This is to certify that the

thesis entitled

PERMEATION OF 2-NONANONE VAPOR THROUGH LLDPE AFFINITY FILMS AS APPLY TO MODIFIED ATMOSPHERE PACKAGING

presented by

MOHD ARIFF WAHID

has been accepted towards fulfillment
of the requirements for

MASTER degree in PACKAGING

Major professor

Date FEBRUARY 5, 1996

PERMEATION OF 2-NONANONE VAPOR THROUGH LLDPE AFFINITY FILMS AS APPLY TO MODIFIED ATMOSPHERE PACKAGING

By

Mohd Ariff Wahid

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

School of Packaging

1996

ABSTRACT

PERMEATION OF 2-NONANONE VAPOR THROUGH LLDPE AFFINITY FILMS AS APPLY TO MODIFIED ATMOSPHERE PACKAGING

By

Mohd Ariff Wahid

The sorption, diffusion and permeation of 2-nonanone in LLDPE was characterized at different concentrations, vapor activities and temperatures. The permeability was measured by quasi-isostatic method, and solubility and sorption profile data for 2-nonanone in LLDPE were determined by using microbalance technique. The results of this study showed concentration and temperature dependencies for the diffusion and permeability of 2-nonanone through LLDPE over the temperature range studied. Sorption behavior of 2-nonanone by LLDPE showed two mode sorption phenomena as a function of concentration and vapor activity at the temperature tested.

A model for modified atmosphere packaging of minimally processed fresh produced can be developed in relation to the permeant transport process. The mass transfer model includes the permeability and equilibrium solubility of 2-nonanone in the polymer material and be used to calculate the amount of the package area needed to maintain target concentrations in the headspace of the package.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Efficient packaging is a necessity for almost every type of product. Therefore, packaging materials usually been selected on the basis of their performance. Barrier property is one of the most important parts of the spectrum of properties needed in a protective packaging material. Containers are usually designed to provide the most complete protection against penetration from oxygen and other gases, loss or gain of water vapor, loss of distinct aroma, and risk of absorptions of alien odors. Glass and metal easily handled this problem. Due to economic and technical reasons, plastic becomes an alternative to glass and metal packaging because of their processability, light weight and relatively low cost, but their limitation is in barrier performance.

Packaging that serves a specific process function for the product which is an additional or different function from the common processing of product is sometimes called `functional packaging' or `active packaging' (Ono ,1990). In some instances certain additives are incorporated into packaging film or within packaging containers to modify the headspace atmosphere and to extend product shelf life. Package design should incorporate mass transfer parameters to control product quality with the added active packaging function. Therefore, it is important to study the permeability, solubility and the diffusion factor of the packaging materials.

Understanding the permeation process of the polymer is critical in order to select suitable flexible packaging materials to protect packaged products. The measurement of the barrier properties has largely been restricted to gas and water vapor permeabilities. Recently it has been recognized that the barrier function of a package to various organic compounds is important, and has lead to the development of a method test to measure permeabilities of various organic vapors (Gillette, 1988; Hernandez, 1986; Zobel, 1988).

Minimally processed fruits are products that can provide convenience and fresh-like quality. In 1995, 3% of the United States sales consisted of fresh-cut produce and by 2000, such ready-to-use produce is projected to fill 25% of shelf space (Leaversuch, 1995). A major factor contributing to the growth of this category is the refinement in the performance of plastic films. Films can be used to modify the package atmosphere and thereby substantially extend the shelf life of fresh produce. In this system, oxygen in air surrounding the product in the package is consumed by the product and carbon dioxide and water vapor are released, leading to a mixture of atmospheric gases different in proportion from that of air. Microbial growth is one of the major concern that can cause spoilage to minimally processed fruits in modified atmosphere packaging (MAP).

Recently the application of antifungal natural volatiles to control decay in minimally processed fruits has been explored (Vaughn et al., 1993; Hamilton-Kemp, 1992; Ding et al., 1992; Davis et al., 1972). 2-Nonanone has been shown to have antifungal activity in packages of strawberry and raspberry fruits

(Vaughn et al., 1993). This natural volatile may function as an effective antifungal compound which might be used commercially to prevent decay of stored fruits. According to (NIOSH, 1979), it has low mammalian toxicity (oral rat LD_{50}, 3200 mg/kg); a pleasant, fruity/floral odor, resistance to rapid decomposition, and adequately volatility (Vaughn et al., 1993). Therefore it has potential for commercial development as a slow-release fungistatic compound in prolong the shelf-life of fresh produce. Decay control using volatile hold some promise where it does not require direct application to the surface of the product, and are volatile in nature, so residue levels would tend to be low. According to Edney (1983), volatile materials can permeate the air spaces around the product more efficiently than liquids, leading to a greater likelihood of contact between the control agent and decay organism. Biologically active volatile materials are frequently encountered in nature and many are found in more than one source. For example, 2-nonanone can be found in attar of rose, clove oil, passion flowers, asparagus, tomato, corn and various fruits like raspberries and strawberries.

The permeation rate and diffusivity through polymer by 2-nonanone is unknown. This information is needed to develop the relationship between film permeability characteristics and the volatility and biological activity of this material. Information on diffusivity, solubility and permeability of organic volatiles can help in developing a better understanding of the mechanism of the movement of organic volatiles through polymer structures. The diffusion and solubility of organic volatile are important in the area of product quality when product quality is related to the effect of organic volatile in the closed environment and the transfer of the vapors out of the system. Knowledge of the organic vapor barrier properties of polymeric films can provide a means of designing a barrier structure for a specific application.

The objectives of the study were as follows:

1. To determine the permeability and sorption of 2-nonanone for linear low density polyethylene (Affinity PL 1880).
2. Evaluation of the concentration and temperature dependencies on the transport process of natural organic penetrant.
3. To develop a better understanding of the mechanism and the variables that affect sorption and diffusivity of natural volatile compound in barrier polymer film.
4. To develop a package design which takes into account the permeant transport process.

LITERATURE REVIEW

Permeation of Organic Vapor Through Polymer Films

The phenomena of mass transfer, includes permeation, absorption and desorption of gases or vapors into polymeric materials and is a very important aspect of packaging design. The permeability of packaging materials to organic vapors is of considerable interest, either to protect the packaged product from foreign odors or to retain its aroma and/or volatile compounds inside the package. According to Gillette (1988), the flux of a permeant through a film is a function of how much of the permeant is present in the film and the mobility of the permeant within the film. In other words, permeability is the product of the thermodynamic parameter of solubility and the kinetic variable of diffusion. For organic vapors, separating the permeability into its two components is important because the diffusion coefficients of these compounds are typically low enough that steady-state permeation is very slow to achieved . The significance of studying the mass transfer properties in polymer film have encouraged the development and application of various tests on the diffusion in polymer films. Solubility can become an important factor when low concentrations of a permeant must be contained in the product or the headspace of the package. Simply increasing the thickness of the packaging material may not prevent loss of the compounds if its solubility in the packaging material is sufficiently high. The compound will be effectively lost from the product by absorption into the packaging material under these circumstances. The sorption of organic vapors in plastic films become quite complex as the penetrant/polymer interaction increases. The sorbed vapors may swell and plasticize the polymer, resulting in increased mobilities of both polymer segments and penetrant molecules (Laine and Osburn, 1971).

There is no standard test for the measurement of organic vapor permeability, although there are a number of methods have been described for vapor permeability measurements. An apparatus that could permit permeability measurements to be made at very low vapor levels was described by Zoebel (1982). An instrument for studying the transport of aromas in polymer films has been described (DeLaussus et al., 1988) which utilizes a mass spectrometer to detect the permeant. Modern Controls, Inc has recently introduced the Permatran-O to measure the permeation of organic vapors through polymeric materials. Various procedures for quantifying the rate of diffusion of organic penetrants through polymeric films have been described by Hernandez et al. (1986). These authors describe the isostatic and quasi-isostatic methods.

Because the permeation rate of organic compounds is not as fast as that of the permeant gases, the slope of the straight part of the permeation curve is very flat for organic substances. Therefore, in the permeation rate of organic vapors, the extrapolation to the time axis is very uncertain and the lag time can lead to negative diffusion constant (Robertson, 1972). In instances where swelling of the polymer occurs by organic vapors, both diffusion and solubility constant become concentration and time dependent. Because these effects cannot be separated by combining time lag and steady state data, it is necessary to study the sorption behaviour as a function of time (Naylor, 1989). For this reason, it has been recommended (Kiszinowski, 1986) that the solubility constants of organic compounds should be determined by other methods such as sorption/desorption experiments. This is commonly done by suspending the polymer sample from a balance under a uniform concentration of vapor at a known temperature and pressure (Hernandez et al., 1986). The permeability and solubility of d-limonene vapor in package liners was studied by (Mohney et al.,1988) showed that the loss of aroma moieties can be result of sorption and permeation through the packaging material. Holland and Santangelo (1988) introduced the `laminate film' method for measuring vanilin transmission rates through food packaging films. The Plaque method (Kiszinowski, 1986) has been introduced when the organic compounds are sorbed from liquids.

The Nature of Permeant

The Mechanism of Diffusion and Sorption

The mechanism of permeation of a vapor through a polymer involves several steps (Van Amerongen, 1950). First, a diffusing molecule condenses on the high pressure side of the polymer. Then, this is followed by solution of the condensed vapor by the polymer. Next, the solution process is followed by diffusion through the polymer, which takes place by the movement of a permeant molecule through a tangled mass of polymer chains and holes which are constantly forming and reforming as the result of thermal vibrations. Usually the holes are smaller than the permeant molecule, hence, several jumps in the same direction must be made before the molecule is displaced by a distance equal to its length. According to Robertson (1992), diffusion of a dissolved permeant in a polymer is viewed as a series of activated jumps from one vaguely defined cavity within the polymer matrix to another. Qualitatively, it is possible to increase the number or the size of cavities in a polymer or give chain segments more mobile increases the rate of diffusion. This can be achieved for instance, by increasing temperature or by the use of plasticizers.

Following the diffusion process, there is desorption of the permeate on the low pressure side of the film by evaporation. Organic vapors diffuse by a more complicated mechanism which is dependent on the motions of both the polymer and diffusant molecule, which are comparable in size or larger than polymer chain segments. The total operational sorption process will likely involve one or more sorption modes. The nature of interactions between permeants and polymer is an important factor in which the molecule of permeants are distributed in the polymer may results in cluster formation, or randomly dispersed permeant. The sorption of organic vapors in polymer films becomes more complex as the penetrant-polymer interaction increases. The sorbed vapor swells and plasticizes the polymer, resulting in increased mobilities of both polymer segments and permeant molecules. The absorption of vapor is sometimes accompanied by time-dependent processes in the polymer which are slower than the micro-Brownian motion which promotes diffusion. These processes depend upon the nature of the polymer, the temperature, and the concentration of the permeant (Meares, 1965). Therefore polymer structure, free volume, chain stiffness of segmental mobility, and the availability of specific sites of interaction in the polymer, plus the physiochemical characteristics of the permeant determined the mode and mechanism of sorption and transport of the permeant within the polymer (Liu et al., 1991).

Variables Affecting Sorption and Diffusion

The size, shape and polarity of the permeate molecule, together with its facility of condensation, have important effects on permeability. Size and shape particularly affect diffusivity while solubility is influenced by polarity and ease of condensation of the molecule. The solubility of the permeate generally depends on its compatibility with the polymer (Pascat, 1986).

According to Murray (1985), important permeant properties include volatility and the size and shape of the molecule. Volatility controls the maximum concentration; size and shape relate to the movement through temporary holes which develop in the polymer. Linear molecules will penetrate more readily than cyclic molecules. The diffusion of most organics and water is complicated by concentration dependence, although gas transport at low pressure in polymer films is not concentration dependent (Hopfenberg, 1978). For the most systems, the diffusivity and permeability are generally higher when the polymer and permeant are similar. In polyethylene, which is a nonpolar material, the permeability is lowest for polar materials and highest for nonpolar materials such as hydrocarbons (Pinsky, 1957).

According to Laine and Osburn (1971), the diffusion coefficient at zero activity, pressure and concentration, D_o, generally decreases as the volume of the penetrant molecules increases, but branching has a greater effect than does molecular size. For example, addition of a methyl group on a given paraffin reduces the valve of D_o more than does increasing the chain length by one carbon atom. This suggests that diffusion occurs preferentially along the direction of greatest length of the permeant molecule. The solubility coefficient, S_o, on the other hand, increases exponentially with the increase in molecular volume and crossectional area of the penetrant molecule. As a result of this compensating dependence of D_o and S_o on permeant size and shape, the zero concentration permeability coefficient, P_o, which equals the product of D_o and S_o, is much less dependent on the size and shape of the penetrant than either term separately (Roger, 1965).

The Nature of Polymer

The barrier properties of films depend on the specific molecular structures of the polymers involved (Pascat, 1986). A fairly systematic correlation has been established (Paine and Paine, 1983) between the activation energy for diffusion, E_d, the size of penetrant molecules and the T_g of polymers for a wide range of gases and low molecular weight organic vapors. There is a greater dependence of both sorption and diffusion processes on the size and shape of the penetrant molecule in the glassy state than in the rubbery state. The low densities of plastic materials with their open structures allows small molecules pass through the structure without being affected by the diffusion process. In higher density polymers, the initialy sorbed vapor breaks up some of the more imperfectly ordered crystalline regions which would be proportional to the vapor concentration (Roger et al., 1956). Diffusion proceeds exclusively in the amorphus regions of the polymers which pass through the voids in these polymer regions. These voids are created by segmental motion of the polymer chains. Segmental mobility of the polymer chains increases with temperature (Roger et al., 1956). The diffusion process takes place in the amorphus domains of the polymer and is dependent upon the mechanical and thermal history of the polymer (Zobel,1985). Crystallites may reduce polymer chain segment mobility in the interstitial amorphus phase, thereby raising the energy barrier of diffusional transport of permeants. Futhermore, the degree of segment immobilization will become greater as the volume fraction of crystalline phase increases and/or the average crystallite size decreases. The number and length of side chain branches in polymers are also important to the barrier properties.

