, Two and Four Layers of Low Density Polyethylene with Vanillin
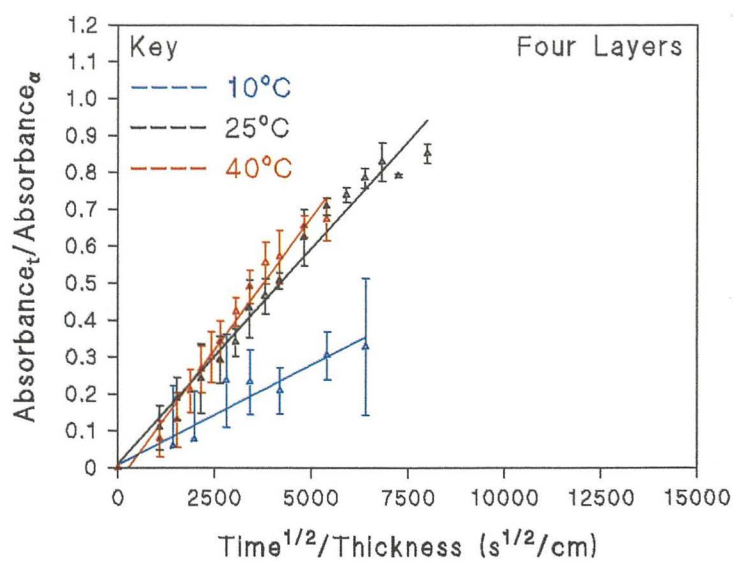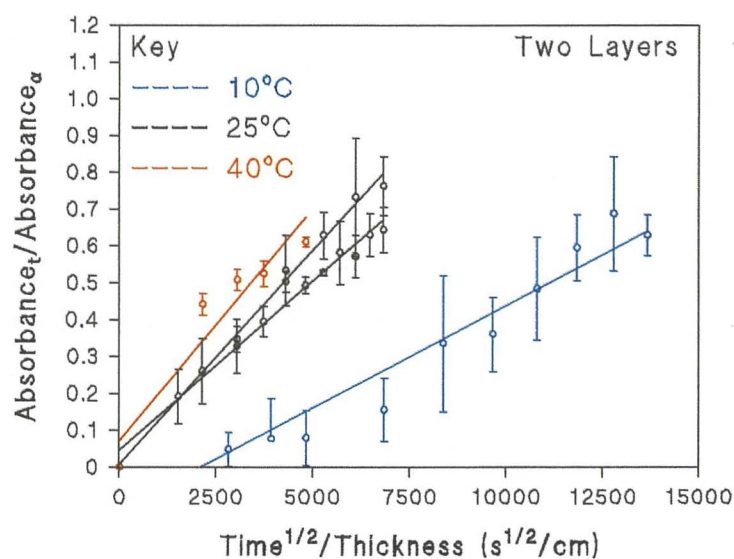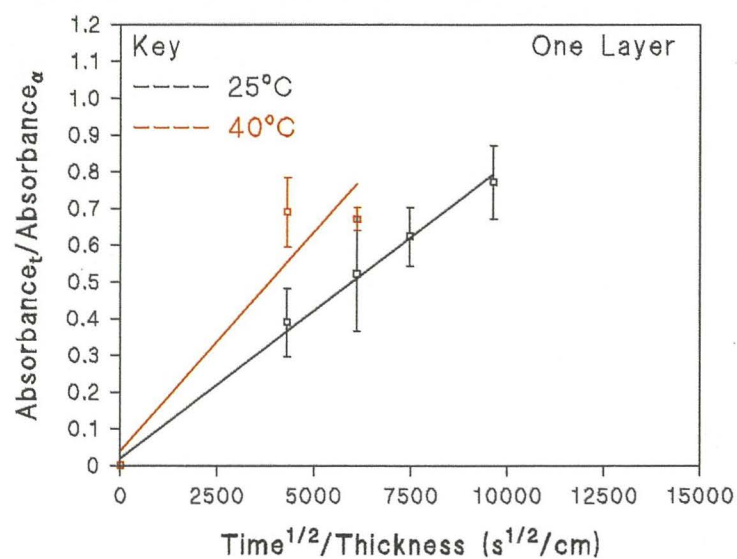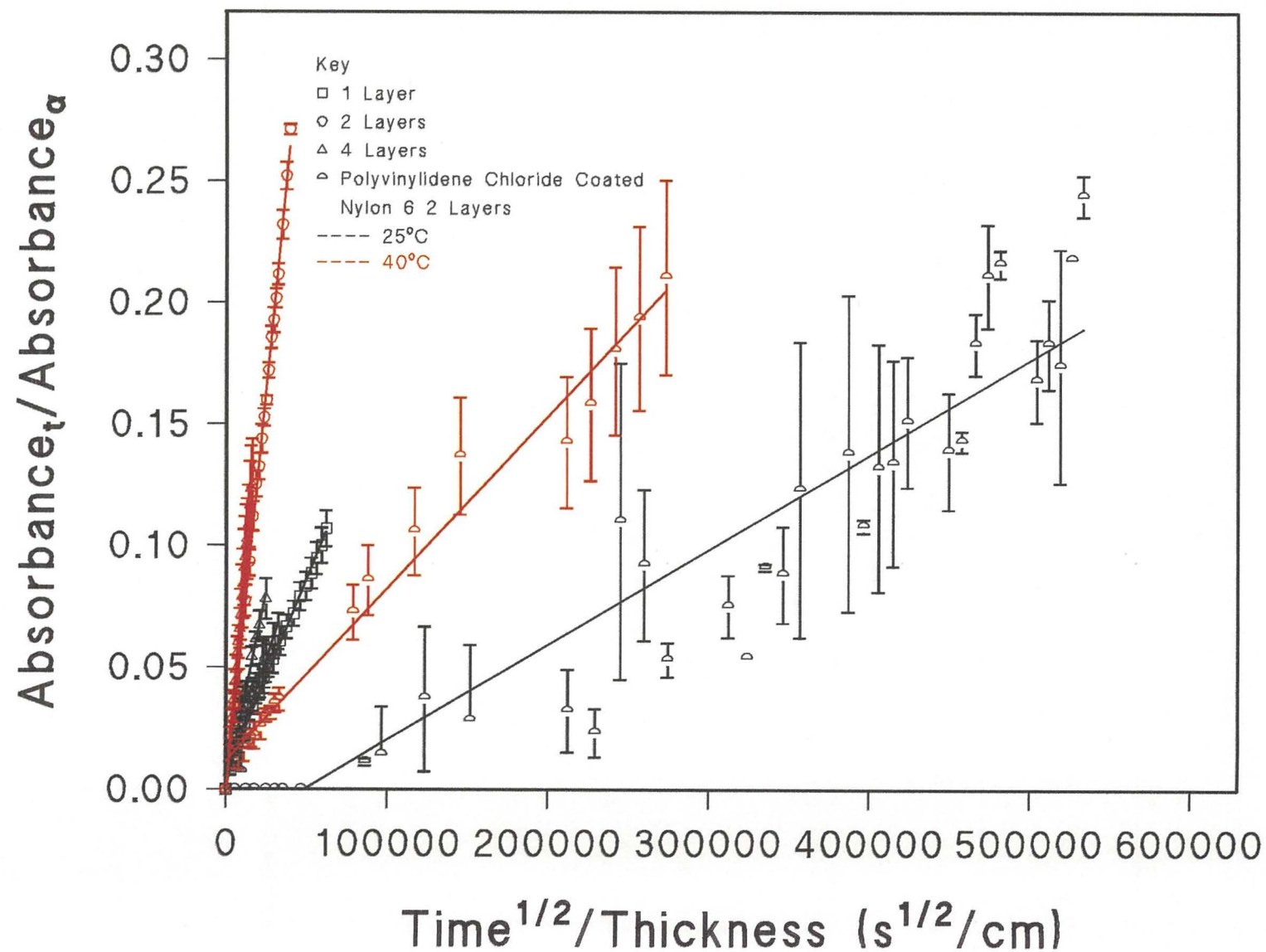
For nylon 6, it can be seen that increasing the number of layers had little effect on the rate of sorption. Also, it was obvious that temperature again increased the rate and amount of vanillin sorbed. Increasing the temperature had more effect on sorption than increasing the number of layers.

Sorption graphs confirmed the effects already observed from the absorbance versus time graphs, but more detailed information about what occurred as sorption progressed can be obtained by examining the short time data more closely. For example, compared to LDPE, nylon 6 had a much slower rate of uptake of vanillin, which was not obvious from the absorbance versus time graphs. Four layers of nylon 6 at 40°C had an absorbance of 0.275 nm at 35000 $s^{1/2}$ /cm, (Figure 4.9). Four layers of LDPE at 40°C had an absorbance of 0.275 at 20000 $s^{1/2}$ /cm, (Figure 4.8). Therefore, more flavour scalping of vanillin would occur if nylon 6 was used as the packaging material.

4.2.3 Ethylene-Vinyl Alcohol Films

The initial 40 hours of the absorbance versus time graph for EVOH films and vanillin is shown in Figure 4.10.

There was very little change in absorbance up to 10 hours after which there was a large and rapid increase. EVOH is moisture sensitive and it loses its barrier properties when it becomes wet. DeLassus and Hilker, 1987 and DeLassus et al., 1988a, 1988b; found that permeability of EVOH polymers increased as RH increased.

These experiments were carried out at 90% RH, but the films were not conditioned before the experiment began. Therefore, it appeared that during the first 10 hours the EVOH films were picking up moisture. Once they equilibrated, vanillin began to be sorbed. The moisture plasticised the film and EVOH rapidly sorbed vanillin.

The sorption graphs shown in Figure 4.11 were taken between 10 and 100 hours when sorption of vanillin appeared to have begun. The same trends observed in the absorbance versus time graphs were also shown by the sorption plot.

This experiment demonstrated the importance of relative humidity when dealing with moisture sensitive barrier films. Films should be conditioned before they are brought into contact with the flavour compounds to get an accurate estimation of the permeability of the moist film.

Figure 4.10 Changes in Absorbance with Time for Ethylene-Vinyl Alcohol Films with Vanillin at 25°C and 90% RH for 40 Hours
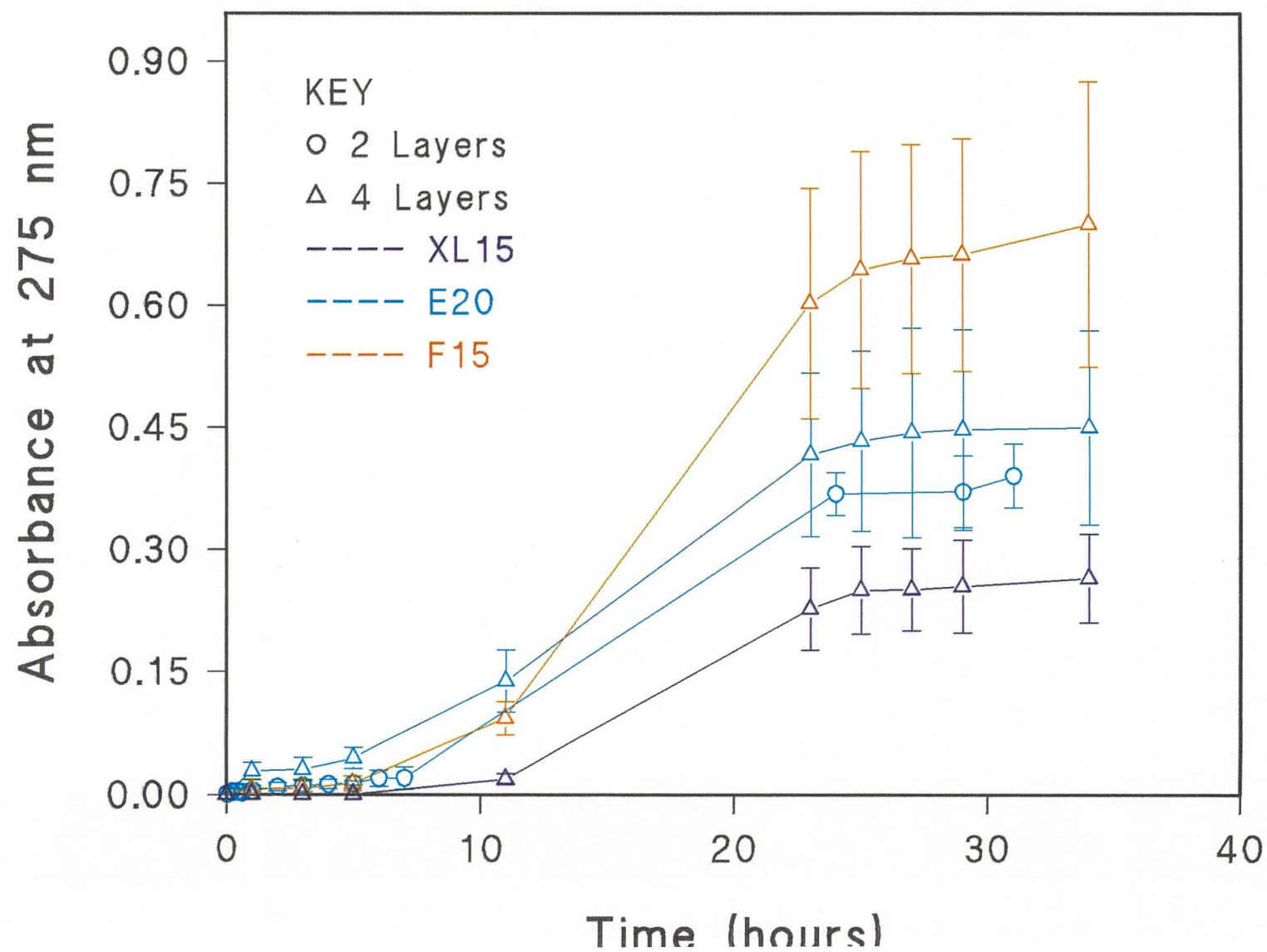
Figure 4.11 Sorption Plot for Ethylene-Vinyl Alcohol Films with Vanillin at 25°C and 90% RH
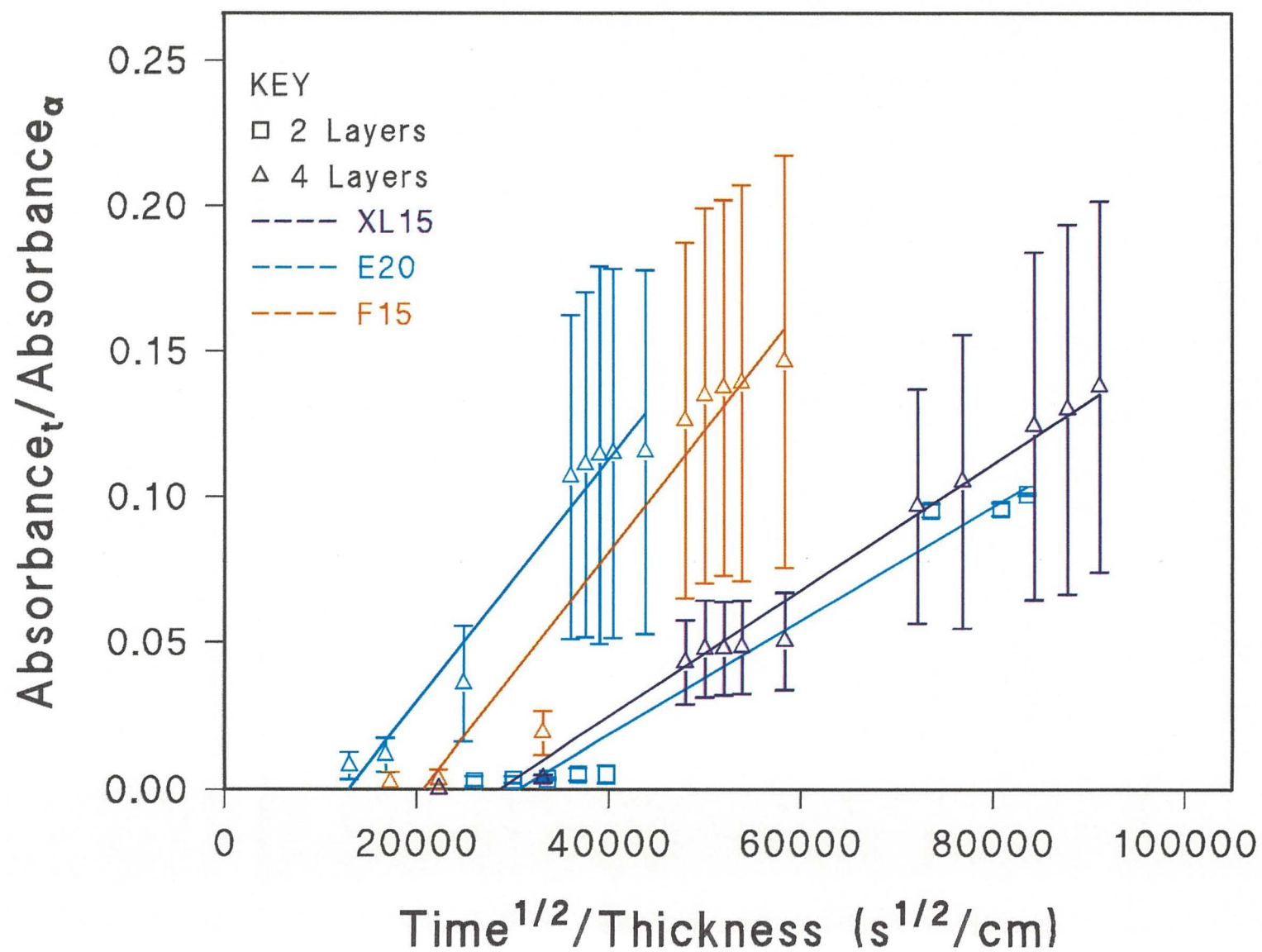
4.3 DEVIATIONS FROM EXPECTED CHANGES IN ABSORBANCE WITH TIME FOR VANILLIN

Anomalous absorbance versus time curves were found for some experiments with two layers of nylon 6 and PVDC coated nylon 6 with vanillin at 25°C. Deviations were also found for experiments with one, two and four layers of nylon 6 and two layers of PVDC coated nylon 6 at 10°C with vanillin. These are included to illustrate the types of anomalies that can occur. Further analysis was not performed on this data as it showed some unusual trends.

4.3.1 Nylon 6 and Polyvinylidene Chloride Coated Nylon 6 at 10°C

Figure 4.12 shows the changes in absorbance with time for two layers of PVDC coated nylon 6 and one, two and four layers of nylon 6 at 10°C. There was a large scatter of points and large variation in the replicate samples which was shown by the large error bars at each point. The concentration of vanillin in the film was very low, indicated by the small absorbance values. Such low absorbances may have been reaching the limits of detection and accuracy of the spectrophotometer which may account for some of the error.

Oxidation of vanillin may also have occurred after such a long time. Oxidation would have a more pronounced effect at such low concentrations, as a very small amount of oxidised vanillin would affect the absorbance dramatically.

There was a period of rapid uptake, indicated by a vertical line, followed by a long period with only a small change in absorbance. Again, the error bars were very large due to variations in replicate samples that have been discussed in Section 4.1.2.

It was possible that there was a layer on the surface of the nylon 6 that held the vanillin. As the surface of the nylon 6 had been corona treated to roughen it, the vanillin could easily have been sorbed into the voids on the surface. Anomalous permeation curves with nylon 6 were also found by Hatzidimitriu et al., 1988. They attributed the high initial rates to microcracks, internal pores and regions of low

Figure 4.12 Changes in Absorbance with Time for Nylon 6 and Polyvinylidene Chloride Coated Nylon 6 with Vanillin at 10°C
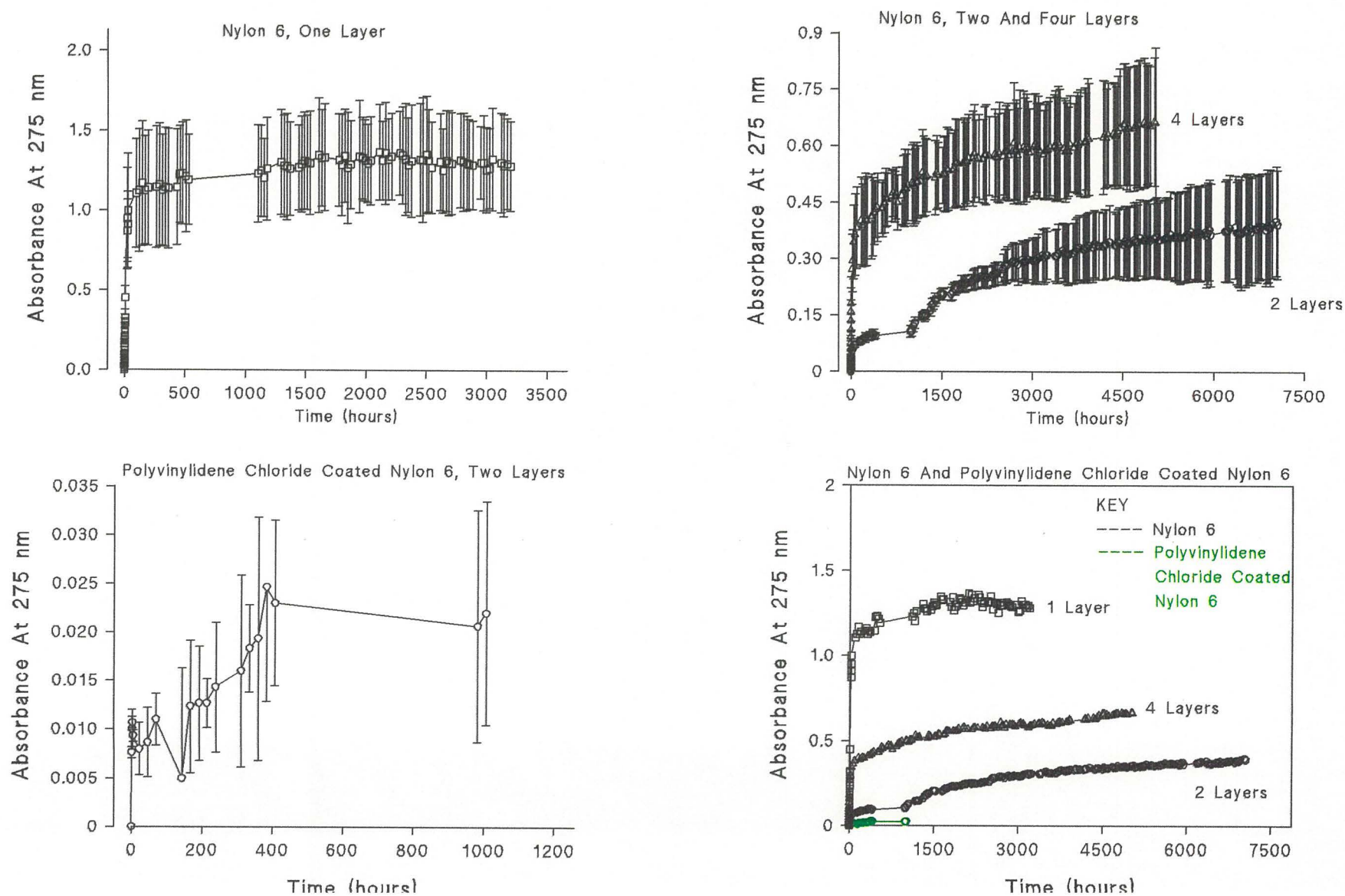
density in the polymer. As sorption proceeded the imperfections were reduced by swelling and rearrangement of the polymer structure and a final steady state was reached.