Polymer Material : Polyethylene

The Ziegler-Natta or, often, Ziegler catalysts polymerize a wide variety of monomers to linear or stereoregular polymers. Ziegler (1955) introduced the polymerization of ethylene with aluminium alkyls and chlorides of transition metals of group IV and VI, which produce polyethylene with a catalyst system of anhydrous aluminium chloride and titanium tetrachloride under pressure and elevated temperature. According to Diedrich (1975), the original Ziegler type catalyst systems were of low activity, generating as little as 1500 g of polymer per gram of transition metal. Thus, Ziegler processes of the first generation required large quantities of catalyst and insufficient flexibility of the polymerization process to produce products for a wide range of application. Second generation Ziegler polyethylene processes has been developed by introducing high yield catalyst systems, which are capable of producing polyethylene without removal of catalyst and no need for additional processing steps. The catalyst can control the basic physical parameters of the polymer, for example, molecular weight, molecular weight distribution and the proportion of long and short side chains.

According to Billmeyer (1984), the physical properties of polyethylene are functions of three independent structural variables: molecular weight, molecular weight distribution or long chain branching and short chain branching. Properties dependent on crystallinity, such as stiffness, tear strength, hardness, chemical strength, softening temperature and yield point, increase with increasing density or decreasing amount of short chain branches in the polymer, whereas permeability to liquids and gases, toughness and flex life decrease under the same conditions. The effect of long chain branching on the properties of polyethylene is evaluated in terms of the breadth of the molecular weight distribution. A decrease in molecular weight distribution causes in a decrease in ease of processing but an increase in tensile strength, toughness and impact strength, and resistance to environmental stress cracking. Most of the differences in properties between branched and linear polyethylenes can be attributed to the high crystallinity of the latter polymers. Linear polyethylenes are stiffer and have a higher crystalline melting point and greater tensile strength and hardness then the branched material.

Recently, a new polyolefin polymerization catalyst technology has been developed based on metallocene catalysts. This technology is based on a constrained geometry ligand attached to a group IV transition metal (eg., Ti) catalyst center. The catalyst structure allows a significant increase in the flexibility for incorporating ethylene and other alpha olefin comonomers into the polymer structure. A new family includes homopolymers and copolymers of olefin polymers has been produced. This new constrained geometry catalyst technology can produced an excellent physical and mechanical properties and excellent melt processability (Swogger, 1992). According to Leaversuch (1995) metallocene-based polyethylene will be central to minimally processed fruit and vegetable market growth. Metallocene polyethylene is suitable to maintain the optimal balance of oxygen, carbon dioxide and moisture necessary. It can be made at densities as low as 0.89 g/ml. Metallocene polyethylene delivers a higher oxygen and moisture vapor transmission rates than other polyethylene, thus highly efficient in allowing oxygen in and carbon dioxide out. Moisture control allows designers to minimize wilting. Metallocene polyethylene can provide clarity, toughness, extended heat sealing and FDA compliance for food use.

Studies of organic vapor-polyethylene systems have been made by Rogers et al. (1960) and McCall and Slichter (1958) for the diffusion of saturated vapors in several polyethylenes at various temperatures. Michael and Parker (1959) studied the sorption of gases through polyethylene films. The authors found that the solubility depends primarily on the amount of crystallinity presents. The magnitude reflects both the volume fraction of amorphus polymer and the area fraction of amorphus material available for flow. Temperature dependence of branched polymer permeability is somewhat greater than linear polymer due to the increase in diffusional activation energy caused by the short chain branches (Michael et al., 1959). Polymers at temperatures below the glass transition exhibit anomalous non-Fickian diffusion behaviour. The discussion of this phenomena can be found in the literature (Roger et al., 1956).

Affinity PL 1880 polyolefin plastomer is the first family of homogenous ethylene alpha-olefin copolymer with 12% octene comonomer developed by the Dow Chemical Company using in-site technology, for use in a variety of demanding packaging applications, including high speed, form-fill seal products. It has narrower molecular weight distribution compare to linear low density polyethylene produced by Ziegler-Natta process. It has excellent ultimate hot tack strength and low temperature seal initiation, outstanding optics and abuse resistance. This film has excellent compatibility with other polyolefins, allowing efficient blending and coextrusion.

Modified Atmosphere Packaging For Minimally Processed Fruits

Modified atmosphere packaging involves modification of atmospheric conditions, via the commodity's respiration as it responds to the surrounding physical environment. Initial modification can be made by the replacement of the air in the headspace of the package with a mixture of atmospheric gases different in proportion from that of air or passively modified by fresh produce inside the package. The recommended concentration of oxygen and carbon dioxide for modified atmosphere storage of fruits and vegetables can be found in the published literature (Kader, 1985). Minimally processed fruits and vegetables contribute 3% to the United States fresh produce sales in 1995 and by 2000 such ready-to-use produce is projected to fill 25% of shelf space (Leaversuch, 1995). These products have the attributes of convenience and fresh-like quality. The key importance of minimally processed fruits and vegetables is the control of enzymes from the produce itself or from the invading microorganisms (Robertson, 1993), to maintain the firm, crisp texture, bright and light color. According to King and Bolin (1989), the primary spoilage mechanisms are the metabolism of the tissue and microbial growth; both will cause deterioration of the tissue and must be controlled to maintain tissue viability. Decay control can be achieved through the application of chemical food additives such as SO_2 or the use of heat or irradiation. The use of natural preservative compound has a greater appeal and increase in interest in the use of organic volatiles to control decay. In a modified atmosphere packaging system, natural organic compounds can be used to control decay by adding the compound in the packaging film of by flushing into the headspace of the package. 2-Nonanone is a promising organic volatile that effectively controls fungal growth on minimally processed fruits (Vaughn et al., 1993).

Properties of Organic Vapor : 2-Nonanone

2-Nonanone is a natural volatile compound found in various fruits like raspberries and strawberries (Vaughn et al., 1993). The formula of

2-nonanone is $CH_3(CH_2)_6COCH_3$, with a -C=O functional group, known as the carbonyl group in the chemical structure. It is a colorless liquid with a melting point of -9 °C and boiling point of 194 °C. The density of 2-Nonanone is 0.832 g/ml. This natural volatile may function as an effective antifungal agent if sufficient concentration could be maintained in the gas space surrounding the fruit. According to (NIOSH, 1979), it has low mammalian toxicity (oral rat LD_{50}, 3200 mg/kg); a pleasant, fruity/floral odor; resistance to rapid decomposition and adequate volatility (Vaughn et al., 1993).

Theory of Permeation.

According to Jost (1960), diffusion through polymer materials at constant pressure and temperature can be expressed by Fick's Law. The first Fick's Law described the rate (J) of transfer of diffusing substance through unit area of a section as being proportional to the concentration gradient $\partial C/\partial x$. The equilibrium uinidirectional diffusion along the x axis can be expressed as,

$$J = -D\,\partial c/\partial x \qquad (1)$$

where J represent the mass of the substance which passed through a unit area perpendicular direction during a unit of time, D is the diffusion coefficient and c is the concentration of the permeant substance. Diffusion as a function of time on a reference volume is given by Fick's second Law.

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial c}{\partial x}\right) \qquad (2)$$

Equation (2) is also valid if D is a function of penetrant concentration and/or time. When D varies with time, t , the diffusion is often called non-Fickian. Integration of Fick's first law gives an expression relating flux (J) to the diffusion coefficient (D), and gas concentration c_2 and c_1, the steady state concentration of the permeant at the two surfaces of a gas barrier to thickness, L, by,

$$J = (x^{-1}) \int_{c1}^{c2} D.\partial c = D\,(c2-c1)x^{-1} \qquad (3)$$

Similarly, for a given plastic barrier at equilibrium, the steady state due to permeation is given by,

$$J = (x^{-1}) \int_{p1}^{p2} P.\partial p = P(p2-p1)L^{-1} \qquad (4)$$

where p_1 and p_2 are the partial pressure of the permeating species on either side of the barrier, and P is the permeability coefficient. From these expressions, the total amount of permeating substance (Q) passed through the polymer area (A) during time (t) can be evaluated thus,

$$Q = DAt\,\frac{(c2-c1)}{L} = PAt\,\frac{(p2-p1)}{L} \qquad (5)$$

To relate the concentration of the substance (c) within the polymer barrier to the concentration of substance in the gas or vapor phase in equilibrium with the polymer, Henry's Law is assumed,

$$c = Sp \qquad (6)$$

where S is the solubility constant of the gas or vapor in the polymer. Therefore, the gas or organic vapor barrier characteristics of plastics may be expressed by reference to three coefficients as mention by (Gillette, 1988), permeability is the product of the thermodynamic parameter of solubility and the kinetic variable of diffusion.

$$P = DS \qquad (7)$$

where, the diffusion coefficient, D, the permeability coefficient, P, and the solubility constant characteristize the process of gas transfer through a polymer.

The diffusion coefficient is a kinetic term that describes how fast a permeant moves in a polymer and it also measure of how much time is required to reach steady state. The value of the diffusion coefficient for a selected penetrant/polymer, is determined by the size of the permeant and the size and frequency of fluctuations of polymer molecules. It is a combination of geometry and thermal effects. Ng (1985) summarized the dependence of diffusion on concentration in polymers as follows;

$$D = K \exp(A\beta c) f_o^{-2} \qquad (8)$$

where,

K = a jumping frequency factor

A = a factor related to the minimum hole size for a jump to occur

F_o = the polymer free volume fractioning in the absence of the vapor

β = a measure of the ability of the migrating compound to increase the free volume of the polymer

c = the concentration of the compound

The solubility coefficient is a thermodynamic term that describes how many permeant molecules move in a polymer. It can be determined by temperature, chemical activities, and intermolecular interactions plus the state of the polymer relative to its glass transition temperature (De Lassus and Strandburg, 1991).

Factors Affecting the Diffusion and Solubility Coefficients

Pressure

The permeability coefficient is independent of the pressure of the diffusing gases and vapors provided there is no interaction between the polymer and diffusing material. However, where there is strong interaction, the permeability is found to be pressure dependent and, in general, it increases as the pressure increases. This is due to an increase in diffusion coefficient, D, promoted by the plasticizing effect of the sorbed permeant, and an increase in the solubility coefficient, S, due to the shape of the sorption of permeant (Robertson, 1992).

Sorption behavior

The term sorption is used to describe the initial penetration and dispersal of permeant molecules into the polymer matrix and includes both adsorption and absorption as well as cluster formation (Naylor, 1989). Sorption behaviour has been classified on the basis of the relative strengths of the interactions between the permeant molecules and the polymer, or between the permeant molecules themselves within the polymer. Three major types of sorption behavior are Henry's Law sorption, Langmuir-Type sorption and Dual-mode sorption.

Temperature

At low pressures or at enhanced temperature, the solubility of gases in a polymer is dependent of the pressure, and the Equation (6) is analogous to Henry's Law (Stepek et al., 1987). An increase in temperature contribute energy to increase the segmental motion of the polymer chains, which increases the permeability of permeants through the polymeric films. The temperature dependence of the solubility coefficient over relatively small ranges of temperature can be represented by an Arrhenius-type relationship:

$$S = S_o \exp(-\Delta H_s)/RT \qquad (9)$$

where S_o is a constant, ΔHs is the heat of solution of the gas in the polymer. For condensable vapors ΔH_s is negative due to the contribution of the heat of condensation, and thus S decrease with increasing temperature. R and T stand for the universal gas constant and absolute temperature, respectively.

The temperature dependence of the diffusion coefficient can also be represented by an Arrhenius-type relationship:

$$D = D_o \exp(-E_d)/RT \qquad (10)$$

where D_o is a constant, and E_d is the activation energy of diffusion which is usually a linear function of temperature. E_d is associated with the energy required for hole formation against the the cohesive forces of the polymer plus the energy necessary to force the molecule through the surrounding structure. For organic liquids in polymer, this value is generally between 10 to 40 kcal/mole (Laine and Osburn, 1971).

From the above two equations it follows that:

$$P = P_o \exp(-E_p)/RT \qquad (11)$$

$$P = (D_oS_o) \exp [-(E_d+H_s)/RT] \qquad (12)$$

where E_p (= E_d + H_s) is the apparent activation energy for permeation. Generally, the solubility coefficient decreases for vapors, and the diffusion coefficient increases with temperature for both gases and vapors (Brown, 1981). Therefore, permeability coefficients of different polymers for one type of permeant determined at one temperature may not be in the same relative order at other temperatures.

Measurements of Transport Properties

Permeability Measurements

A quasi-isostatic test method or accumulation technique has been developed (Hilton and Nee, 1978) for determining the permeability of organic vapors through barrier films. The polymer film is mounted in a permeability cell and the vapor permeating through the film is monitored such that the total quantity permeated can be plotted as a function of time. Baner et al. (1986) described a method based on a quasi-isostatic procedure for determining the diffusion of organic penetrants through polymeric films. Baner et al. (1986) employed a continous flow of organic vapor through the high concentration cell chamber to assure a constant vapor gradient. A gas chromatographic method was developed for the permeation rate measurements. Barrer (1939) presented a solution of Equation (2) which allowed an approximative determination of D, the diffusion coefficient:

$$D = L^2/6\theta \tag{13}$$

where θ is the intersection of the projection of the steady-state portion of the transmission curve and is called the lag-time (Figure 1). The steady state permeability coefficient (P) can be determined from the quasi-isostatic method by using the Equation (14),

$$P = yL/Ab \tag{14}$$

where y is the slope of the straight portion of the transmission rate curve (mass/time), L is a thickness of the film, A is an area of the film exposed to the permeant in the permeability cell and b is driving force given by the concentration or partial pressure gradient. By plotting $\log[t_{1/2}(\ dM/dt)]$ as a function of 1/t, it is possible to obtain information about the concentration dependency of the diffusion coefficient, D (Baner, 1987).

Sorption Measurements

Sorption measurements have been used to select potential barrier polymer films for specific applications. Fujita (1961) described the general behavior of sorption and permeability of organic vapors. Baner (1987) applied the equilibrium vapor pressure and microbalance gravimetric technique to study the sorption and diffusion of toluene vapor through polymeric films as a function of penetrant concentration. Solubility of vapors is usually determined in sorption apparatus by measuring gravimetrically the equilibrium amount of the vapor absorbed by a known volume or weight of polymer. A gravimetric technique carried out at equilibrium vapor pressure can continually measure the weight gain and loss by the sample film as a function of time. The solubility coefficient and diffusivity coefficient are thus determined by sorption measurement (Hernandez et al., 1986). Crank (1975) described the diffusion equation appropriate for the sorption of penetrant by a polymer film as:

$$Mt/M_\infty = 1 - (8/\pi^2)\,[\exp(-D\pi^2 t)/L^2 + 1/9\,\exp(-9D\pi^2 t)/L^2] \quad (15)$$

where M_t and M_∞ are the amount of penetrant sorbed or desorbed from the polymer film sample at any time (t) and the equilibrium sorption level after infinite time, respectively, t is the time to attain M_t, and L is the thickness of the film sample.

The sorption diffusion coefficient (D_s) and diffusion coefficient for desorption (D_d) can be calculated from Equation (16), where $M_t/M_\infty = 0.5$ (Figure 2).

$$D_d = D_s = 0.049L^2/t_{1/2} \quad (16)$$

Where $t_{1/2}$ is equal to the time required to reach a sorption level equal to half of the equilibrium value, M_∞.

Solubility coefficient (S) values can be calculated from sorption experiments by yhe following equation.

$$S = \frac{M_\infty}{wb} \quad (17)$$

Where S is the solubility coefficient expressed as mass of vapor sorbed at equilibrium per mass of polymer per driving force . M_∞ is the total amount (mass) of vapor absorbed by the polymer at equilibrium for a given temperature, w is the weight of the polymer sample under test and b is a value of the permeant driving force.

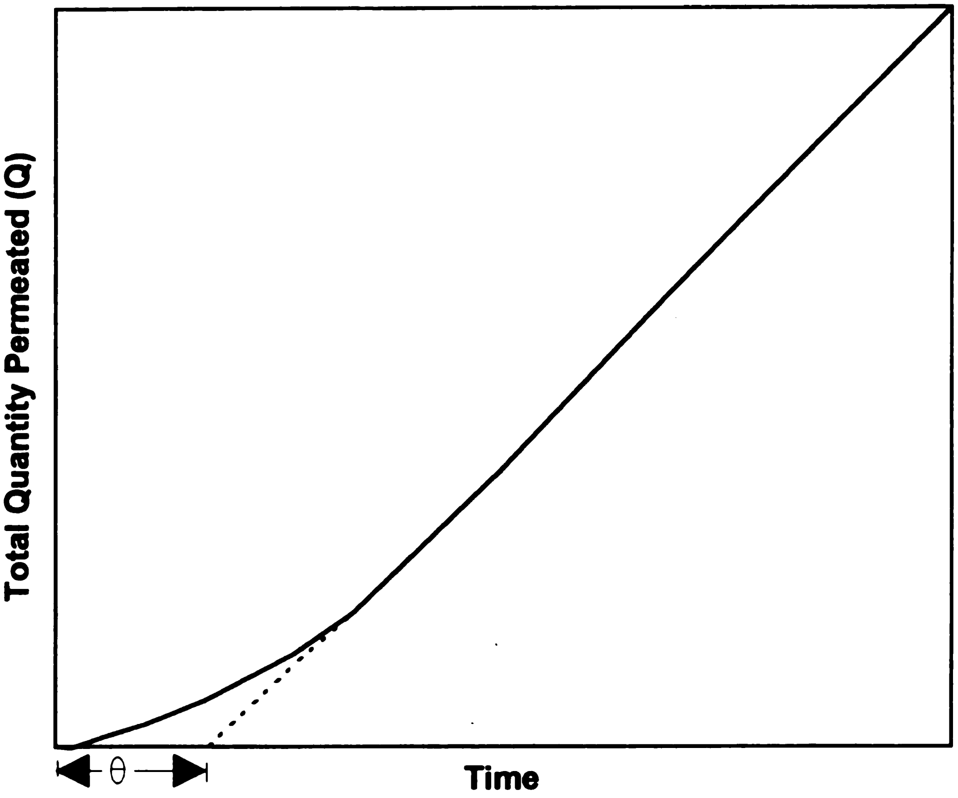


Figure 1. Transmission rate profile of the quasi-isostatic method

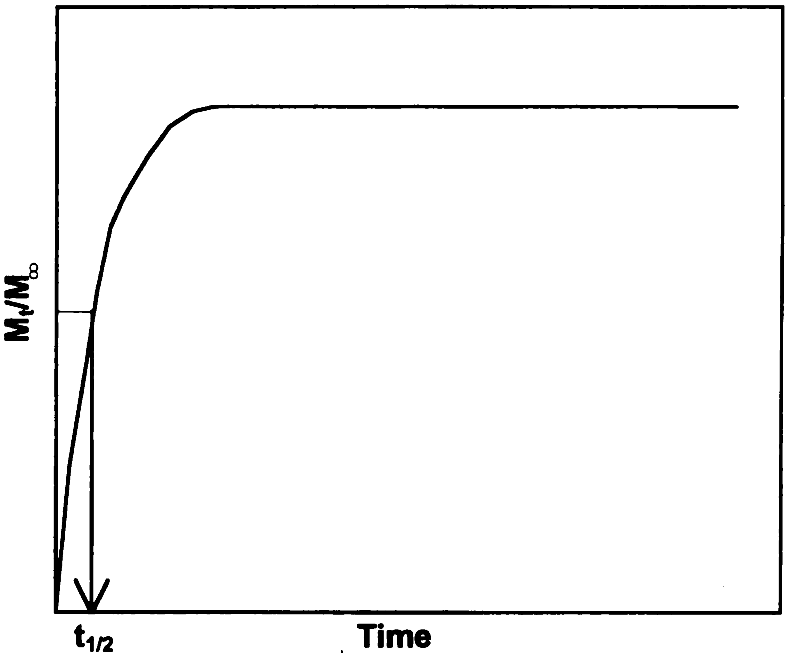


Figure 2. Generalized sorption profile curve

MATERIALS AND METHODS

Materials

Polymer Film

Linear low density polyethylene, polyolefin plastomer called Affinity PL 1880, 1.9 mil thick from Dow Chemical Company with 12% octene comonomer group was used in the experiments. The polymer had a density of 0.902 g/cc. The physical properties was illustrated in Table 2. This material was selected based on the structural properties, highly permeable to oxygen which is suitable for fresh produce, and relatively inexpensive.

Penetrants

Research grade 2-nonanone ($CH_3(CH_2)_6COCH_3$) from Adrich Chemical Company (purity greater than 99 %, boiling point of 192 °C/743 mm, molecular weight 142.24 g/mol and density 0.832 g/cc) was employed through out, as the permeant molecule.

Acrylonitrile

Used as a solvent for constructing a 2-nonanone calibration curve.

Nitrogen Gas

Used as a carrier gas. High purity dry nitrogen 99.98%.

Experimental Procedures

Permeability Measurement

The permeability test based on the quasi-isostatic method (Figure 3) was used to collect the permeation data at different concentrations of the volatile compound through a sample film at 22, 30 and 40 °C (Hernandez et al., 1986). The film to be tested has been mounted in the permeability cell which was comprised of two aluminium cell chambers and placed in constant temperature chamber. A constant concentration of permeant vapor was passed through the center cell chamber at a constant rate. The center cell was separated from the two edge chambers by the test film. This cell design allows the permeability of two film samples to be determined concurrently, under identical conditions.

A constant concentration of a permeant vapor was generated by bubbling nitrogen gas through liquid permeant maintained at constant temperature. The vapor permeating through the film into the lower chambers was then quantified by sampling and analysis by gas chromatography, until the permeation rate attained steady state. At predetermined time intervals an aliquot (500 μl) of headspace was withdrawn from the low concentration cell chambers with a gas tight high performance syringe (Hamilton, No. 1750) and injected directly into the gas chromatograph with flame ionization detection. An equal volume of nitrogen was replaced into the cell in order to maintain a constant total pressure (1 atm).

To determine the diffusivity and permeability values, the increase in penetrant quantity in the lower concentration cell chamber was plotted as a function of time and the resultant transmission rate profile was related to the permeability of the film sample.

Sorption Measurement

The sorption measurement system was obtained by using an equilibrium vapor pressure and microbalance gravimetric technique (Figure 3). A Cahn Electrobalance (Cahn Instruments, Inc., Cerritos, CA) will be employed for the gravimetric technique (Hernandez et al., 1986). The electrobalance and sample tube were placed in the temperature controlled chamber, which maintained at 22 °C, 30 °C and 40 °C. A film sample was cut into small pieces and a weight between 30 to 50 mg was used since the sensitivity of the system is 5 μg for a sample mass of approximately 30 mg. The nichrome wire was hooked to one end of the sample, and tube assembly with the sample hanging freely in hangdown tube. The wire hooked to the sample was also hooked to the balance arm. This system allows continous collection of sorption data until equilibrium is reached as a function of penetrant concentration and temperature. A constant concentration of permeant vapor was flowed continously through the hangdown sample tube.

A constant concentration permeant vapor can be produced by using a vapor generator system. Before actual testing was conducted, rotameter settings were determined to provide a range of vapor activities. Vapor activity was calculated by dividing the experimentally determined vapor pressure by the saturated vapor pressure (Appendix B). Rotameters were used to provide an indication of the settings required for the desired vapor activities. The gas flows to the rotameters were regulated by Nupro \`M' series needle valves. For the calculation of vapor activity, a standard calibration curve for 2-nonanone was prepared. A detailed procedure to measure the calibration factor is presented in Appendix A and Figure 4 shows the standard calibration curve of 2-nonanone. Sorption profiles and solubilities were obtained by a continuous recording of weight-gain measurement at 22 °C, 30 °C and 40 °C until the system reached steady state. After this stage was reached, the desorption profiles was measured by closing the valve that attached to the vapor generator system that carried a constant concentration of permeant vapor through the tube. This would allow the permeant to desorbed out of the sample. To determine whether the initial portion of the sorption of the sorption curve followed Fickian behavior, and to estimate the diffusion coefficient, the following method was applied with the aid of a computer assisted fitting point. The values of M_∞ were selected by refering to a plot of the experimental M_t vs time, t, data. The M_∞ value for a Fickian diffusion process was assigned, the $t_{1/2}$ value can be obtained from a plot of M_t/M_∞ versus time value and the diffusion coefficient (D_s) calculated by refering to Equation (16). By substituting the D_s value into Equation (15), calculated values of M_t were obtained. By using minimum sum of square between the calculated and experimental values, the calculated values were selected to plot M_t/M_∞ versus time and compared with the experimental values.

Gas Chromatographic Analysis

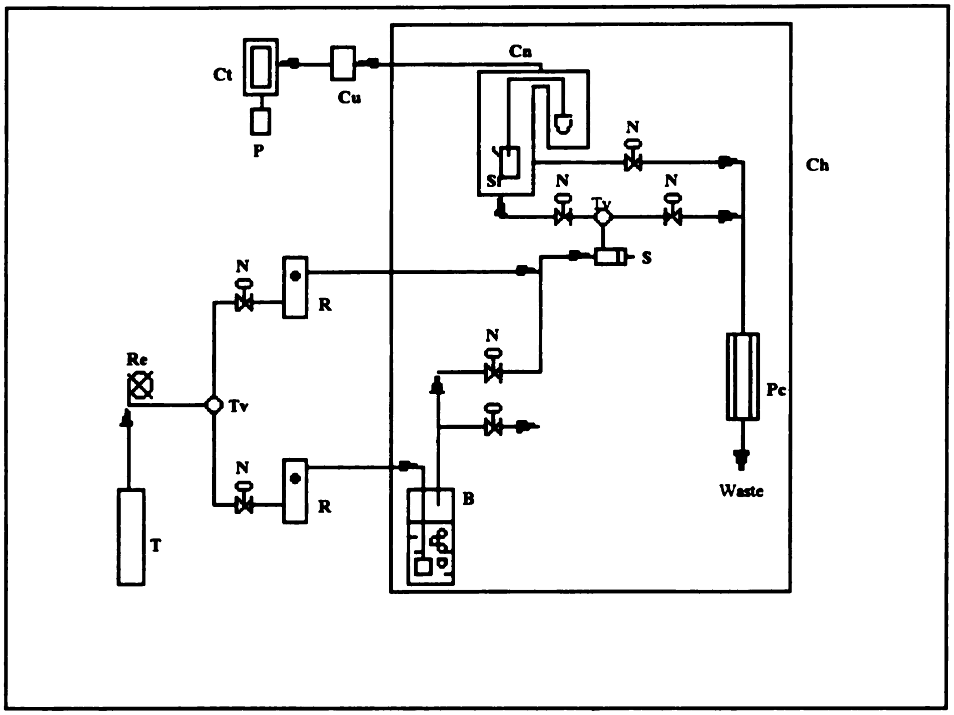
Analysis of permeant concentration was carried out by a gas chromatographic procedure with flame ionization detection. A Hewlett-Packard Model 5890A gas chromatograph equipped with flame ionization detector interfaced to a Hewlett-Packard Model 3392A integrator was employed for quantification. The gas chromatographic conditions are presented in Table 1. A standard curve of detector response versus quantity has been constructed from standard solutions of known concentration. Figure 4 shows the standard curve, where response is plotted as a function of 2-nonanone quantity. Elution time for 2-nonanone was at 11.7 min.