Alternatively, the nylon 6 may have picked up a surface layer of a contaminant from benches when it was cut.

Another possibility is that at this temperature, water dissolved vanillin on the surface of the nylon 6. As these experiments were carried out when the room temperature was 25-30°C, there was condensation forming on the film when the absorbance was measured.

As nylon 6 is moisture sensitive and relative humidity was not controlled in these experiments, it is possible that ambient RH could have been very different between experiments and may have had more effect on some days (if it was much higher or lower) than on other days.

Figure 4.12 also shows that PVDC coated nylon 6 sorbed less vanillin at a slower rate than nylon 6. This trend was found in the typical change in absorbance with time plots in Figures 4.1 and 4.2 and still occurs here even though the data shows other deviations from the norm.

4.3.2 Nylon 6 and Polyvinylidene Chloride Coated Nylon 6 at 25°C

The results for two layers of nylon 6 and PVDC coated nylon 6 at 25°C are shown in Figure 4.13.

Some trends observed in Figures 4.1 and 4.2 for nylon 6 and PVDC coated nylon 6 at 25°C were also demonstrated. PVDC coated nylon 6 sorbed less vanillin at a slower rate than nylon 6. Breakthrough of the PVDC coating still occurred and absorbance increased rapidly as the nylon 6 absorbed the vanillin.

However, both PVDC coated nylon 6 and nylon 6 showed similar deviations to the 10°C data. There was a period of rapid uptake of vanillin shown by a vertical line

Figure 4.13 Changes in Absorbance with Time for Two Layers of Nylon 6 and
Polyvinylidene Chloride Coated Nylon 6 with Vanillin At 25°C
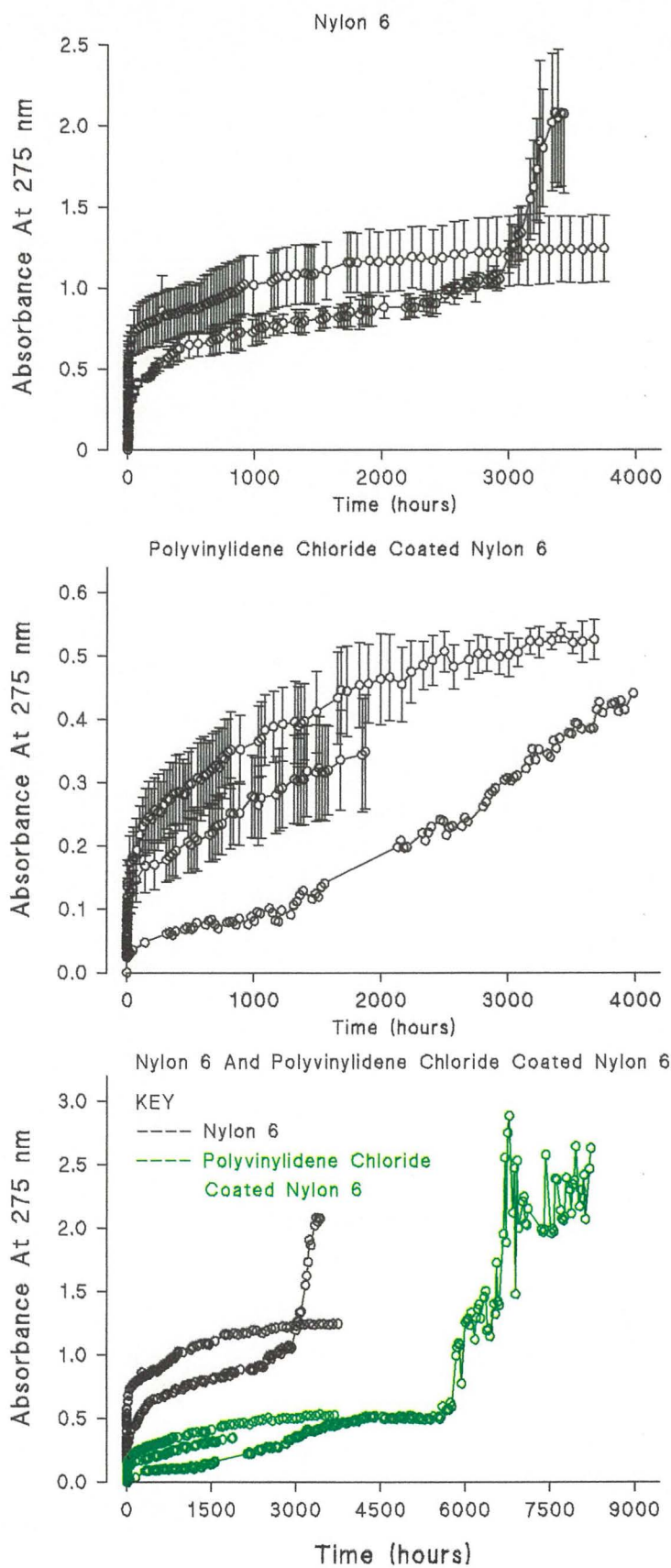
and then the graph levelled off as the rate of uptake decreased. The same explanations given in Section 4.3.1 could apply to these results also. It appeared that once the surface layer had become saturated, the nylon 6 began to sorb vanillin normally, that is, after 3000 hours, the absorbance began to rise rapidly again and the graph began to resemble the nylon 6 data shown in Figures 4.1 and 4.2.

Once again, the error bars were very large for the reasons discussed in Section 4.1.2.

Further studies need to be carried out to determine the exact cause of these anomalous results.

4.4 PREDICTION OF EQUILIBRIUM ABSORBANCE VALUES

The method described by Hayakawa, 1974; was used to estimate the absorbance value at steady state for all EVOH and vanillin experiments and nylon 6 and vanillin experiments. To get an indication of how appropriate this method was, it was then applied to the LDPE data.

Table 4.1 shows the experimental and predicted results. The values were the means of three replicates $\pm$ one standard deviation (SD_{n-1}). The method appeared to work. Values obtained agreed within $\pm$ one standard deviation with those obtained experimentally.

There are numerical conditions that must be met if the method is to be used, but there is also one other condition that should be checked. The procedure was developed by assuming that a major portion of a semilog arithmetic curve consisted of one or more straight lines. Data should be examined for the applicability of the proposed procedure by calculating a rate of change in y values at each of the uniform time intervals. If this rate decreases progressively with increase in time values, the proposed procedure may be used (Hayakawa, 1974).

Table 4.1 Experimental and Predicted Equilibrium Absorbance Values for Low
Density Polyethylene and Vanillin

Sample	Maximum Absorbance	
	Experimental	Predicted
10°C 2 Layers	0.05 ± 0.01	0.05 ± 0.01
10°C 4 Layers	0.10 ± 0.01	0.08 ± 0.01
25°C 1 Layer	0.05 ± 0.01	0.05 ± 0.01
25°C 2 Layers	0.14 ± 0.01	0.10 ± 0.01
25°C 2 Layers	0.14 ± 0.02	0.12 ± 0.02
25°C 4 Layers	0.27 ± 0.00	0.24 ± 0.01
40°C 1 Layer	0.13 ± 0.02	0.13 ± 0.01
40°C 2 Layers	0.30 ± 0.03	0.28 ± 0.04
40°C 4 Layers	0.55 ± 0.04	0.52 ± 0.06

4.5 DIFFUSION, SOLUBILITY AND PERMEABILITY COEFFICIENTS

The diffusion coefficient indicated how quickly the flavour moved through the film. The saturation solubility indicated how much flavour could be lost. The partition coefficient which is the solubility coefficient, showed the relevant efficiencies of vanillin extraction by the films. The permeability coefficient allowed comparison of the ease of transport of vanillin in the films. The flux gave the maximum transmission rate.

4.5.1 Calculation of Permeation Coefficients

These coefficients were calculated for all films and temperatures with vanillin. Sample calculations are given in Appendix 4.1.

The diffusion coefficients were calculated by both the initial slope and half time methods. Sample calculations are shown in Appendix 4.1 and the coefficients are shown in Appendices 4.6 to 4.9. The diffusion coefficients from the half time method were calculated on one data point only, while those from the initial slope method were based on several data values. Therefore, it was felt that the diffusion coefficients from the initial slope method would be more accurate.

The coefficients for LDPE, in Appendix 4.6, calculated by the two methods were fairly similar. For nylon 6 and PVDC coated nylon 6 (Appendices 4.7 and 4.8), respectively), the diffusion coefficients from the half time method were larger. For ethylene-vinyl alcohol films, the half time method gave much larger diffusion coefficients (Appendix 4.9).

Therefore, this shows there is a large difference in values estimated from only one point and using more points would give a more accurate estimate of the diffusion coefficient.

Also, for EVOH films, it was not always possible to obtain the $t_{\frac{1}{2}}$ value, (the time taken to reach a value that is half of the maximum absorbance at steady state). This was due to the absorbance being off scale well before this time and therefore the

graph did not contain the data needed.

The diffusion coefficients from the initial slope method were used in further calculations of permeability coefficients and fluxes.

4.5.2 Low Density Polyethylene

Table 4.2 shows the coefficients calculated for LDPE and vanillin. These again confirm the trends already seen from the absorbance versus time graphs and the sorption plots.

The diffusion coefficient increased with temperature and only varied slightly with number of layers. Therefore, temperature was the most important effect. Murray, 1987; Salame, 1990 and Salame and Steingiser, 1977; also reported that the rate of diffusion increased as temperature increased, because movement of polymer chains increased and it became easier for the penetrant to move through the polymer structure.