Injection temperature	220 °C
Max. oven temperature	250 °C
Final temperature	200 °C
Detect temperature	250 °C
Rate	7.5 °C/min
He carrier gas	45 l/min
Initial time	1 min
Final time	30 min
Column	SPB-5 Fused silica capillary column 30 m, 0.32 mm ID 0.25 μ film thickness

Table 1. Setting condition of gas chromatograph

Physical Properties		**Values**
Percent comonomer, octene		12.0
Melt index, dg/min		1.0
Density, gm/cc		0.902
DSC Melting Point, °C		100
Film Properties, 2.0 mil		
Puncture Resistance, J/cm^3		26.0
Dart Impact, g		>830
Elmendorf Tear Strength, g	MD	355
	CD	500
Ultimate Tensile, psi	MD	7170
	CD	3800
Ultimate Elongation, %	MD	570
	CD	560
Seal Initiation Temperature, °C		85

Table 2. Physical properties of linear low density polyethylene Affinity PL 1880



B - Organic Vapor Bubbler
Ch - Control Temperature Chamber
Cn - Cahn Electrobalance
Ct - Computer Terminal
Cu - Control Unit
N - Needle Valve
P - Plotter

Pc - Permeability Cell
R - Rotameter
Re - Regulator
S - Sampling Port
Sf - Sample Film
T - Nitrogen Tank
Tv - Three Way Valve

Figure 3. Schematic Diagram of Sorption and Permeability Test Apparatus

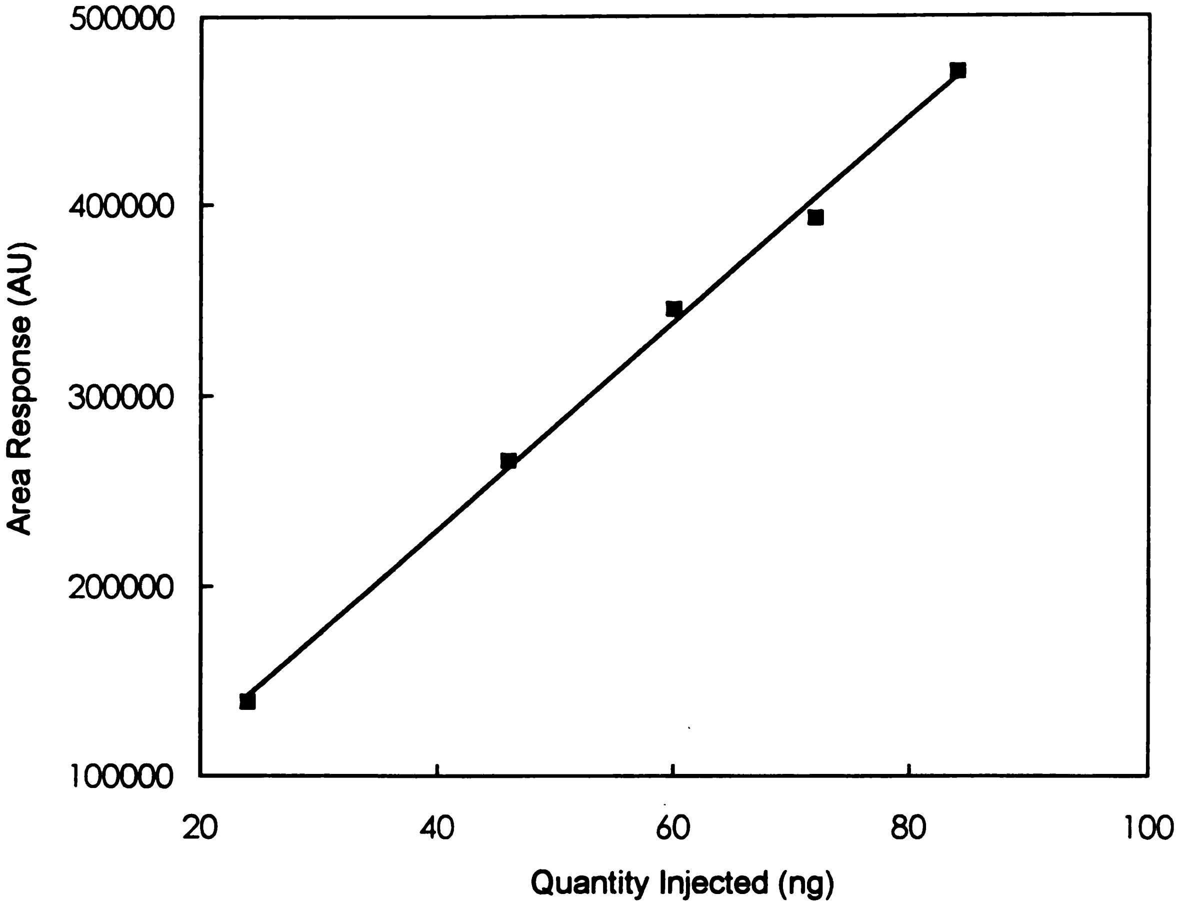


Figure 4. Standard Calibration Curve of 2-Nonanone at 23°C

RESULTS AND DISCUSSION

Solubility of 2-Nonanone Vapor in LLDPE Affinity PL 1880 Film.

Plots of M_t/M_∞ vs time for sorption of 2-nonanone in Affinity PL 1880 film at 22 °C are shown in Figures 5 to 11. The experiments were conducted at the vapor activities of the permeant ranging from 0.13 to 0.58. Superimposed on the experimental data is the calculated curve according to Equation (15) with the diffusion coefficient, Ds, as calculated from Equation (16). Similar plots were prepared for solubility of 2-nonanone at 30 °C and 40 °C and are shown in Figures 12 to 17 and Figures 18 to 23, respectively. The vapor activities ranged from 0.13 to 0.66 at 30 °C and 0.18 to 0.53 at 40 °C. For these cases, the calculated curves were also compared to the Fickian model. At 22 °C, at a concentration of 2-nonanone less than 2 ppm (w/v) or vapor activity less than 0.38, equilibrium times of less than 10 hours were observed for the Fickian diffusion process. As shown, the theoretical curve fits the experimental data very well and the initial portion of the curve is approximated by a straight line. The Fickian diffusion pathway may be assumed to be completed before applicable stress-relaxation has occured. It can be seen that in the early stage of sorption, the 2-nonanone vapor gradient provides the major driving force and the transport process is dominated by Fickian diffusion. At 22 °C, as the concentration of 2-nonanone increase above 2 ppm or vapor activity above 0.38, the agreement between the experimental and calculated results, following the same procedure as above, is quite poor as shown in Figures 10 and 11. This trend occurred at vapor activities above 0.33 as shown in Figures 15 to 17, at 30 °C, and vapor activities above 0.28, as shown in Figures 20 to 23, at 40 °C. The sorption process is sufficient to develop a significant swelling stress which produces gradual swelling of the polymer structure and allows additional sorption. Therefore the level of vapor concentration determines sorption behavior. Berens (1977) and Mohney et al. (1988) also observed this behavior and suggested that this behavior involved a `two-stage' sorption process with a non-Fickian, relaxation-controlled mode of sorption superimposed on the Fickian diffusion.