Saturation solubility also increased with temperature and did not vary significantly with the number of layers. The partition coefficient showed the same trend. DeLassus, 1987; stated that solubility may increase, decrease or remain constant as temperature increases.

Permeability coefficients increased with temperature and also with number of layers at 40°C. DeLassus et al., 1988a; said that depending on the relative magnitudes of change of the diffusion and solubility coefficients, permeability can either increase or decrease with temperature. As diffusion and solubility of vanillin both increased with temperature in LDPE, it was expected that permeability would also have shown an increase.

The flux increased with temperature, but decreased with number of layers. Reducing the concentration gradient, reduced the transmission loss.
The calculated coefficients agreed with those determined by Holland and Santangelo, 1988.

Table 4.2 Permeation Coefficients for Low Density Polyethylene Film and Vanillin

Test Film	Thickness x (cm)	Diffusion Coefficient D (cm^2/s)	Saturation Solubility C_i^l		Partition Coefficient $PC = C_i^l/C_1$	Permeability Coefficient $D^\cdot = PC(D)$ (cm^2/s)	Flux/Area $F = DC_i^l/x$	
			(g/cm^3)	(moles/l)			(g/cm^{2}s)	(g/m^{2}h)
10°C 2 Layers	0.0088	0.6×10^{-9}	0.9×10^{-4}	0.6×10^{-3}	0.9×10^{-3}	0.5×10^{-12}	0.6×10^{-11}	0.2×10^{-3}
10°C 4 Layers	0.0176	0.6×10^{-9}	0.8×10^{-4}	0.5×10^{-3}	0.8×10^{-3}	0.5×10^{-12}	0.3×10^{-11}	0.1×10^{-3}
25°C 1 Layer	0.0044	1.3×10^{-9}	1.7×10^{-4}	1.1×10^{-3}	1.7×10^{-3}	2.2×10^{-12}	4.9×10^{-11}	1.8×10^{-3}
25°C 2 Layers	0.0088	2.2×10^{-9}	2.3×10^{-4}	1.5×10^{-3}	2.3×10^{-3}	4.9×10^{-12}	5.7×10^{-11}	2.1×10^{-3}
25°C 4 Layers	0.0176	2.7×10^{-9}	2.3×10^{-4}	1.5×10^{-3}	2.3×10^{-3}	6.1×10^{-12}	3.5×10^{-11}	1.2×10^{-3}
40°C 1 Layer	0.0044	2.8×10^{-9}	4.3×10^{-4}	2.9×10^{-3}	4.3×10^{-3}	12.1×10^{-12}	27.4×10^{-11}	9.9×10^{-3}
40°C 2 Layers	0.0088	3.1×10^{-9}	5.0×10^{-4}	3.3×10^{-3}	5.0×10^{-3}	15.6×10^{-12}	17.7×10^{-11}	6.4×10^{-3}
40°C 4 Layers	0.0176	4.0×10^{-9}	4.7×10^{-4}	3.1×10^{-3}	4.6×10^{-3}	18.5×10^{-12}	10.5×10^{-11}	3.8×10^{-3}

4.5.3 Nylon 6

Table 4.3 shows the coefficients calculated for nylon 6. Again, the diffusion coefficient increased with temperature and also with number of layers.

The saturation solubility decreased with number of layers at 25°C but did not vary at 40°C. The partition coefficient also followed the same pattern.

The permeability coefficient increased with temperature. This was expected as the diffusion coefficient increased more than solubility decreased with temperature.

The flux also increased with temperature but decreased with number of layers as it did with LDPE.

The coefficients were close to those calculated by Holland and Santangelo, 1988; for nylon 11.

The diffusion coefficients were much smaller for nylon 6 than for LDPE. Therefore, vanillin would be detected almost immediately through LDPE but nylon 6 would have a longer lag time before vanillin could be detected. The saturation solubilities and partition coefficients indicated that nylon 6 is a better solvent for vanillin than LDPE and would extract vanillin very effectively from the food.

LDPE was more permeable than nylon 6 but not by as much as might have been expected when looking at the diffusion coefficient. LDPE had larger diffusion coefficients than nylon 6, 10^{-9} and 10^{-12} respectively. The permeability coefficients were approximately the same, 10^{-12} and 10^{-13} respectively. Therefore, the flow through nylon 6 was delayed for longer than in LDPE but it was still a significant rate at steady state.

Table 4.3 Permeation Coefficients for Nylon 6 Film and Vanillin

Test Film	Thickness x (cm)	Diffusion Coefficient D (cm²/s)	Saturation Solubility C_1^1 (g/cm³)	(moles/l)	Partition Coefficient $PC=C_1^1/C_1$	Permeability Coefficient $D'=PC(D)$ (cm²/s)	Flux/Area $F=DC_1^1/x$ (g/cm²s)	(g/m²h)
25°C[#] 1 Layers	0.0016	0.5×10^{-12}	23.0×10^{-3}	15.4×10^{-2}	23.4×10^{-2}	1.2×10^{-13}	7.5×10^{-12}	2.7×10^{-4}
25°C[#] 2 Layers	0.0032	0.8×10^{-12}	13.0×10^{-3}	8.4×10^{-2}	12.8×10^{-2}	1.0×10^{-13}	3.3×10^{-12}	1.2×10^{-4}
25°C[#] 4 Layers	0.0064	2.1×10^{-12}	7.0×10^{-3}	4.6×10^{-2}	7.0×10^{-2}	1.5×10^{-13}	2.3×10^{-12}	0.8×10^{-4}
40°C[#] 2 Layers	0.0032	9.1×10^{-12}	6.4×10^{-3}	4.2×10^{-2}	6.4×10^{-2}	5.8×10^{-13}	18.2×10^{-12}	6.6×10^{-4}
40°C[#] 4 Layers	0.0064	12.5×10^{-12}	7.6×10^{-3}	5.0×10^{-2}	7.6×10^{-2}	9.5×10^{-13}	14.8×10^{-12}	5.3×10^{-4}

[#] calculated from prediction of equilibrium values

4.5.4 Polyvinylidene Chloride Coated Nylon 6

Table 4.4 shows the coefficients for PVDC coated nylon 6. As the calculations were performed on the short time data points only, it is assumed that these were values for the PVDC coating only and that the vanillin had not come into contact with the nylon 6.

All coefficients increased with temperature. The diffusion coefficients were much smaller than for both LDPE and nylon 6 so PVDC coated nylon 6 would have a much longer lag time before vanillin permeation would be detected.

The saturation solubility and partition coefficients were similar to nylon 6 at 40°C and much lower than nylon 6 at 25°C. Increasing the temperature increased the solubility of vanillin in PVDC.

The permeability coefficients were much lower than nylon 6 and LDPE due to the small diffusion coefficients. The flux at steady state was also much smaller. Therefore, as previously indicated, PVDC coated nylon 6 was a much better barrier to vanillin than LDPE or nylon 6.

Table 4.4 Permeation Coefficients for Polyvinylidene Chloride Coated Nylon 6 and Vanillin

Test Film	Thickness x (cm)	Diffusion Coefficient D (cm^2/s)	Saturation Solubility C_1^s (g/cm^3)	 (moles/l)	Partition Coefficient $PC = C_1^s/C_1$	Permeability Coefficient $D' = PC(D)$ (cm^2/s)	Flux/Area $F = DC_1^s/x$ (g/cm^2s)	 (g/m^2h)
25°C 2 Layers	0.0034	3.0×10^{-14}	2.1×10^{-3}	1.4×10^{-2}	2.1×10^{-2}	0.6×10^{-15}	2.0×10^{-14}	7.2×10^{-7}
40°C 2 Layers	0.0034	9.8×10^{-14}	8.7×10^{-3}	5.7×10^{-2}	8.7×10^{-2}	8.6×10^{-15}	26.7×10^{-14}	96.0×10^{-7}

4.5.5 Ethylene-Vinyl Alcohol Films

Table 4.5 shows the coefficients calculated for EVOH films and vanillin.

The diffusion coefficient was lowest for the oriented film, XL15. This was expected as it would be more difficult for the vanillin to permeate through the more crystalline film.

The saturation solubilities and partition coefficients were the lowest for the film with the highest ethylene content, E20. This was expected as the film would have less affinity for the slightly polar vanillin molecule and less would dissolve in it. There was no difference in the saturation solubilities and partition coefficients for the oriented XL15 film and the 32 mole % ethylene film, F15.

As expected, the permeability coefficient was lowest for the biaxially oriented XL15 film due to the small diffusion coefficient for this film. Therefore, oriented films were better barriers than unoriented films. The next lowest permeability was for E20 which contained 44 mole % ethylene. The low permeability was due to the small solubility coefficient in this case. F15 had the highest permeability of all the EVOH films.

The lowest flux was found for the oriented XL15 film and the highest for F15 film.

The diffusion coefficients were intermediate between nylon 6 and PVDC coated nylon 6.
The partition coefficients and saturation solubilities were similar to those of nylon 6. Moist EVOH behaved in a similar manner to nylon 6 films, as the permeability coefficients were similar in magnitude. The fluxes were again similar to those for nylon 6.

To be a good barrier to vanillin, EVOH films should be oriented and contain a high proportion of ethylene.

Test Film	Thickness x (cm)	Diffusion Coefficient D (cm²/s)	Saturation Solubility C_i^1 (g/cm³)	(moles/l)	Partition Coefficient $PC = C_i^1/C_1$	Permeability Coefficient $D^* = PC(D)$ (cm²/s)	Flux/Area $F = DC_i^1/x$ (g/cm²s)	(g/m²h)
E20# 2 Layers	0.004	7.5×10^{-13}	1.4×10^{-2}	5.5×10^{-2}	8.3×10^{-2}	0.6×10^{-13}	2.6×10^{-12}	0.9×10^{-4}
E20# 4 Layers	0.008	34.1×10^{-13}	0.8×10^{-2}	5.3×10^{-2}	8.1×10^{-2}	2.8×10^{-13}	3.5×10^{-12}	1.3×10^{-4}
F15# 4 Layers	0.006	34.5×10^{-13}	1.3×10^{-2}	8.7×10^{-2}	13.2×10^{-2}	4.6×10^{-13}	7.5×10^{-12}	2.7×10^{-4}
XL15# 4 Layers	0.006	9.2×10^{-13}	1.4×10^{-2}	9.3×10^{-2}	14.1×10^{-2}	1.3×10^{-13}	2.1×10^{-12}	0.8×10^{-4}

calculated from prediction of equilibrium values

4.6 COMPARISON OF FILMS WITH D-LIMONENE

The absorbance versus time graphs for one and two layers of low density polyethylene and d-limonene at 25°C are shown in Figure 4.14. The plots show the absorbances up to 600 hours and also the initial 10 hours. Absorbance versus time graphs for one and two layers of ethylene-vinyl alcohol films with d-limonene at 25°C and 90% RH are shown in Figure 4.15. The graphs show the absorbances up to 900 hours and the initial 10 hours.

There was a large scatter of points for LDPE and EVOH films with d-limonene (Figures 4.14 and 4.15). The large error bars showed the lack of reproducibility of these replicates compared to two layers of LDPE and vanillin at 25°C in Figure 4.5. The absorbance values were very low and again may have been reaching the limits of detection of the spectrophotometer.

With EVOH films there was also no clear indication of a trend and the absorbance values were very low. Two layers of E20 did show a slight trend but the error bars still indicated a lack of reproducibility in the replicates.

It was not possible to measure d-limonene in nylon 6 and PVDC coated nylon 6 at the wavelength used, 215 nm. The nylon 6 film began to absorb at this wavelength and interfere with the readings. It was not possible to zero the spectrophotometer.

D-Limonene was not a good compound to measure with this method. It is not as strongly absorbing as vanillin. It has a low extinction coefficient, ε = 257, compared with vanillin, ε = 10,233. Therefore, much greater amounts of d-limonene would need to be present in the film before it could be detected.

D-Limonene began desorbing from the film as it was being measured, making it difficult to get a consistent reading. Adsorption rather than absorption may have been occurring. Kwapong and Hotchkiss, 1987 and Halek and Meyers, 1989; found that adsorption followed by absorption occurred when LDPE sorbed d-limonene. Therefore, if adsorption was occurring, d-limonene would readily desorb from the surface of the LDPE when it was exposed to the air for absorbance readings.

One Layer For 600 Hours

One Layer For 10 Hours

Two Layers For 600 Hours

Two Layers For 10 Hours
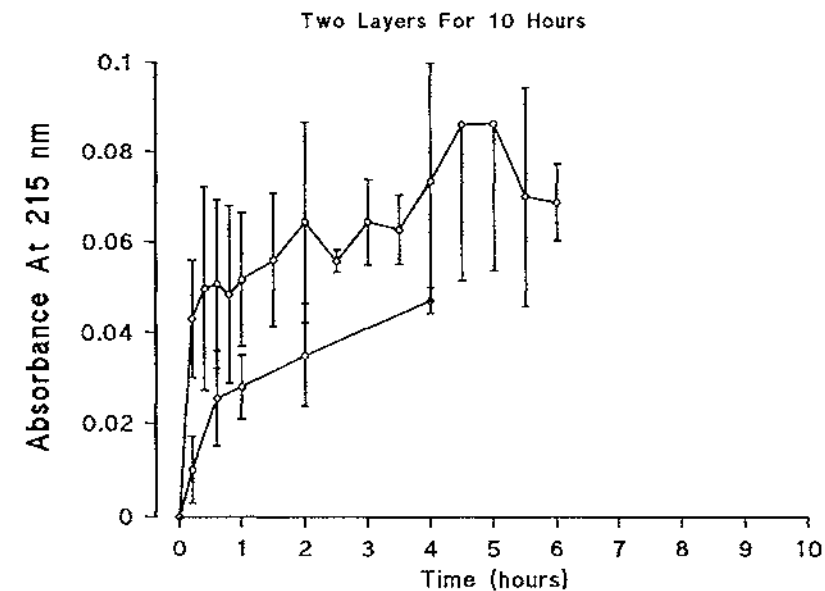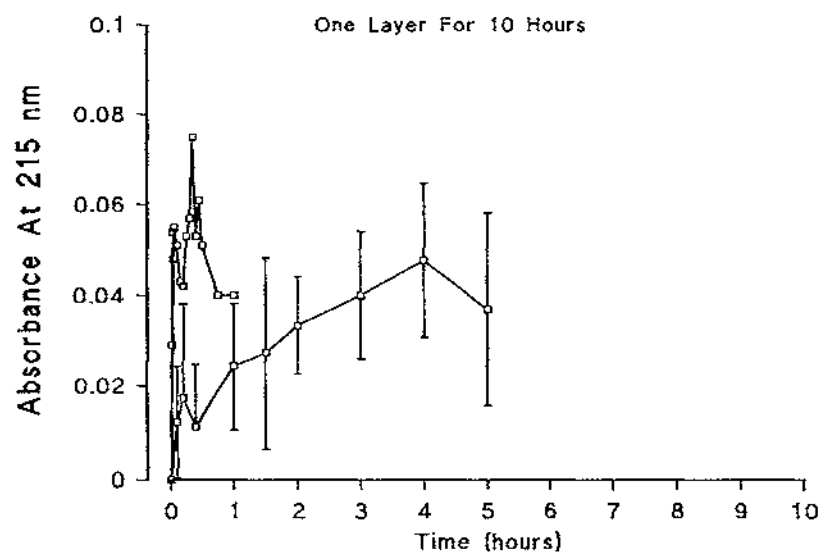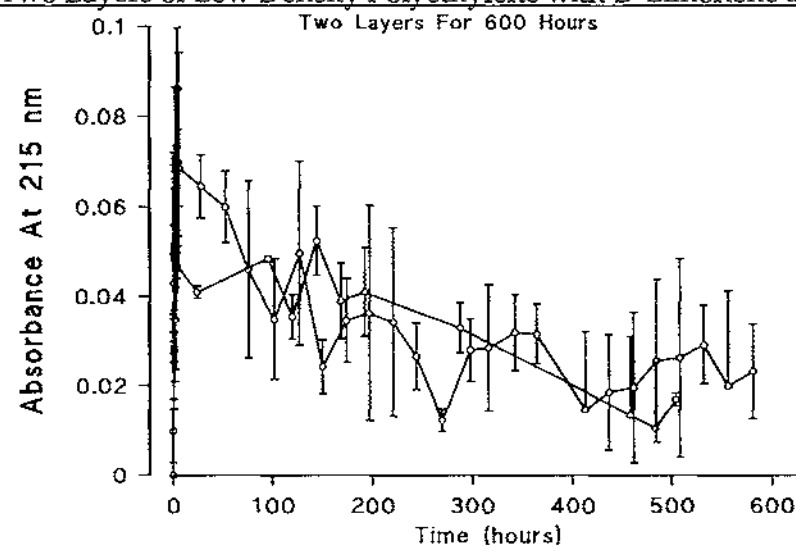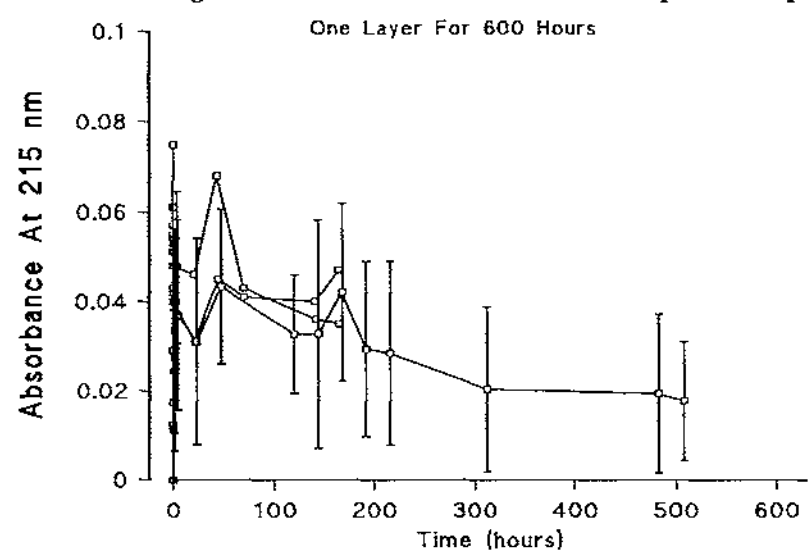
Figure 4.15 Changes in Absorbance with Time for One and Two Layers of
Ethylene-Vinyl Alcohol Films with D-Limonene at 25°C and 90% RH
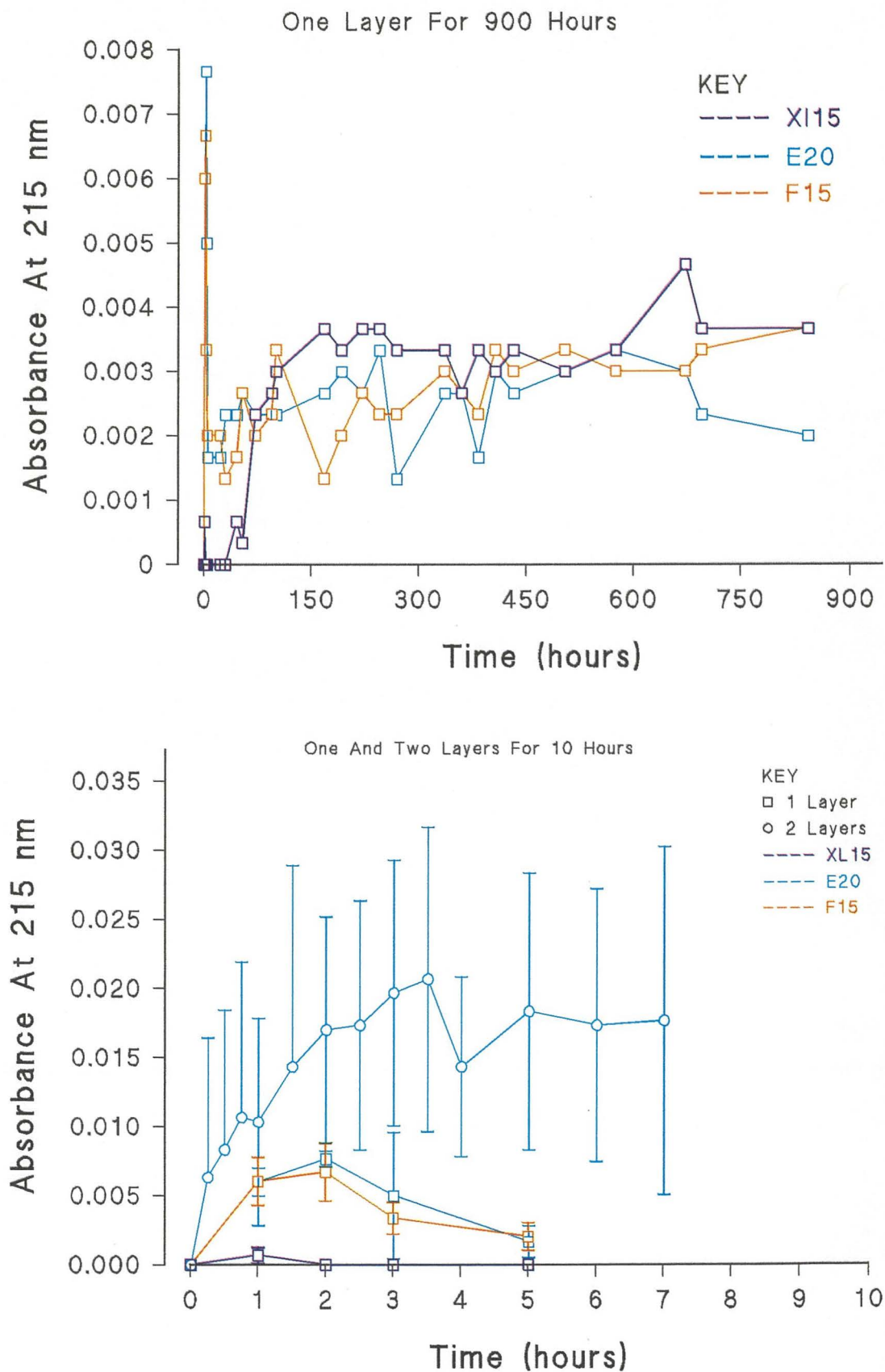
Figure 4.16 Structures of the Polymers and D-Limonene
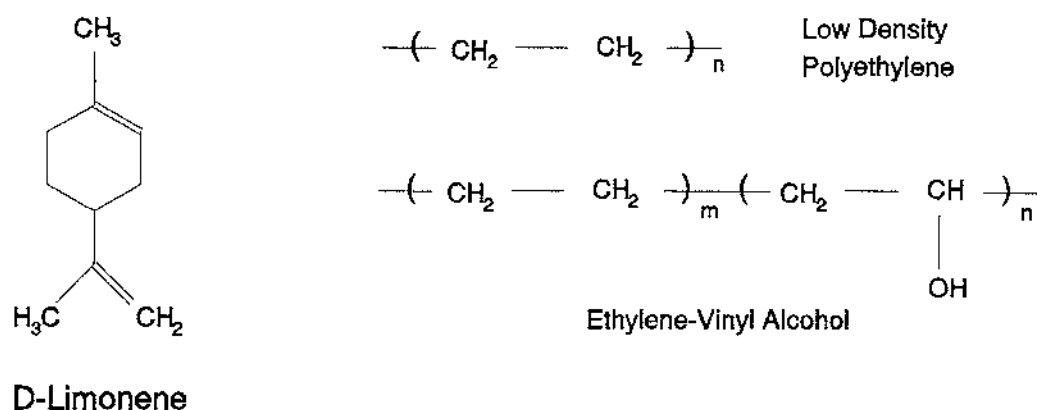
D-Limonene