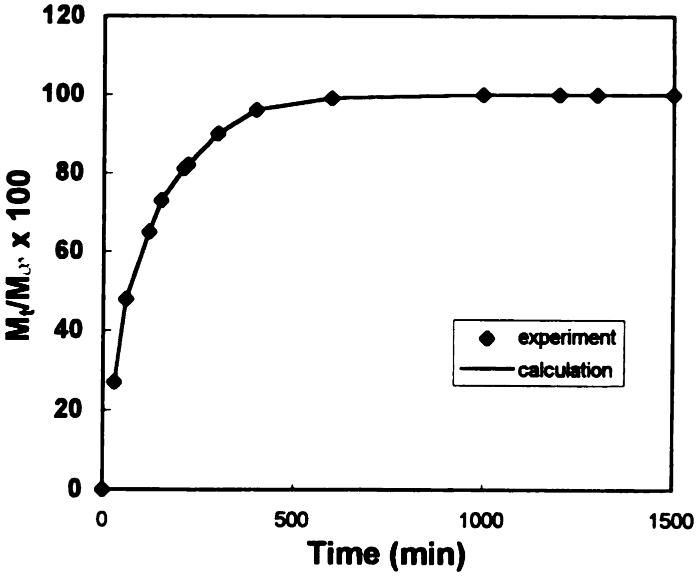


Figure 5. M_t/M_∞ vs Time at 22 °C and Av = 0.13

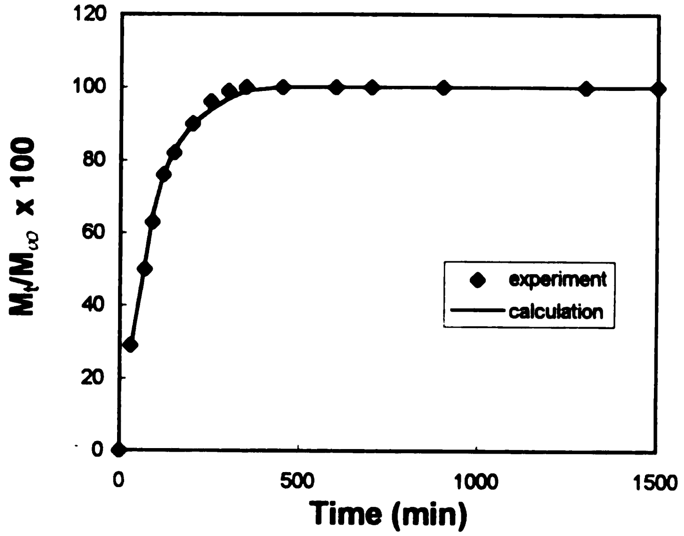


Figure 6. M_t/M_∞ vs Time at 22 °C and Av = 0.15

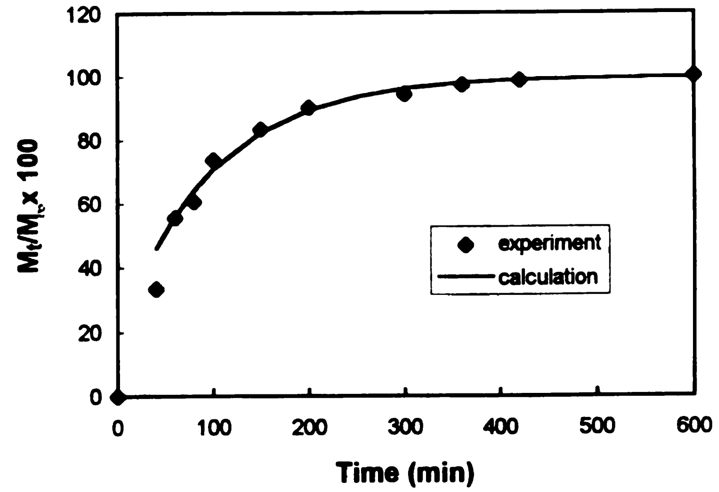


Figure 7. M_t/M_∞ vs Time at 22 °C and Av = 0.18

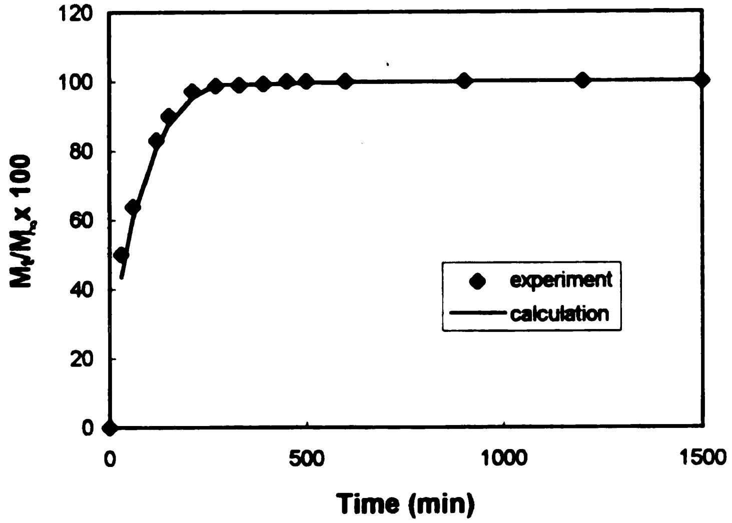


Figure 8. M_t/M_∞ vs Time at 22 °C and Av=0.23

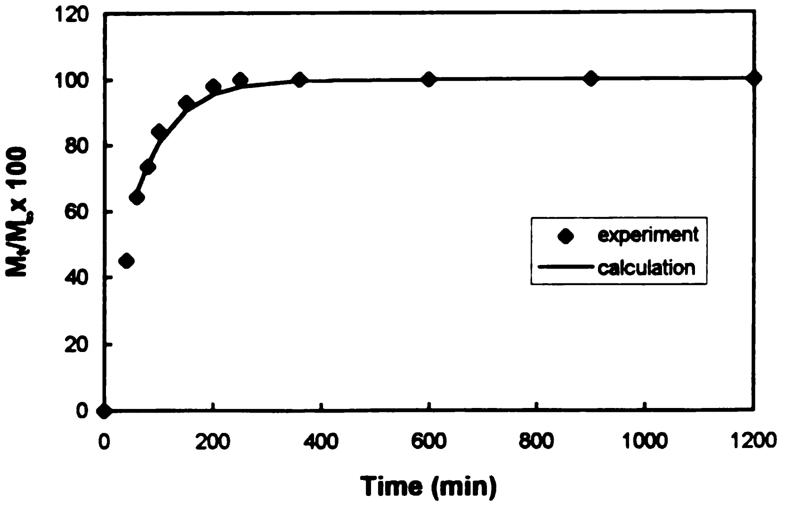


Figure 9. M_t/M_∞ vs Time at 22 °C and Av = 0.38

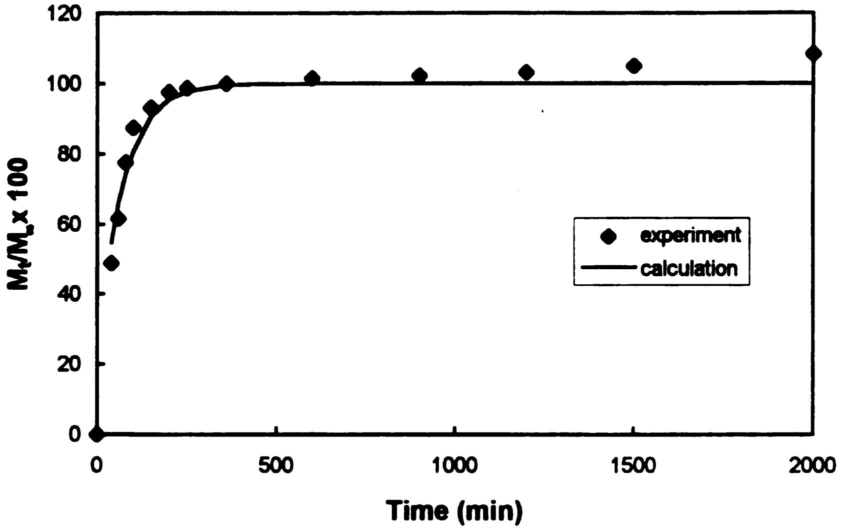


Figure 10. M_t/M_∞ vs Time at 22 °C and Av = 0.48

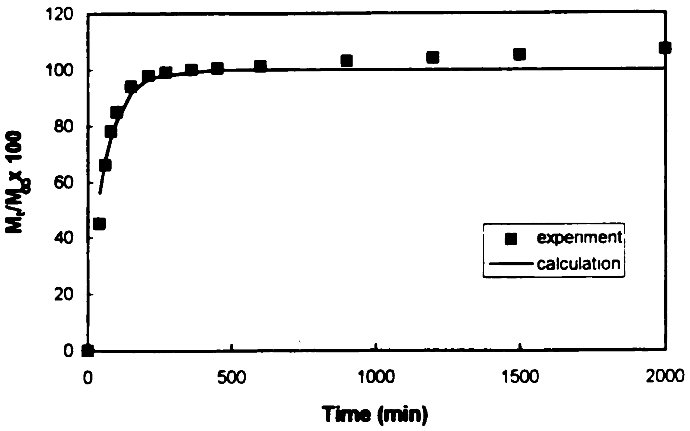


Figure 11. M_t/M_∞ vs Time at 22 °C and Av = 0.58

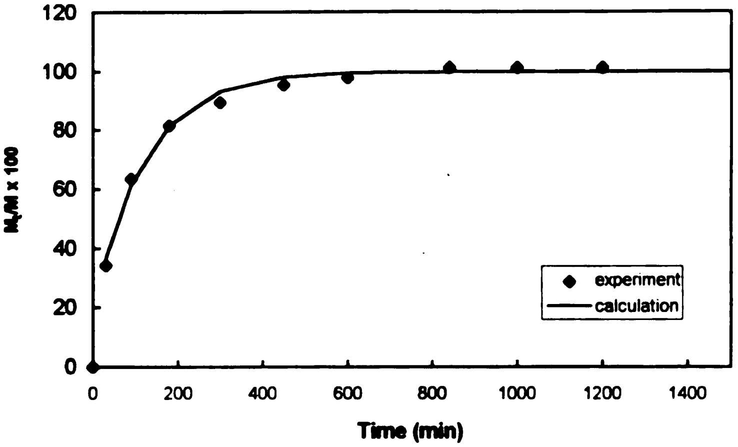


Figure 12. M_t/M_∞ vs Time at 30 °C and Av = 0.13

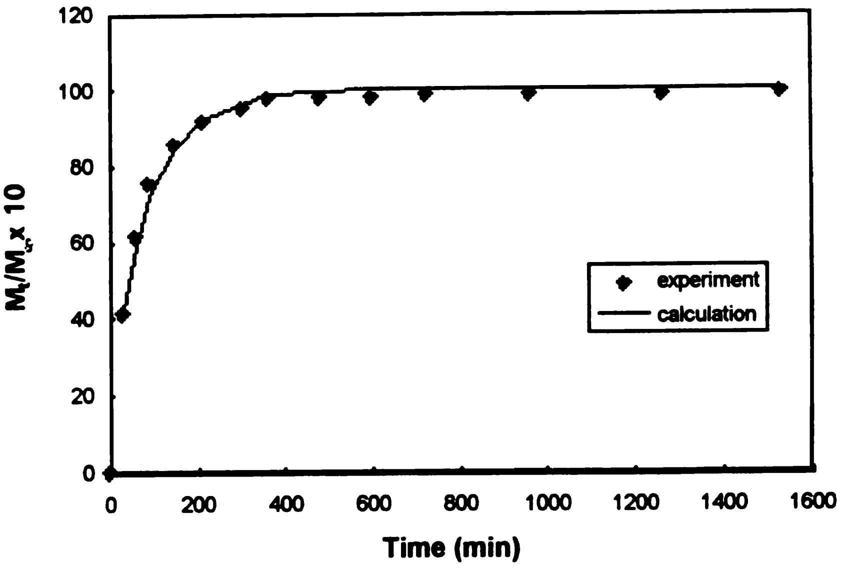


Figure 13. M_t/M_∞ vs Time at 30 °C and Av = 0.18

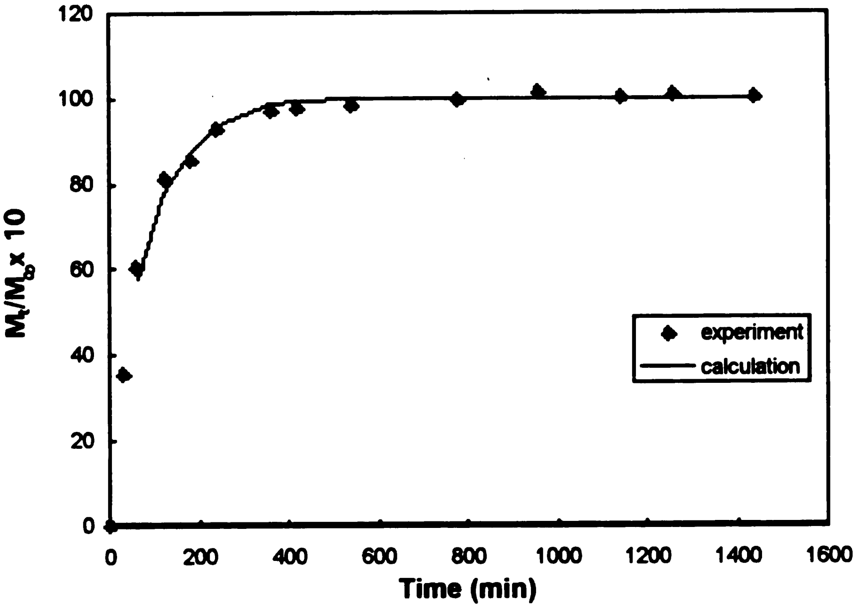


Figure 14. M_t/M_∞ vs Time at 30 °C and
Av = 0.24

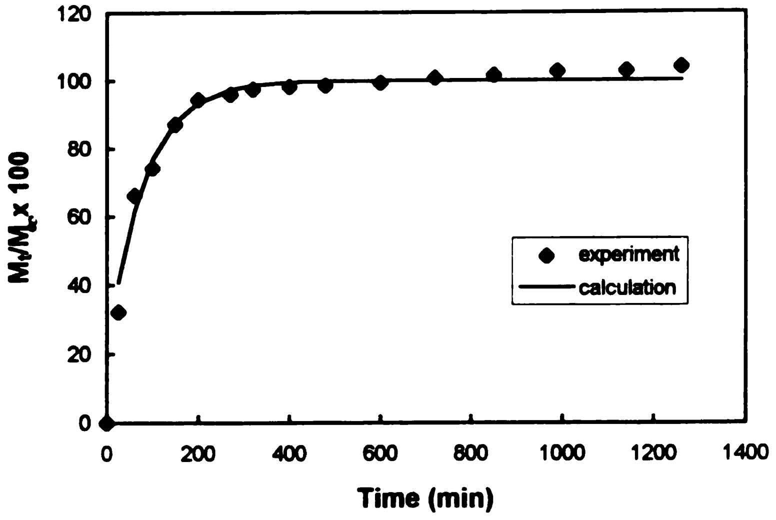


Figure 15. M_t/M_∞ vs Time at 30 °C and Av =0.33

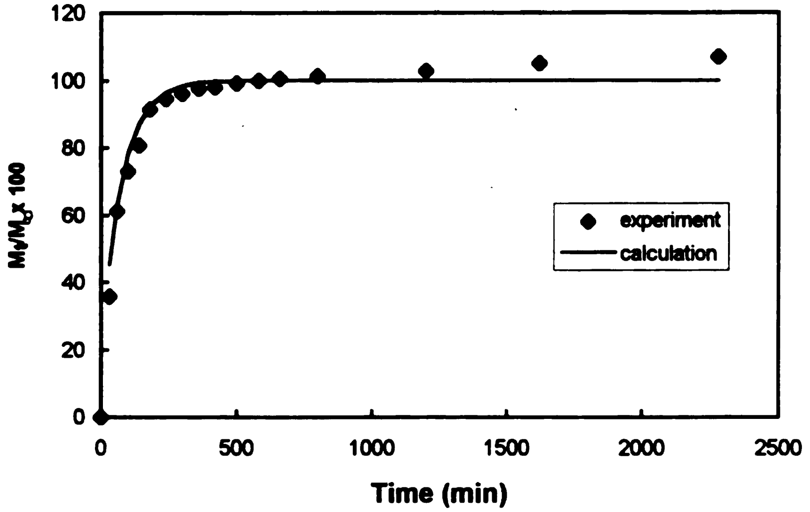


Figure 16. M_t/M_∞ vs Time at 30 °C and Av = 0.49

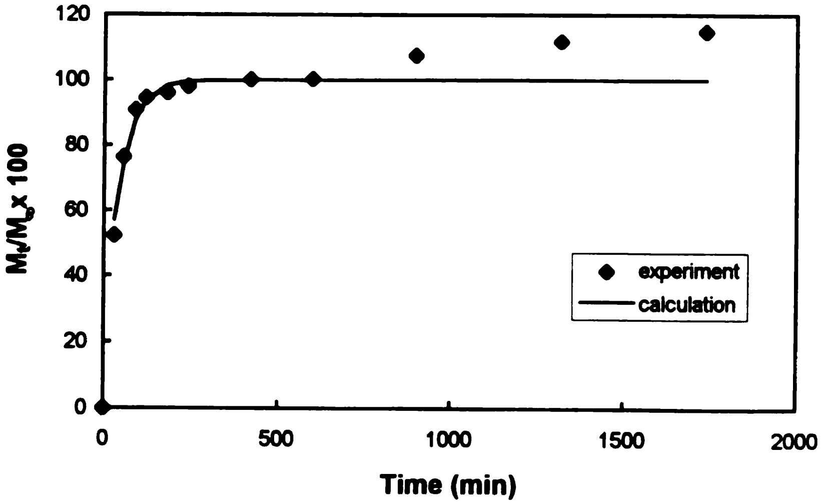


Figure17. M_t/M_∞ vs Time at 30 °C and Av = 0.66

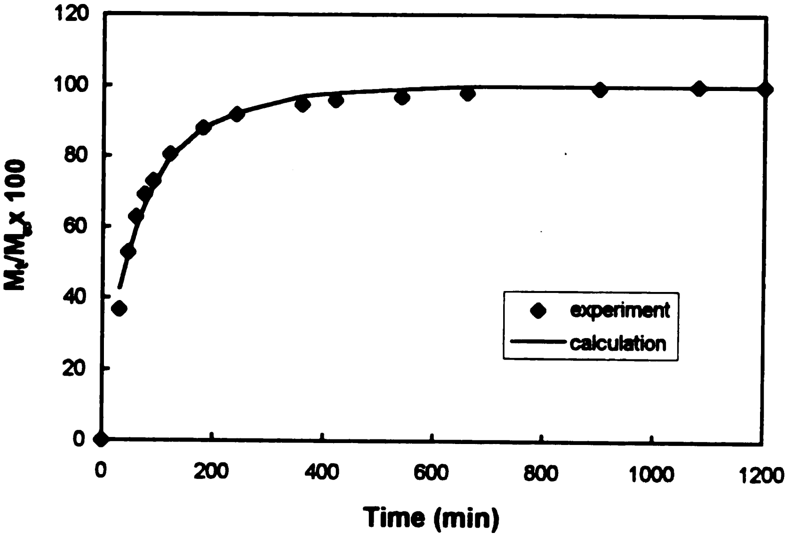


Figure 18. M_t/M_∞ vs Time at 40 °C and Av = 0.18

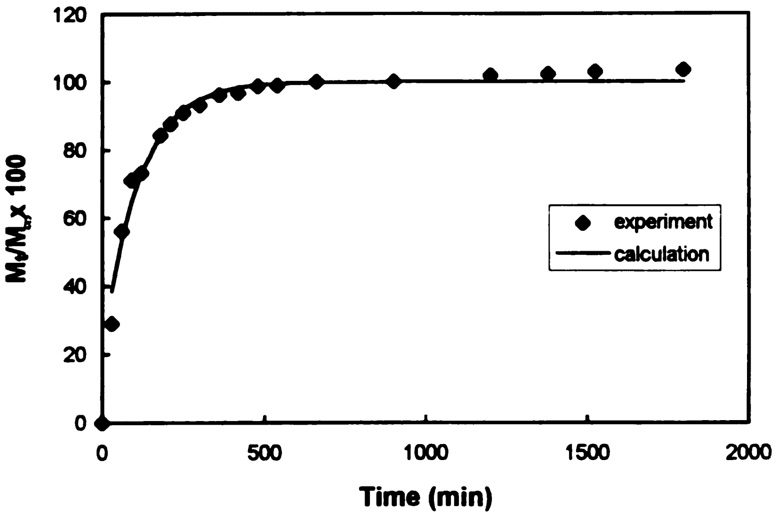


Figure 19. M_t/M_∞ vs Time at 40 °C and Av = 0.21

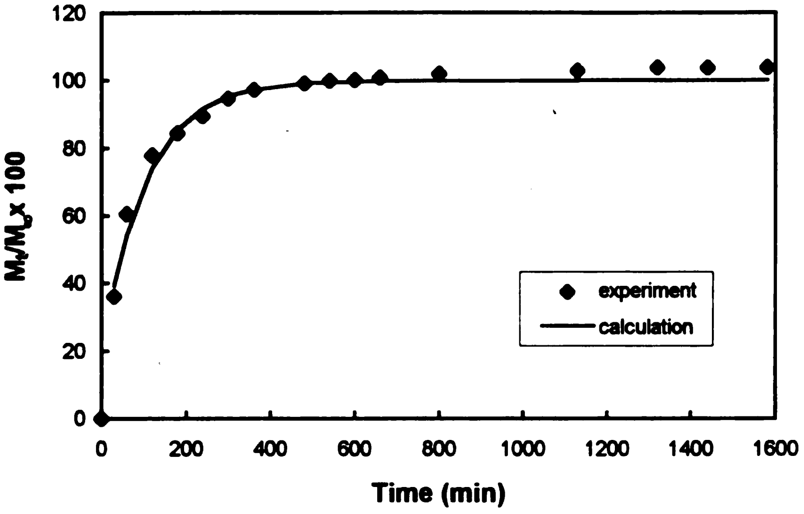


Figure 20. M_t/M_∞ vs Time at 40 °C and Av = 0.28

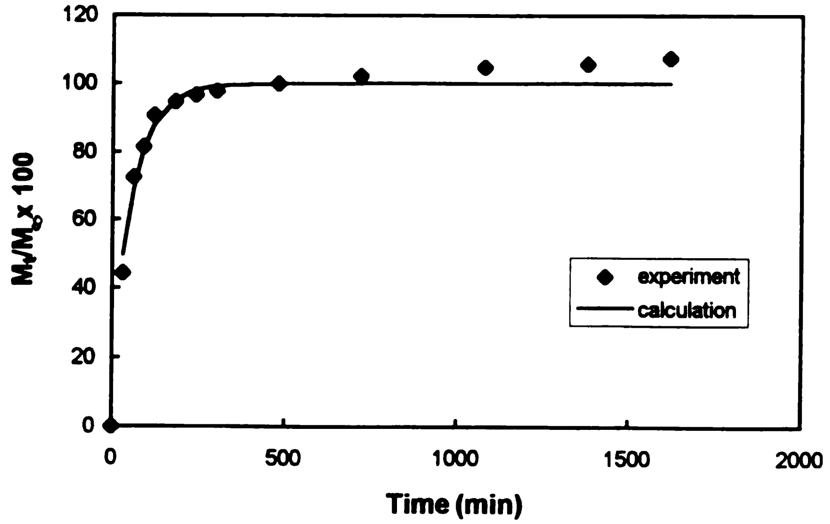


Figure 21. M_t/M_∞ vs Time at 40 °C and Av = 0.31

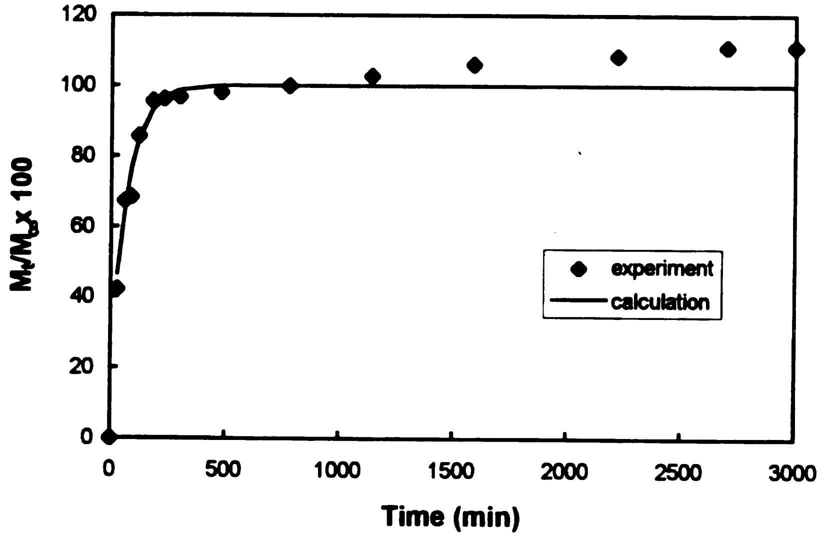


Figure 22. M_t/M_∞ vs Time at 40 °C and Av = 0.46

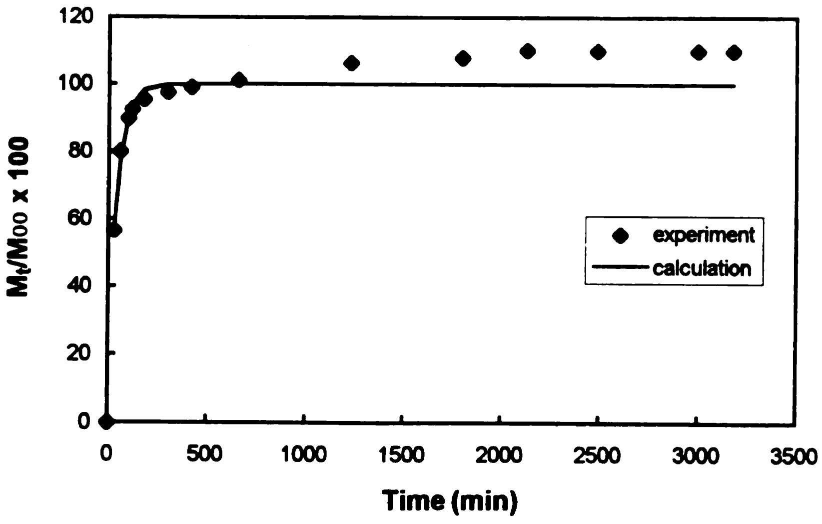


Figure 23. M_t/M_∞ vs Time at 40 °C and Av = 0.53

Equilibrium Solubility of 2-Nonanone in Affinity PL 1880 as a Function of Partial Pressure.

The equilibrium solubility of 2-nonanone vapor diluted in nitrogen gas in polyethylene film sample was determined by measuring the uptake of 2-nonanone at different values of partial pressure and temperature. Figure 24 presents the plot of equilibrium solubility of 2-nonanone in the films expressed as gram of 2-nonanone per gram of polymer at 22 °C, 30 °C and 40 °C. From the plot, it can be seen that there is a linear relationship between the 2-nonanone equilibrium solubility in the polymer and 2-nonanone partial pressure. Table 3 presents values of 2-nonanone partial pressure and concentration. The range of concentration studied was between 0.46 to 4.21 mg/L. At this short range of concentration, the linear behavior indicates that the equilibrium solubility of this compound obey Henry's law (Equation 6). This agreement also observed at 30 °C and 40 °C, as shown in Figure 24. At 30 °C and 40 °C, as the partial pressure increases, so does the equilibrium solubility, resulting in a higher concentration of 2-nonanone in the polymer. The total penetrant sorption process will