If the structures of the polymers and d-limonene are compared, (Figure 4.16), it would be expected that LDPE would sorb large amounts of d-limonene as they have similar structures; both the polymer and the penetrant are hydrocarbons. There are many studies in literature that demonstrate this (Kwapong and Hotchkiss, 1987; Halek and Meyers, 1989; Hotchkiss, 1987). However, the results of these experiments did not demonstrate this.

It would be expected that EVOH would sorb less d-limonene than LDPE as it is a more polar film. This has been shown by Imai et al., 1990. The results shown in Figures 4.14 and 4.15 also show that EVOH films sorbed less d-limonene than LDPE.

The results with d-limonene demonstrate a worst case situation where this method is not applicable. Gravimetric measurement or the transmission technique of the "laminate film" method may make it possible to measure d-limonene permeation more simply than the traditional methods and use of these should be investigated.

4.7 USE OF THE "LAMINATE FILM" METHOD

Plots of the changes in absorbance with time gave a general overview of what was happening as the compound was sorbed. They also gave a preliminary indication of how effective the films were as barriers to vanillin. On the basis of the absorbance changes with time, nylon 6 and moist EVOH films could be discarded as barrier materials to vanillin as they sorbed larger amounts of vanillin more quickly than LDPE and PVDC coated nylon 6. Results could therefore be obtained in a very short time, that is, hours or days, compared to the weeks or months required for traditional methods. Sorption plots and the coefficients calculated from them, confirmed trends already observed from changes of absorbance with time, such as increases in permeation with increased temperature. However, because the plots allowed closer examination of the earlier data points, some effects stood out that were not obvious or very clearly shown in the absorbance graphs. For example, sorption plots showed that nylon 6 had a slower rate of uptake of vanillin than LDPE.

If more detailed information such as diffusion, solubility and permeability coefficients for the film and penetrant are required, for example, to enable a choice to be made between LDPE and PVDC coated nylon 6, then these coefficients can be obtained from the same data in the absorbance versus time plots without the need for further experimentation.

The relative magnitudes of change in the diffusion (D) and solubility (S) coefficients due to some change in conditions could dramatically affect the permeation of a compound in a film and hence the shelf life of a food. This might not be obvious if the permeability coefficient, P, alone was examined. For example, P may not change but D may decrease and S may increase so flavour scalping could occur if some change in environmental conditions occurred. Therefore, all three parameters need to be known in order to select the most suitable packaging film for a particular application. Some factors that were important in these experiments were:

Temperature

The results demonstrated that temperature dramatically affected permeation. Temperature had a large effect between 10 and 25°C but not such a great effect between 25 and 40°C. Past research had indicated that D would increase with increased temperature and S could increase, decrease or remain constant. Permeation could therefore increase or decrease with temperature depending on the relative magnitudes of change in D and S (Murray, 1987; Salame, 1990; Salame and Steingiser, 1977; DeLassus, 1987). Temperature fluctuations could cause large variations in the estimation of permeabilities of films. Also, temperature changes may be responsible for some of the anomalous results due to condensation forming on the film. To eliminate these errors and problems, tests using the "laminate film" method should be carried out in temperature controlled rooms to accurately measure the permeation of compounds in polymers.

Relative Humidity

Hatzidimitriu, 1987; DeLassus et al., 1988a, 1988b and Landois-Garza et al., 1988; have all demonstrated the effects of RH on the permeabilities of films. The effect of RH on permeation was demonstrated with EVOH films. Increasing the RH decreased the barrier properties of EVOH to vanillin. If a moisture sensitive or hydrophilic barrier film is used in a package, for example, nylon 6 or EVOH and if it is not part of a multilayer polymer structure, that is, it is not protected by moisture barrier films; then the film should be equilibrated at the RH of interest before it is tested with penetrant, to enable a true estimation of the permeability of the film to be obtained.

Nature of the Film and the Penetrant

Salame, 1977 and Brody, 1989; stated that compounds with structures or functional groups similar to those of the polymer would be readily sorbed by the polymer. This was the case for both vanillin and limonene in these experiments.

Therefore, methods of estimating permeation such as the permachor value (Salame and Steingiser, 1977; Salame, 1961, 1986, 1990) the solubility parameter (Hall, 1981) could be applied to permeation of volatile organic compounds. This would give an indication of the best polymers and eliminate others, before they were tested with the "laminate film" method.

Layers

As demonstrated in these experiments, the number of layers used did not affect the rate or way in which the film sorbed the penetrant. Therefore, more layers can safely be used to enable more accurate estimation of diffusion coefficients for polymer-penetrant combinations which have very short lag times.

Increasing the number of layers, increased the amount of penetrant sorbed, but this did not affect the calculation of diffusion coefficients. Increasing the number of layers, decreased the maximum transmission rate (flux) so it may be useful to use thicker gauges of films in some cases to decrease the amount of penetrant that could be lost.

Units

The calculations were simple to perform and gave results with realistic and workable units such as cm^2/s and g/m^2h rather than the cumbersome units generated by traditional methods of permeation measurement (DeLassus et al., 1988a, 1988b; Yasuda, 1975). The advantage of the units used, is that it does not matter if the penetrant is a solid, liquid or vapour and therefore, comparison of results for different penetrants is straightforward and no conversion of results is necessary.

The "laminate film" method allowed a quick, qualitative estimate of the best barrier film for a particular packaging application to be made. For example, from the results obtained, if a food was packaged in two containers, one of nylon 6 and the other of LDPE, vanillin would be lost in both cases but 'flavour scalping' would

occur with nylon 6, (higher partition coefficient). Nylon 6 was a more effective barrier to vanillin permeation in the short term than LDPE, (lower D coefficient), but vanillin is still being sorbed by the film and lost from the product even though it took some time for the vanillin to permeate through the film. PVDC is a good food contact material, (no scalping of vanillin) and a good barrier to vanillin, (low D and P coefficients). LDPE is a good contact material, but a poor barrier, (high flowrate). Nylon 6 would be a good barrier to taints from the environment as they would take a long time to contact the product.

The "laminate film" method required inexpensive equipment and did not require skilled personnel to carry out the tests.

When testing a product and polymer for flavour permeation, the appropriate compound must be carefully chosen. The penetrant tested should be the major component that contributes to quality and acceptability of the product, as flavours and aromas are made up of many compounds and it is not possible to measure all of them.

Compounds to be tested need to have a high molar absorptivity so that small quantities can be accurately measured. The polymer must be transparent and must not absorb at the wavelength used to measure changes in absorbance.

If the compounds and polymers are suitable for use with the "laminate film" method, then the method provides a fast, inexpensive and simple way of determining the best polymer for a packaging application. However, before this can become a standard method, there are some areas that require further investigation.

These are :

- the effect of concentration on permeation. This could easily be tested by using supply films cast with different concentrations of the penetrant.

- the results at 10 and 25°C for nylon 6 and polyvinylidene coated nylon 6 that deviated from the expected trends in changes of absorbance with time. These need to be repeated in more detail to find the true cause of the deviations.

- long term effects should be considered if the sorption method is used. If oxidation of the penetrant or degradation of the polymer could be a problem, for example, then the transmission method could be used, as steady state can take a long time to reach for some polymer-penetrant combinations.

- the transmission technique and gravimetric measurement should also be investigated as alternatives to the sorption technique for polymers and compounds that are not suited to testing by the sorption method.

- As the experiments with d-limonene were not successful, it was not possible to compare the permeation coefficients with those obtained from traditional methods. Other flavour compounds need to be tested, so the coefficients obtained can be compared to results from the existing methods for testing permeation.

5.0 CONCLUSIONS

The sorption technique of the "laminate film" method was simple to use and gave results more quickly than traditional methods. The results obtained were used to easily choose the most appropriate barrier film for a particular penetrant.

Therefore, it would be a good method for use in industry where a simple, quick and cheap method for testing the barrier properties of polymers to flavours and aromas is needed.

The units used for the diffusion, solubility and permeability coefficients made calculations simple and comparison of results for penetrants straightforward, regardless of whether the penetrant was a solid, liquid or gas, as no conversion was necessary.

The compound of interest should have a large extinction coefficient so sorption can be accurately measured and the test polymer should be transparent.

The main factors affecting the polymer-penetrant permeation were temperature, RH and nature of the polymer and penetrant. Therefore, temperature needs to be strictly controlled when carrying out tests and if the polymer is moisture sensitive, it should be conditioned at the RH of interest before the test is carried out.

More layers of the polymer can safely be used to accurately measure very small diffusion coefficients without affecting the permeation behaviour of the penetrant.

Some further work is required before this can become a standard test method, particularly with different penetrants at varying concentrations. There are some organic volatiles and polymers which cannot be used with this method and alternative techniques such as transmission and gravimetric measurement need to be tested with them.

REFERENCES

Allison, H.L. (1985) High Barrier Packaging - What Are The Options?
Packaging 30 (3) : 25-29

Anon. (1987) Aroma Sorption.
Food Engineering 59 (4) : 39,42

Apostolopoulos, D; Winters, N. (1991) Measurement of Permeability for Packaging Films to d-limonene Vapour at Low Levels.
Packaging Technology and Science 4 : 131-138

Baner, A.L; Hernandez, R.J; Jayaraman, K; Giacin, J.R. (1986) "Isostatic and Quasi-isostatic Methods For Determining The Permeability Of Organic Vapours Through Barrier Membranes" in M.L. Troedel, ed, Current Technologies In Flexible Packaging - an ASTM Special Technical Publication 912.