likely involve one or more sorption modes as the penetrant molecules are sorbed within the polymer in different modes (Rogers, 1965). Futhermore, the specific sorption process may be described as a function of penetrant concentration and temperature. The relationship between concentration and temperature on the solubility of 2-nonanone can be described as a function vapor activity of the permeant. Figure 25 shows a linear relation between the vapor activity and the equilibrium solubility of 2-nonanone. As the vapor activity increase, the equilibrium solubility of 2-nonanone increase at 22 °C, 30 °C and 40 °C. Temperature has a profound impact on equilibrium solubility of 2-nonanone, as shown in Figure 25. As the temperature increase, the equilibrium solubility decrease at one level of vapor activity, due to an increase in saturated partial pressure. The curves at 22 °C, 30 °C and 40 °C were closed each other due to short range of temperature studied.

22 °C		30 °C		40 °C	
Partial Pressure (Pa)	Concentration 2-Nonanone (mg/L)	Partial Pressure (Pa)	Concentration 2-Nonanone (mg/L)	Partial Pressure (Pa)	Concentration 2-Nonanone (mg/L)
7.97	0.46	14.55	0.82	26.13	1.43
9.19	0.53	20.14	1.14	30.49	1.67
11.03	0.64	26.85	1.52	40.65	2.22
14.09	0.82	36.92	2.08	45.01	2.46
23.28	1.35	54.83	3.09	66.79	3.65
29.41	1.71	73.85	4.17	76.95	4.21

Table 3. The partial pressure and concentration of 2-nonanone at 22 °C, 30 °C and 40 °C

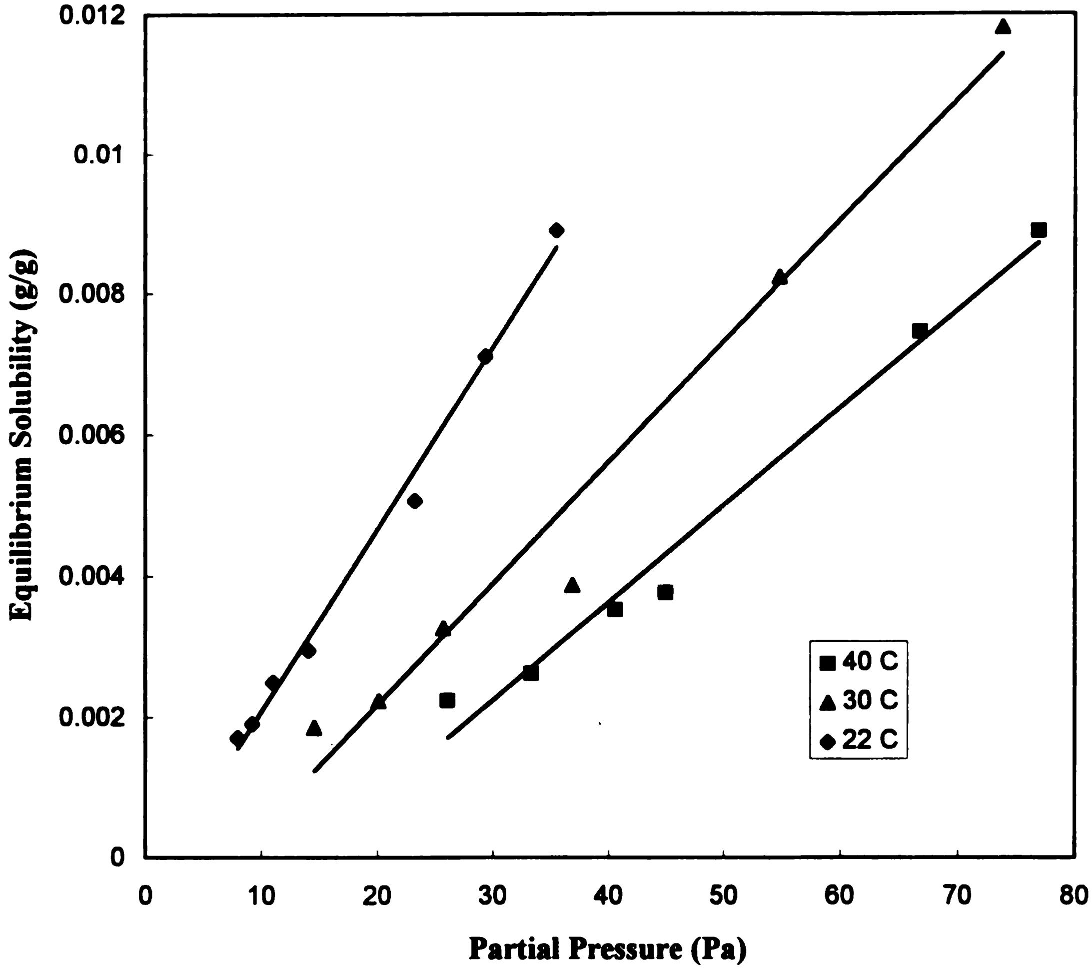


Figure 24. The effect of partial pressures and temperatures on the concentration of 2-Nonanone

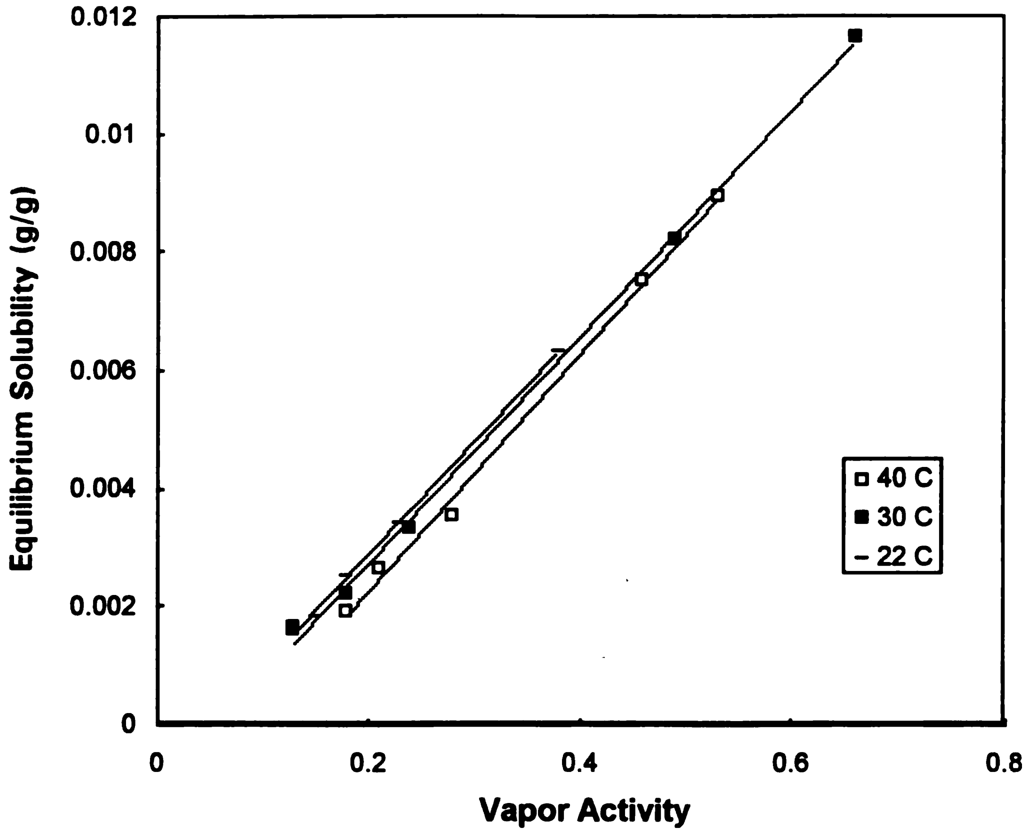


Figure 25. The effect of vapor activity and temperature on the concentration of 2-nonanone

The Effect of Concentration on the Solubility Coefficient of 2-Nonanone

The effect of concentration on the solubility coefficient of 2-nonanone in the test polymer sample at 22 °C, 30 °C and 40 °C is shown graphically in Figure 26. It was found that the sorption data could be represented by a linear function of the logarithm of the soubility coefficient versus the concentration of 2-nonanone. At 22 °C, the solubility coefficient is constant with the increase in vapor concentration from 0.4 to 2.1 ppm (w/v). There is no significant increases in solubility coefficient as the concentration increase. The same trends were observed at 30 °C and 40 °C, with the concentration ranging from 0.8 to 4.2 ppm (w/v) and 1.4 to 4.2 ppm (w/v) respectively. Table 4, 5 and 6 summarized the effect of 2-nonanone concentration on permeability coefficient, diffusion coefficient and solubility coefficient of Affinity PL 1880 at 22 °C, 30 °C and 40 °C using gravimetric technique. Figure 26 also ilustrates the effect of temperature on the solubility coefficient of 2-nonanone. As the temperature increased, the solubility coefficient of 2-nonanone decreased probably due to an increase in saturated partial pressure and relatively large heat of condensation.

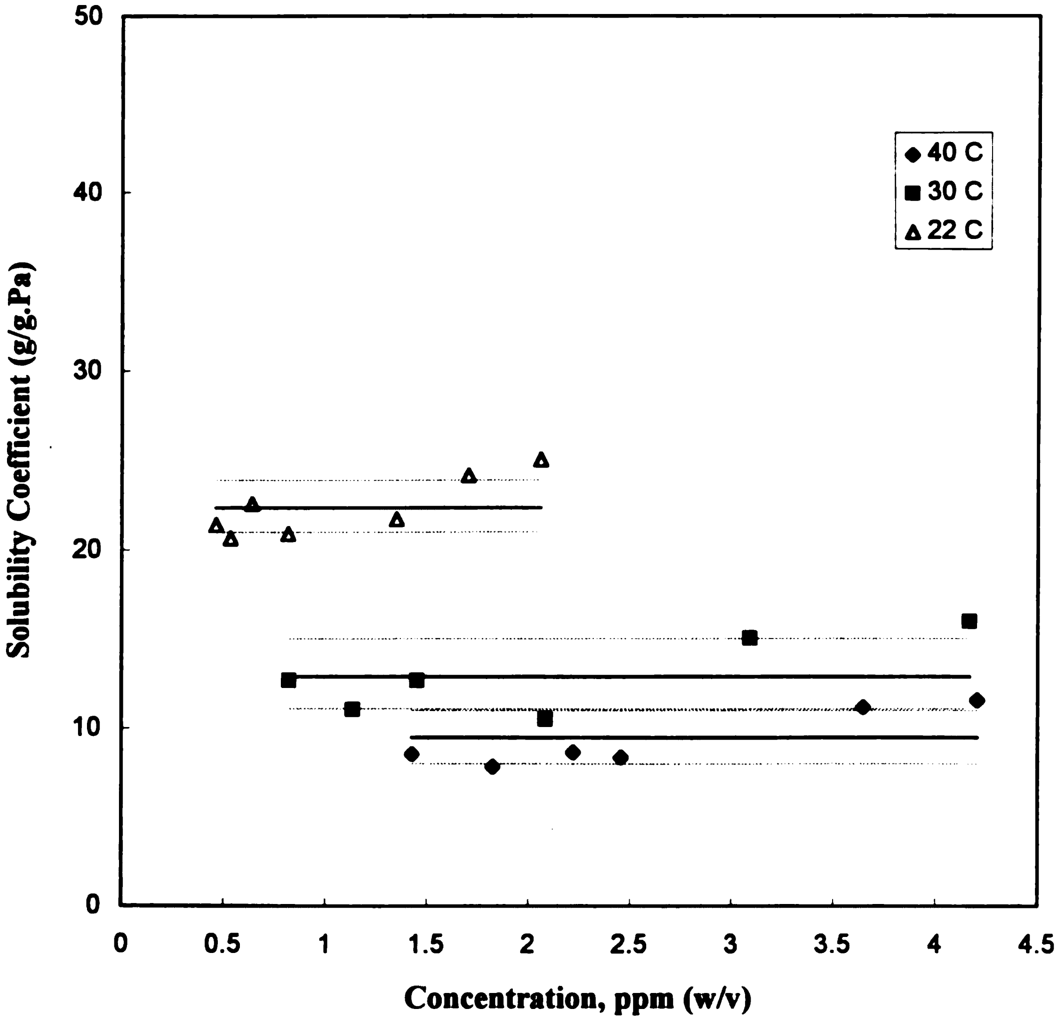


Figure 26. The effect of the concentration on solubility coefficient of 2-Nonanone at different temperatures

Vapor Activity	Concentration 2-Nonanone (ppm) (w/v)	Equilibrium Solubility, C* (x 10^{-3}) (g/g)	Solubility Coefficient, S (x 10^{-5}) (g/g.Pa)	Diffusion Coefficient, D (x 10^{-14}) (m^2/sec)
0.13	0.4 ± 0.03	1.7 ± 0.5	21.4 ± 0.5	3.1 ± 0.3
0.15	0.5 ± 0.04	1.8 ± 0.4	20.7 ± 0.4	3.3 ± 0.5
0.18	0.6 ± 0.02	2.5 ± 0.5	22.6 ± 0.5	3.8 ± 0.2
0.23	0.8 ± 0.05	2.9 ± 0.6	20.9 ± 0.6	4.0 ± 0.5
0.38	1.4 ± 0.04	5.1 ± 0.3	21.7 ± 0.3	4.2 ± 0.5
0.48	1.7 ± 0.03	7.1 ± 0.6	24.2 ± 0.6	4.4 ± 0.4
0.58	2.1 ± 0.06	8.9 ± 0.4	25.0 ± 0.7	4.8 ± 0.3

Table 4. The effect of vapor activity on the sorption of 2-nonanone at 22 °C

Vapor Activity	Concentration 2-Nonanone (ppm) (w/v)	Equilibrium Solubility, C* (x 10^{-3}) (g/g)	Solubility Coefficient, S (x 10^{-5}) (g/g.Pa)	Diffusion Coefficient, D (x 10^{-14}) (m^2/sec)
0.13	0.8 ± 0.02	1.8 ± 0.4	12.7 ± 0.4	4.1 ± 0.3
0.18	1.1 ± 0.05	2.2 ± 0.4	11.0 ± 0.4	4.2 ± 0.2
0.24	1.5 ± 0.04	3.3 ± 0.2	12.1 ± 0.2	4.5 ± 0.4
0.33	2.1 ± 0.03	3.9 ± 0.3	10.4 ± 0.3	4.9 ± 0.6
0.49	3.1 ± 0.05	8.2 ± 0.3	15.0 ± 0.3	5.1 ± 0.5
0.66	4.2 ± 0.04	11.8 ± 0.5	15.9 ± 0.5	5.6 ± 0.4

Table 5. The effect of vapor activity on the sorption of 2-nonanone at 30 °C

Vapor Activity	Concentration 2-Nonanone (ppm) (w/v)	Equilibrium Solubility, C* (g/g)	Solubility Coefficient, S ($\times 10^{-5}$) (g/g.Pa)	Diffusion Coefficient, D ($\times 10^{-14}$) (m^2/sec)
0.18	1.4 ± 0.2	2.2 ± 0.3	8.5 ± 0.3	4.4 ± 0.4
0.21	1.7 ± 0.4	2.6 ± 0.3	8.6 ± 0.3	4.5 ± 0.3
0.28	2.2 ± 0.5	3.5 ± 0.4	8.7 ± 0.4	4.8 ± 0.1
0.31	2.5 ± 0.3	3.8 ± 0.3	8.4 ± 0.3	4.9 ± 0.4
0.46	3.7 ± 0.4	7.5 ± 0.1	11.2 ± 0.1	5.4 ± 0.5
0.53	4.2 ± 0.3	8.9 ± 0.5	11.6 ± 0.5	6.3 ± 0.5

Table 6. The effect of vapor activity on the sorption of 2-nonanone at 40 °C

Effect of the Temperature on the Solubility and Permeability Coefficients of 2-Nonanone

Temperature has a profound impact on both the solubility and permeability of the organic volatile compound, as indicated in Equations (9) and (11). Figure 27 shows the Arrhenius plot of the solubility coefficient of 2-nonanone at vapor activity, Av = $0.18\underline{+}0.005$. The heat of solution of 2-nonanone was determined to be 32 kcal/mole. An increase in temperature contributes energy resulting in an increase in segmental mobility of the polymer chains, thus a decrease in the solubility coefficient of 2-nonanone. An Arrhenius plot of the permeability constant, P, of 2-nonanone vapor through Affinity PL 1880 film vs. 1/T (^{o}K) is shown in Figure 28. From this figure, the temperature dependency of the permeability constant can be represented by Equation (11). From the slope of Figure 28, the activation energy of the permeation process, Ep, was determined to be 37 kcal/mole. When compared with the activation energy of oxygen through LDPE above Tg (E_p = 10.18 kcal/mole) (Mannapperuma et al., 1989), the activation energy of 2-nonanone vapor is high. A possible explanation for these results is that the molecular size of 2-nonanone is relatively large as compared to oxygen and requires a higher activation energy for diffusion. The strong temperature dependence on permeability of 2-nonanone which enhances polymer chain conformational mobility may affect the swelling of the polymer. Although this study was conducted at 20 °C, 30 °C and

40 °C respectively, the permeability coefficient at lower temperature can be extrapolated from Figure 28.

Effect of the Temperature on the Diffusion Coefficient of 2-Nonanone

An Arrhenius plot of the diffusion coefficient (D) of 2-nonanone vapor through polyethylene film vs 1/T (°K) is shown in Figure 29. From the slope of this figure, the activation energy of the diffusion process (E_d) was determined to be 14 kcal/mole. The activation energy appeared to be higher than the activation energy of a permeant gas, such as oxygen through LDPE above Tg (E_d = 9.58 kcal/mole) (Mannapperuma et al., 1989). This result may be explained considering that the molecular size of 2-nonanone is larger than oxygen molecule. Michael et al., (1959) indicated that the side chain branches in the polymer chain may required a higher activation energy for diffusion. The activation energy value determined for the 2-nonanone/polyethylene system was similar in order of magnitude to the activation energy of diffusion determined for other data of organic vapor/LDPE systems. According to Laine and Osburn (1971), the activation energy of 15 organic vapors tested ranging from 6 to 30 kcal/mole. In addition to molecular size, a further explanation for the strong temperature dependence of 2-nonanone diffusion through the polyethylene sample is the swelling effect by the sorbed permeant.

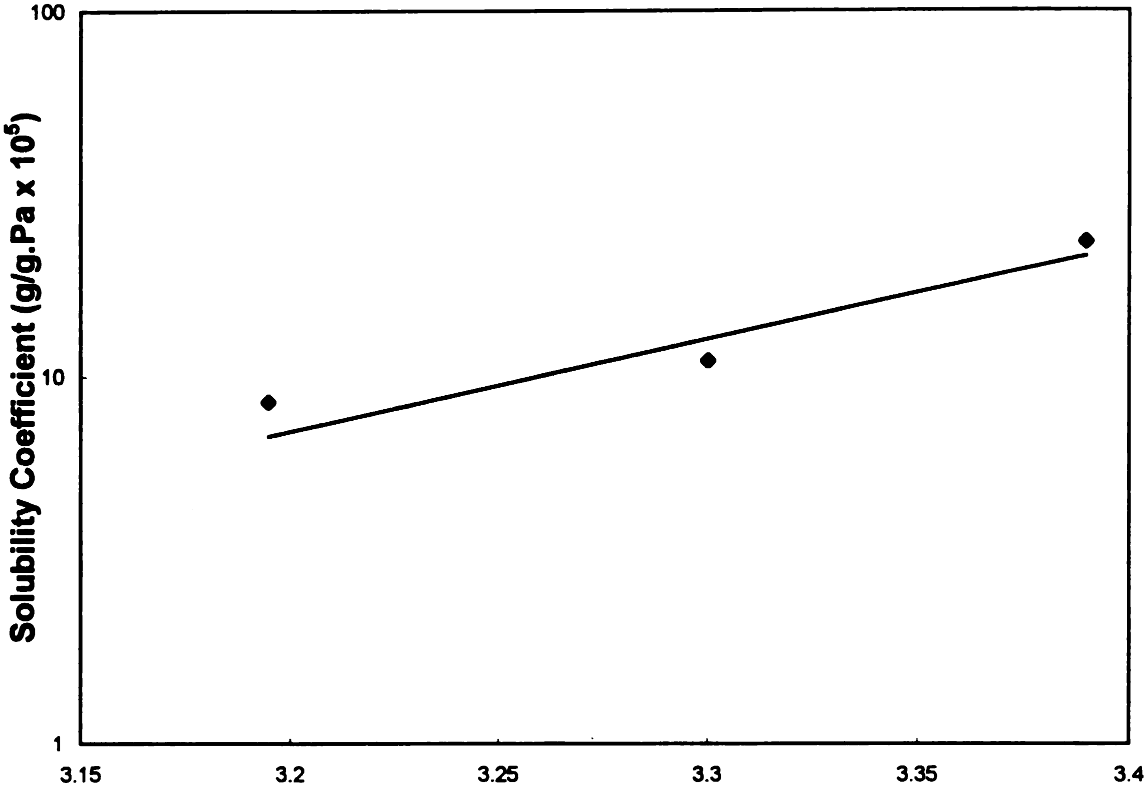


Figure 27. Temperature dependence of the solubility coefficient for 2-Nonanone at Av = 0.18

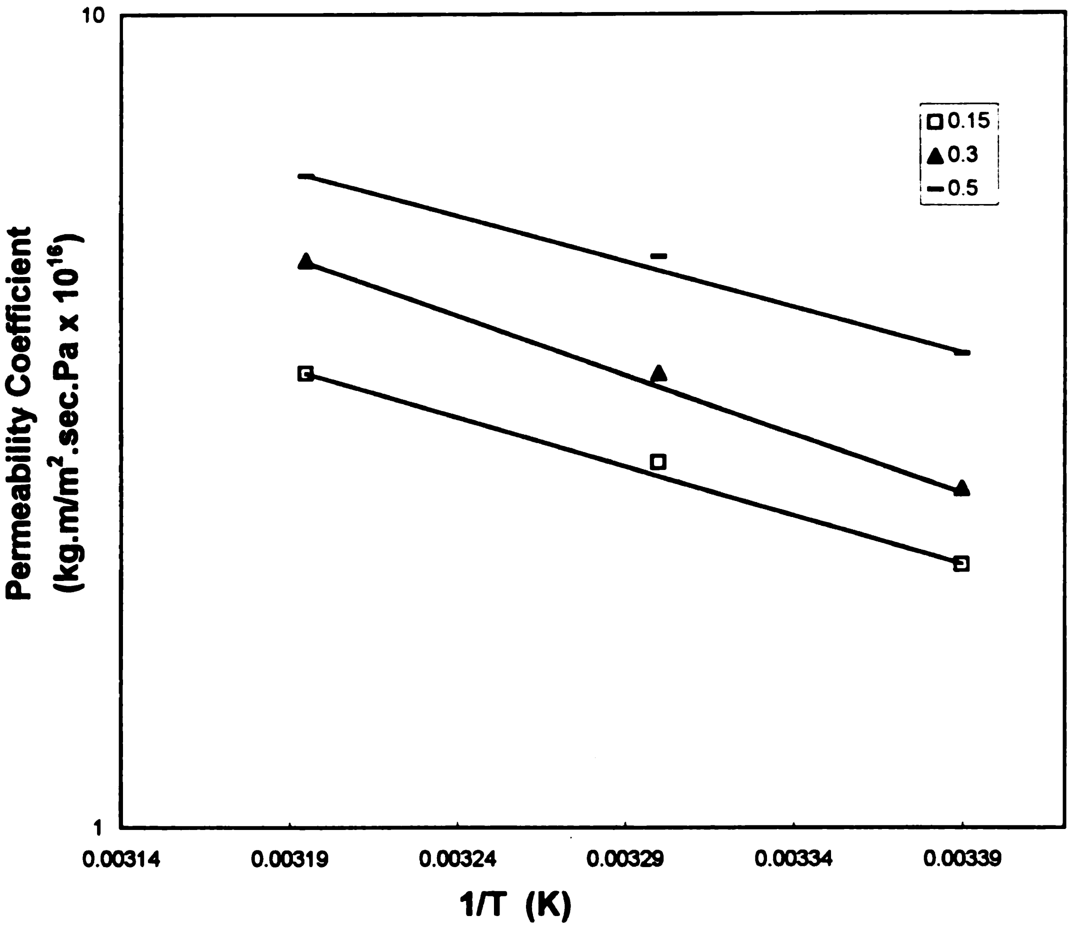


Figure 28. Temperature dependence of the permeability coefficient for 2-nonanone at vapor activity = 0.15, 0.3 and 0.5