Briston, J.H; Katan, L.L. (1974a) "Plastics Quality" in Plastics In Contact With Food, Food Trade Press Ltd, London. pp 239-250

Briston, J.H; Katan, L.L. (1974b) "Appendix II: Diffusion and Permeability" in Plastics In Contact with Food, Food Trade Press Ltd, London. pp 432-438

Brody, A. (1989) Flavor Interacts With Packaging.
Prepared Foods 158 (10) :128-130,132

Combellick, W.A. (1985) "Barrier Polymers", in J.I. Kroschwitz, (ed), Encyclopedia of Polymer Science and Engineering, vol 2, John Wiley & Sons Inc, New York. pp 176-192

DeLassus, P.T; Jenkins, S.R. (1986) Advances in Flavour and Aroma Testing in Relation to Polymer Barrier Performance. Proceedings of the International Seminar on Packaging, Auckland University. pp 116-130

DeLassus, P.T; Hilker, B.L. (1987) "Interaction of High Barrier Plastics With Food: Permeation and Sorption" in J.I. Gray, B.R. Harte, J. Miltz, eds, Food Product-Package Compatibility, Technomic Publishing Co, Inc, Pennsylvania. pp 229-244

DeLassus, P.T. (1987) Diffusion and Sorption of Organic Molecules By Polymer Films. First Australian International Packaging Conference.

DeLassus, P.T; Tou, J.C; Babinec, M.A; Rulf, D.C; Karp, B.K Howell, B.A. (1988a) "Transport of Apple Aromas in Polymer Films" in J. Hotchkiss, ed, Food and Packaging Interactions ACS Symposium Series 365. pp 11-27

DeLassus, P.T; Strandburg, G; Howell, B.A. (1988b) Flavour and Aroma Permeation In Barrier Films: the Effects of High Temperature and High Humidity.
Tappi Journal 71 (11) : 177-181

Durr, P; Schobinger, U: Waldvogel, R. (1981) Aroma Quality of Orange Juice After Filling and Storage in Soft Packages and Glass Bottles.
Alimenta 20 : 91-93

Felder, R.M; Huvard, G.S. (1980) "Permeation, Diffusion, and Sorption of Gases and Vapors", in R.A. Fava, (ed), Methods of Experimental Physics, vol 16 Part C, Academic Press, New York. pp 315-377

Foster, R. (1986) "Ethylene-vinyl Alcohol Copolymers (EVOH)" in M.Bakker (ed), The Wiley Encyclopedia of Packaging Technology, John Wiley & Sons Inc, New York. pp 270-275

Giacin, J.R. (1987) "Chemical Structure and Properties of Polymers" in P.E. Velso, J.V. Chambers, J.H. Rodriguez (eds), Principles of Aseptic Processing and Packaging, Food Processors Institute, Washington. pp 81-96

Giacin, J.R; Hernandez, R.J. (1987) Evaluation of the Aroma Barrier Properties of Polymer Films by Sorption and Permeation Methods.
Activities Report of the R & D Associates 39 (1) : 79-90

Gilbert, S.G; Hatzidimitriu, E; Lai, C; Passy, N. (1983) "Study of Barrier Properties of Polymeric Films to Various Organic Aromatic Vapours" in G. Charalambous; G. Inglett, eds, Instrumental Analysis of Foods: Recent Progress, Vol 1, Academic Press, Inc, New York. pp 405-411

Hagenbaugh, J. (1987) Measurement of Organic Vapour Rates In Oriented Polypropylene Packaging Films. First Australian International Packaging Conference.

Halek, G.W. (1988) "Relationship Between Polymer Structure and Performance in Food Packaging Applications" in J. Hotchkiss, ed, Food and Packaging Interactions ACS Symposium Series 365. pp 195-202

Halek, G.W; Meyers, M.A. (1989) Comparative Sorption of Citrus Flavor Compounds by Low Density Polyethylene.
Packaging Technology and Science (2):141-146

Hall, C. (1981)"Chemical Properties" in Polymer Materials, Macmillan Press Ltd, London. pp 113-118

Hatzidimitriu, E; Gilbert, S.G; Loukakis, G. (1987) Odor Barrier Properties of Multi-Layer Packaging Films At Different Relative Humidities.
Journal of Food Science 52 (2) : 472-474

Hatzidimitriu, E; Gilbert, S.G; Loukakis, G; Paik, S. (1988) "Permeation Studies of Model Flavour Compounds in Nylon 6 Film." in G Charalambous (ed), Frontiers of Flavour, Elsevier Science Publishers, Amsterdam. pp 297-305

Hayakawa, K. (1974) Predicting an Equilibrium State Value from Transient State Data.
Journal of Food Science 39 : 272-275

Hernandez, R.J; Giacin, J.R; Baner, A.L. (1990) "The Evaluation of the Aroma Barrier Properties of Polymer Films" in K.M. Finlayson (ed), Plastic Film Technology High Barrier Plastic Films For Packaging, Technomic Publishing AG, Basel. pp 107-130

Hirose, K.; Harte, B.R; Giacin, J.R; Miltz, J; Stine, C. (1988) "Sorption of d-limonene By Sealant Films and Effect On Mechanical Properties" in J. Hotchkiss, ed, Food and Packaging Interactions ACS Symposium Series 365. pp 28-41

Holland, R.V; Rooney, M.L; Santangelo, R.A. (1981) New Methods of Measuring Permeabilities of Packaging Films.
CSIRO Food Research Quarterly 41 : 47-50

Holland, R.V; Santangelo, R.A. (1984) Packaging Films: New Techniques in Permeability Measurements.
CSIRO Food Research Quarterly 44 : 20-22

Holland, R; Santangelo, R. (1988) The 'Laminate Film' Method for Measuring Odour Transmission Rates Through Food Packaging Films.
CSIRO Food Research Quarterly 48 : 40-46

Hotchkiss, J.H. (1987) Comparative Sorption of Aromatic Flavours by Plastics Used in Food Packaging.
Activities Report of the R & D Associates 39 (1) : 65-70

Hriciga, A.L; Stadelman, D.J. (1988) "Flavour-Polymer Interactions: Coffee Aroma Alteration" in J. Hotchkiss, ed, Food and Packaging Interaction ACS Symposium Series 365. pp 59-67

Ikari, K; Takahashi, T; Yamada, R. (1987) High Gas Barrier Material EVAL. Proceedings of the Sixth International Seminar on Packaging, Auckland University. pp 98-132

Ikegami, T; Nagashima, K; Shimoda, M; Tunaka, Y; Osajima,Y. (1991) Sorption of Volatile Compounds in Aqueous Solution by Ethylene-Vinyl Alcohol Copolymer Films.
Journal of Food Science 56 (2) : 500-509

Imai, J; Harte, B.R; Giacin, J.R. (1990) Partition Distribution of Aroma Volatiles From Orange Juice Into Selected Polymeric Sealant Films.
Journal of Food Science 55 (1) : 158-161

Johnson, E.M. (1989) The Aroma Protectors.
Food Packaging Technology International Issue 1: 223-224

Kail, J.A.E. (1984) Flavour Barrier Evaluation Enhances Material Selection.
Packaging 29 (4) :68-70

Kontominas. (1985) Determination of Permeation Rates of Polymeric Films to Organic Vapours in Relation To Retention of Flavour Quality of Packaged Foodstuffs.
Sciences des Aliments 5 : 321-329

Koszinowski, J; Piringer, O. (1986) "Influence of Packaging Material and the Nature of the Packed Goods on the Loss of Volatile Organic Compounds : Permeation of Aroma Compounds." in M. Mathlouthi, (ed), Food Packaging and Preservation : Theory and Practice, Elsevier Applied Science Publishers Ltd, Essex. pp 325-340

Koszinowski, J; Piringer, O. (1987) Food/Package Compatibility and Migration. Journal of Plastic Film & Sheeting 3 (4) : 96-111

Kwapong, O.Y; Hotchkiss, J.H. (1987) Comparative Sorption of Aroma Compounds By Polyethylene and Ionomer Food Contact Plastics. Journal of Food Science 52 (3) : 761-763,785

Landois-Garza, J; Hotchkiss, J.H. (1988) "Permeation of High Barrier Films By Ethyl Esters: Effect of Permeant Molecular Weight, Relative Humidity and Concentration" in J. Hotchkiss, ed, Food and Packaging Interactions ACS Symposium Series 365. pp 42-58

Liu, K.J; Giacin, J.R; Hernandez, R.J. (1988) The Effect of Relative Humidity On The Permeability of Toluene Vapour Through A Multi-Layer Coextruded Film Containing Hydrophilic Layers. Packaging Technology and Science 1 : 57-65

Long, F.A; Thompson, L.J. (1954) Water Induced Acceleration of the Diffusion of Organic Vapors in Polymers. Journal of Polymer Science 14 : 321-327

Mannheim, C.H; Miltz, J; Letzter, A. (1987) Interaction Between Polyethylene Laminated Cartons and Aseptically Packed Citrus Juice. Journal of Food Science 52 (3) : 737-740

Mannheim, C.H; Miltz, J; Passy, N. (1988) "Interaction Between Aseptically Filled Citrus Products and Laminated Structures" in J. Hotchkiss, ed, Food and Packaging Interactions ACS Symposium Series 365. pp 68-82

Marcus, S.A; DeLassus, P.T; Wence, R.L. (1978) New Developments In Rigid Barrier Applications. Proceedings of the Sixth International Seminar on Packaging, Auckland University. pp 133-160

Mohney, S.M; Hernandez, R.J; Giacin, J.R; Harte, B.R; Miltz, J. (1988) Permeability and Solubility of d-limonene Vapour In Cereal Package Liners.
Journal of Food Science 53 (1) : 253-257

Murray, L.J. (1985) An Organic Vapor Permeation Rate Determination for Flexible Packaging Materials.
Journal of Plastic Film & Sheeting 1 (4) : 104-114

Murray, L.J. (1987) Analytical Methods For Organic Vapour Permeation Studies.
First Australian International Packaging Conference.

Naylor, T. (1989) "Permeation Properties", in Comprehensive Polymer Science - The Synthesis, Characterization, Reactions and Applications of Polymers, Pergamon Press, Oxford. pp 643-668

Pasternak, R.A; Schimscheimer, J.R; Heller, J. (1970) A Dynamic Approach to Diffusion and Permeation Measurements.
Journal of Polymer Science Part A2 (8) : 467-479

Sadler, G.D; Braddock, R.J. (1990) Oxygen Permeability of Low Density Polyethylene as a Function of Limonene Absorption: An Approach to Modelling Flavour "Scalping".
Journal of Food Science 55 (2) : 587-588

Salame, M. (1961) The Prediction of Liquid Permeation in Polyethylene and Related Polymers.
SPE Transactions October : 153-163

Salame, M; Steingiser, S. (1977) Barrier Polymers.
Polymer-Plastics Technology and Engineering 8 (2) : 155-175

Salame, M. (1986) Prediction of Gas Barrier Properties of High Barrier Polymers.
Polymer Engineering & Science 26 (22) : 1543-1546

Salame, M. (1987) New Barrier Materials for Packaging.
Activities Reports of R & D Assoc. 37 (2) : 34-37

Salame, M. (1990) "The Use of Barrier Polymers in Food and Beverage Packaging."
in K.M. Finlayson (ed), Plastic Film Technology High Barrier Plastic
Films For Packaging, Technomic Publishing AG, Basel. pp 132-145

Schwope, A.D; Goydan, R; Reid, R.C; Krishnamurthy, S. (1988) State-of-the-Art
Review of Permeation Testing and the Interpretation of Its Results.
American Industrial Hygiene Association Journal 49 (11) : 557-565

Shimoda, M; Ikegami, T; Osajima, Y. (1988) Sorption of Flavour Compounds in
Aqueous Solution Into Polyethylene Film.
Journal of the Science of Food and Agriculture 42 (2) : 157-163

Stepek, J; Duchacek, V; Curda, D; Horacek, J; Sipek, M. (1987) "Structure and
Properties of Polymers: Permeability of Polymers" in Polymers As
Materials For Packaging, Ellis Horwood Ltd, Chichester. pp 85-89,
154-169

Tarkenton, S. (1989) Coated OPP Films Provide Better Flavour and Aroma Barrier.
Food Engineering (5):93

Toebe, J.M; Hoojjat, H; Hernandez, R.J; Giacin, J.R, Harte, B.R. (1990) Interaction
of Flavour Components From an Onion/Garlic Flavoured Sour Cream
With High Impact Polystyrene.
Packaging Technology & Science 3 : 133-140

Yasuda, H. (1975) Journal of Applied Polymer Science 19 :2529-2536

Zobel, M.G.R. (1982) Measurement of Odour Permeability of Polypropylene
Packaging Films At Low Odourant Levels.
Polymer Testing 3 : 133-142

Zobel, M.G.R. (1985) The Odour Permeability of Polypropylene Packaging Film.
Polymer Testing 5 : 153-165

Zobel, M.G.R. (1988) Packaging and Questions Of Flavour Retention.
Food Technology International Europe : 339-342

APPENDICES

Appendix 3.1 Calculations for a 1 Molar Vanillin Supply Film

Polymer solution volume (Ethyl cellulose in ethyl acetate)	= 20 ml
Volume of ethyl cellulose as 11.7% $^v/_v$ in ethyl acetate	= 20 x 11.7% = 2.34 ml
Density of ethyl cellulose	= 1.15 g/ml
∴ Mass of ethyl cellulose	= 2.34 x 1.15 = 2.69 g
Mass of vanillin (MW = 152.15) as 1M in 2.34 ml of ethyl cellulose	= $\dfrac{1 \times 152.15 \times 2.34}{1000}$ = 0.356 g

Appendix 3.2 Calculations for a 1 Molar D-Limonene Supply Film

Polymer solution volume   = 20 ml
(Ethyl cellulose in ethyl acetate)

Volume of ethyl cellulose as   = 20 x 11.7%
11.7% $^v/_v$ in ethyl acetate   = 2.34 ml

Density of ethyl cellulose   = 1.15 g/ml

∴ Mass of ethyl cellulose   = 2.34 x 1.15
                                                       = 2.69 g

Mass of d-limonene (MW = 136.2)   = $\dfrac{1 \times 136.2 \times 2.34}{1000}$
as 1M in 2.34 ml of ethyl cellulose

                                                       = 0.319 g

Appendix 4.1 Sample Calculations of Coefficients for Two Layers of Low Density Polyethylene and Vanillin at 10°C

a) Calculation of the diffusion coefficient by the half time method.

$$D = 0.04919 / t_{1/2} / x^2$$

where $t_{1/2}$ = time taken to reach an absorbance value that is one half of the steady state value (s)

x = thickness of the film (cm)

D = diffusion coefficient

$$D = 0.04919 / (2.36 \times 3600) / (0.0088)^2$$
$$= 0.5 \times 10^{-9} \ cm^2/s$$

b) Calculation of the diffusion coefficient by the initial slope method.

$$\frac{Abs_t}{Abs_\infty} = 2.257 \ (Dt)^{1/2} / x$$

where Abs_t = absorbance at time t

Abs_∞ = absorbance at steady state

D = diffusion coefficient

t = time (s)

x = film thickness (cm)

Slope of sorption plot = $\frac{Abs_t}{Abs_\infty}$ / ($t^{1/2}$ / x)

∴ $D = (slope)^2 \times 0.1963$
$$= (5.548 \times 10^{-5})^2 \times 0.1963$$
$$= 0.6 \times 10^{-9} \ cm2 /s$$

c) Saturation solubility, C_1, of the vanillin supply film.

Volume of cast supply film = $(18 \times 20 \times 0.0025) \times 3$
$$= 2.7 \text{ cm}^3$$

Weight of vanillin in the film = 0.269 g

$\therefore$ $\quad C_1 = \dfrac{0.269}{2.7}$

$\quad\quad = 0.10 \text{ g/cm}^3$

or $\quad C_1 = 0.10 \times \dfrac{1000}{152.15}$

$\quad\quad = 0.65 \text{ moles/l}$

d) Saturation solubility of vanillin in LDPE, C_1^1.

$$C_1^1 = \frac{A}{\varepsilon b}$$

where $\quad$ A = absorbance at steady state

$\quad\quad \varepsilon$ = molar absorptivity (l/(mole cm))

$\quad\quad$ b = film thickness (cm)

$$C_1^1 = \frac{0.053}{(10233 \times 0.0088)}$$

$\quad\quad = 0.6 \times 10^{-3} \text{ moles/l}$

or $\quad C_1^1 = 0.6 \times 10^{-3} \times \dfrac{152.15}{1000}$

$\quad\quad = 0.9 \times 10^{-4} \text{ g/cm}^3$

e) Partition coefficient, PC.

$$PC = \frac{C_i^1}{C_1}$$

$$= \frac{0.9 \times 10^{-4}}{0.10}$$

$$= 0.9 \times 10^{-3}$$

$$PC = \frac{C_i^1}{C_1}$$

$$= \frac{0.6 \times 10^{-3}}{0.65}$$

$$= 0.9 \times 10^{-3}$$

f) Permeability coefficient, D'.

$$D' = PC(D)$$

$$= 0.9 \times 10^{-3} \times 0.6 \times 10^{-9}$$

$$= 0.5 \times 10^{-12} \ cm^2/s$$

g) Flux / Area, F.

$$F = DC_1^1 / x$$

$$= 0.6 \times 10^{-9} \times 0.9 \times 10^{-4} / 0.0088$$

$$= 0.6 \times 10^{-11} \ g/cm^2 s$$

or

$$F = 0.6 \times 10^{-11} \times 3.6 \times 10^7$$

$$= 0.2 \times 10^{-3} \ g/m^2 h$$

Appendix 4.2 Slopes of Sorption Plots and Average Maximum Absorbances for
Low Density Polyethylene and Vanillin

Sample	Slope	Average Maximum Absorbance
10°C, 2 Layers	5.55×10^{-5}	0.05
10°C, 4 Layers	5.42×10^{-5}	0.10
25°C, 1 Layer	8.04×10^{-5}	0.05
25°C, 2 Layers	1.04×10^{-4}	0.14
25°C, 4 Layers	1.16×10^{-4}	0.27
40°C, 1 Layer	1.19×10^{-4}	0.13
40°C, 2 Layers	1.26×10^{-4}	0.30
40°C, 4 Layers	1.43×10^{-4}	0.55

Appendix 4.3 Slopes of Sorption Plots and Average Maximum Absorbances for
Nylon 6 and Vanillin

Sample	Slope	Average Maximum Absorbance
25°C, 1 Layer	1.62×10^{-6}	2.53
25°C, 2 Layers	2.02×10^{-6}	2.77
25°C, 4 Layers	3.27×10^{-6}	3.00
40°C, 2 Layers	6.80×10^{-6}	1.38
40°C, 4 Layers	8.00×10^{-6}	3.27

Appendix 4.4 Slopes of Sorption Plots and Average Maximum Absorbances for Polyvinylidene Chloride Coated Nylon 6 and Vanillin

Sample	Slope	Maximum Average Absorbance
25°C, 2 Layers	3.91×10^{-7}	0.50
40°C, 2 Layers	7.08×10^{-7}	1.98

Appendix 4.5 Slopes of Sorption Plots and Average Maximum Absorbances for Ethylene-Vinyl Alcohol Films and Vanillin

Sample	Slope	Average Maximum Absorbance
E20, 2 Layers	1.95×10^{-6}	3.88
E20, 4 Layers	4.17×10^{-6}	4.36
F15, 4 Layers	4.20×10^{-6}	5.32
X115, 4 Layers	2.16×10^{-6}	5.73

Appendix 4.6 Diffusion Coefficients for Low Density Polyethylene and Vanillin

Sample	Initial Slope Method	Half Time Method
10°C, 2 Layers	0.6×10^{-9}	0.5×10^{-9}
10°C, 4 Layers	0.6×10^{-9}	0.6×10^{-9}
25°C, 1 Layer	1.3×10^{-9}	1.6×10^{-9}
25°C, 2 Layers	2.2×10^{-9}	3.1×10^{-9}
25°C, 4 Layers	2.7×10^{-9}	3.3×10^{-9}
40°C, 1 Layer	2.8×10^{-9}	2.9×10^{-9}
40°C, 2 Layers	3.1×10^{-9}	5.0×10^{-9}
40°C, 4 Layers	4.0×10^{-9}	3.7×10^{-9}

Appendix 4.7 Diffusion Coefficients for Nylon 6 and Vanillin

Sample	Initial Slope Method	Half Time Method
25°C, 1 Layer	0.5×10^{-12}	0.7×10^{-12}
25°C, 2 Layers	0.8×10^{-12}	2.7×10^{-12}
25°C, 4 Layers	2.1×10^{-12}	8.6×10^{-12}
40°C, 2 Layers	9.1×10^{-12}	14.0×10^{-12}
40°C, 4 Layers	12.5×10^{-12}	7.1×10^{-12}

Appendix 4.8 Diffusion Coefficients for Polyvinylidene Chloride Coated Nylon 6
and Vanillin

Sample	Initial Slope Method	Half Time Method
25°C, 2 Layers	3.0×10^{-14}	7.9×10^{-14}
40°C, 2 Layers	9.8×10^{-14}	34.9×10^{-14}

Appendix 4.9 Diffusion Coefficients for Ethylene-Vinyl Alcohol Films and Vanillin

Sample	Initial Slope Method	Half Time Method
E20, 2 Layers	7.5×10^{-13}	2.9×10^{-12}
E20, 4 Layers	34.1×10^{-13}	$8.3 \times 10^{-12*}$
F15, 4 Layers	34.5×10^{-13}	$8.2 \times 10^{-12*}$
XL15, 4 Layers	9.2×10^{-13}	$2.2 \times 10^{-12*}$

* Average value of only one or two replicates