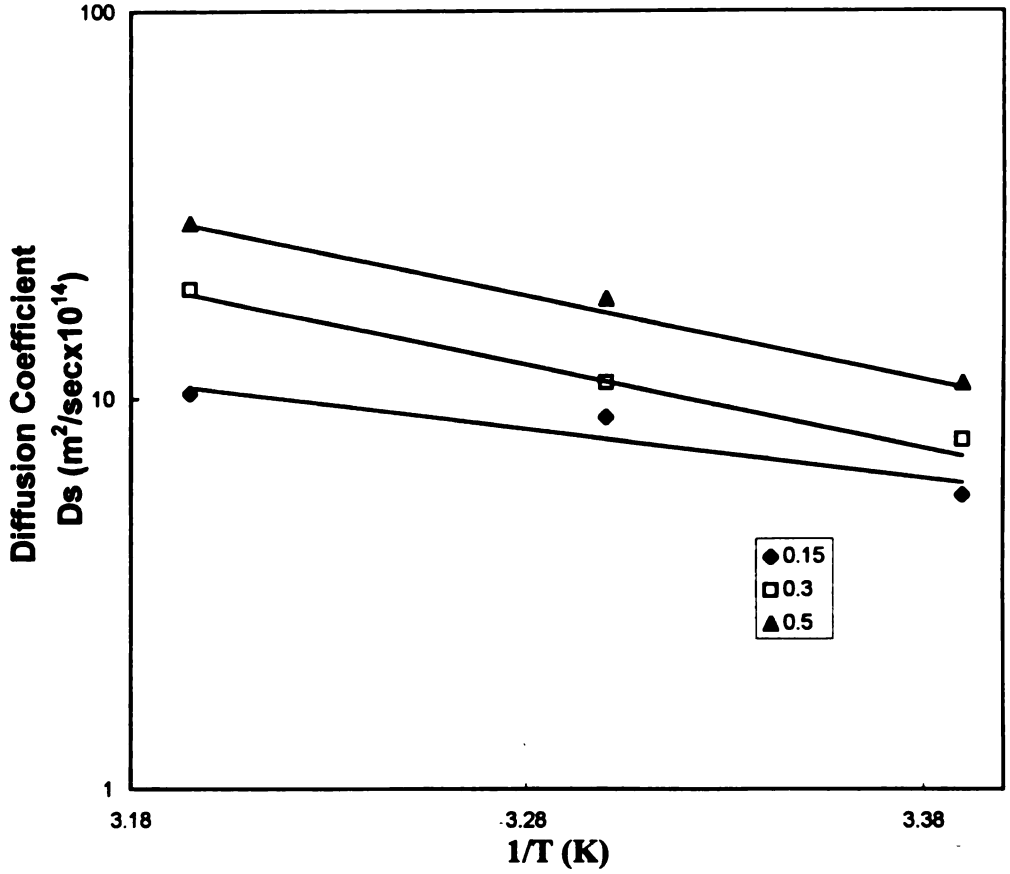


Figure 29. Temperature dependence of the diffusion coefficient for 2-Nonanone at vapor activity = 0.15, 0.3 and 0.5

The Effect of the 2-Nonanone Vapor Concentration on the Penetrant Permeability with a Quasi-Isostatic Technique

Representative transmission rate profile curves for Affinity PL 1880 film samples at 22, 30 and 40 ^{o}C are presented in Figure 30, 31 and 32, respectively, where the total quantity of 2-nonanone permeated (Q) in micrograms is plotted as a function of time over the vapor activity range studied. The transmission rate profile curves as shown are illustrative of the effect of concentration on the permeability and lag time values. The reported data were the average of duplicate studies, since good agreement was shown by the replicate experiments, with an estimate error value of 10%. As shown, an initial induction time, a non-steady state or a time lag occured during the initial stage of the experiment as the permeant passed through the film and established a steady-state profiles. The mass transport parameters at 22, 30 and 40 ^{o}C, that includes lag time, diffusion coefficient and permeability coefficient, calculated from these data, are summarized in Tables 7, 8 and 9, respectively. Figure 33 clearly illustrates the temperature dependence of the permeability coefficient, P, and the lag time diffusion coefficient, D_{lag}, with P increasing and D_{lag} decreasing with an increase in temperature. The observed temperature dependent permeability constants suggest penetrant/polymer interaction, that is swelling of the polymer matrix, resulting in configurational changes and alteration of polymer chain conformational mobility and thus of penetrant diffusivity.

Vapor Activity	Partial Pressure (Pa)	Thickness (mil)	Lag Time (min)	Diffusion Coeff. (x 10^{14}) (m^2/sec)	Permeability Coeff. (x 10^{16}) (kg.m/m^2.sec.Pa)	P (fs)
0.08	4.9	1.9	118	5.5 ±0.3	1.9 ± 0.3	19
0.13	8.0	1.9	100	6.5 ±0.3	2.2 ± 0.2	22
0.23	14.1	1.9	96	6.7 ±0.5	2.3 ± 0.5	23
0.33	20.2	1.9	90	7.2 ±0.3	2.7 ± 0.3	27
0.54	33.1	1.9	50	12.9±0.6	4.8 ± 0.6	48

Table 7. The effect of the 2-nonanone concentration on the permeation at 22 °C

Vapor Activity	Partial Pressure (Pa)	Thickness (mil)	Lag Time (min)	Diffusion Coeff. (x 10^{14}) (m^2/sec)	Permeability Coeff. (x 10^{16}) (kg.m/m^2.sec.Pa)	P (fs)
0.23	25.3	1.9	59	10.9±0.2	2.9 ± 0.4	29
0.30	33.0	1.9	57	11.4±0.4	3.9 ± 0.2	39
0.42	46.2	1.9	45	14.4±0.2	5.3 ± 0.3	53
0.54	59.4	1.9	38	17.0±0.5	5.4 ± 0.3	54

Table 8. The effect of the 2-nonanone concentration on the permeation at 30 °C

Vapor Activity	Partial Pressure (Pa)	Thickness (mil)	Lag Time (min)	Diffusion Coeff. (x 10^{14}) (m^2/sec)	Permeability Coeff. (x 10^{16}) (kg.m/m^2.sec.Pa)	P (fs)
0.13	18.9	1.9	53	12.2± 0.3	3.5 ± 0.4	35
0.23	30.5	1.9	40	16.2± 0.3	3.8 ± 0.2	38
0.29	42.1	1.9	35	18.4± 0.4	4.3 ± 0.4	43
0.44	63.9	1.9	30	21.5± 0.4	5.5 ± 0.3	55
0.56	81.3	1.9	20	32.2± 0.3	7.0 ± 0.3	70

Table 9. The effect of the 2-nonanone concentration on the permeation at 40 °C

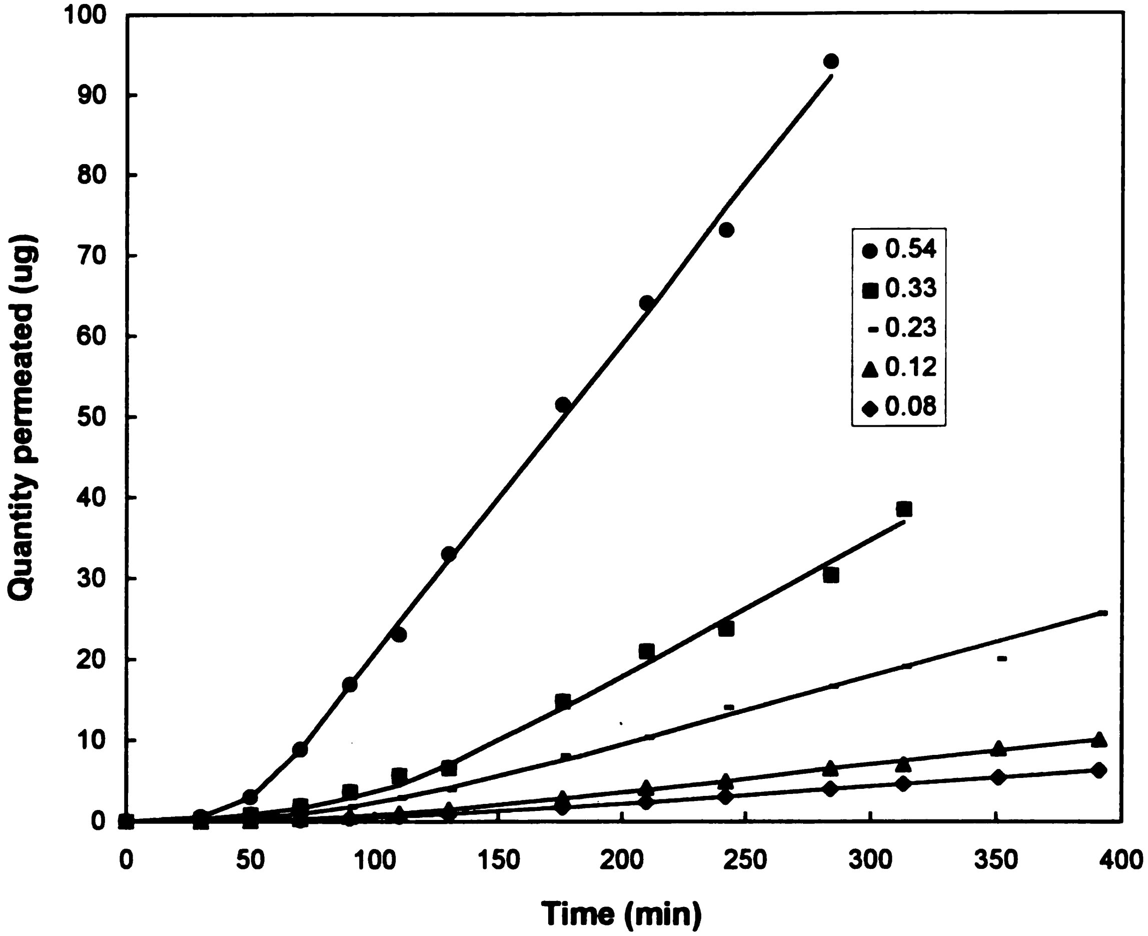


Figure 30. Transmission rate profile of 2-nonanone at 22 °C and various vapor activities

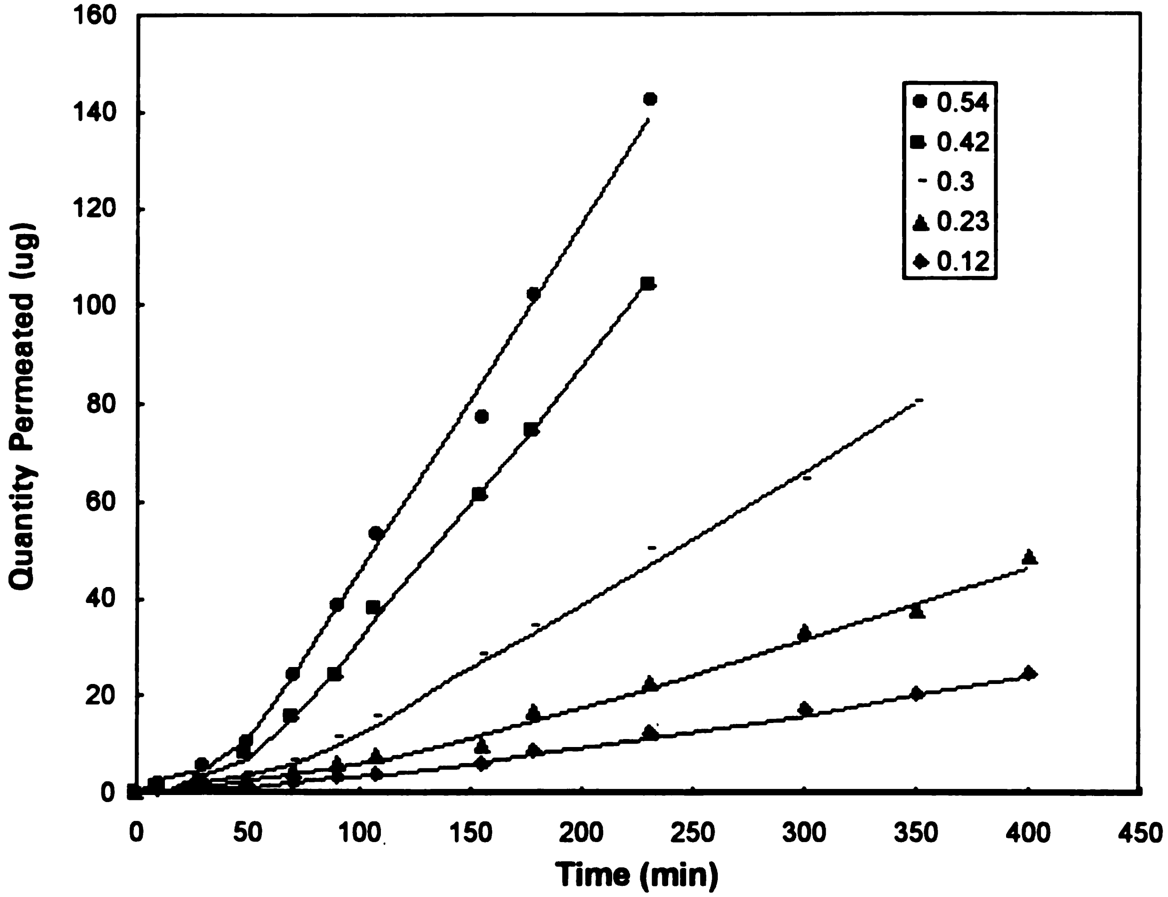


Figure 31. Transmission rate profile of 2-nonanone at 30 °C and various vapor activities

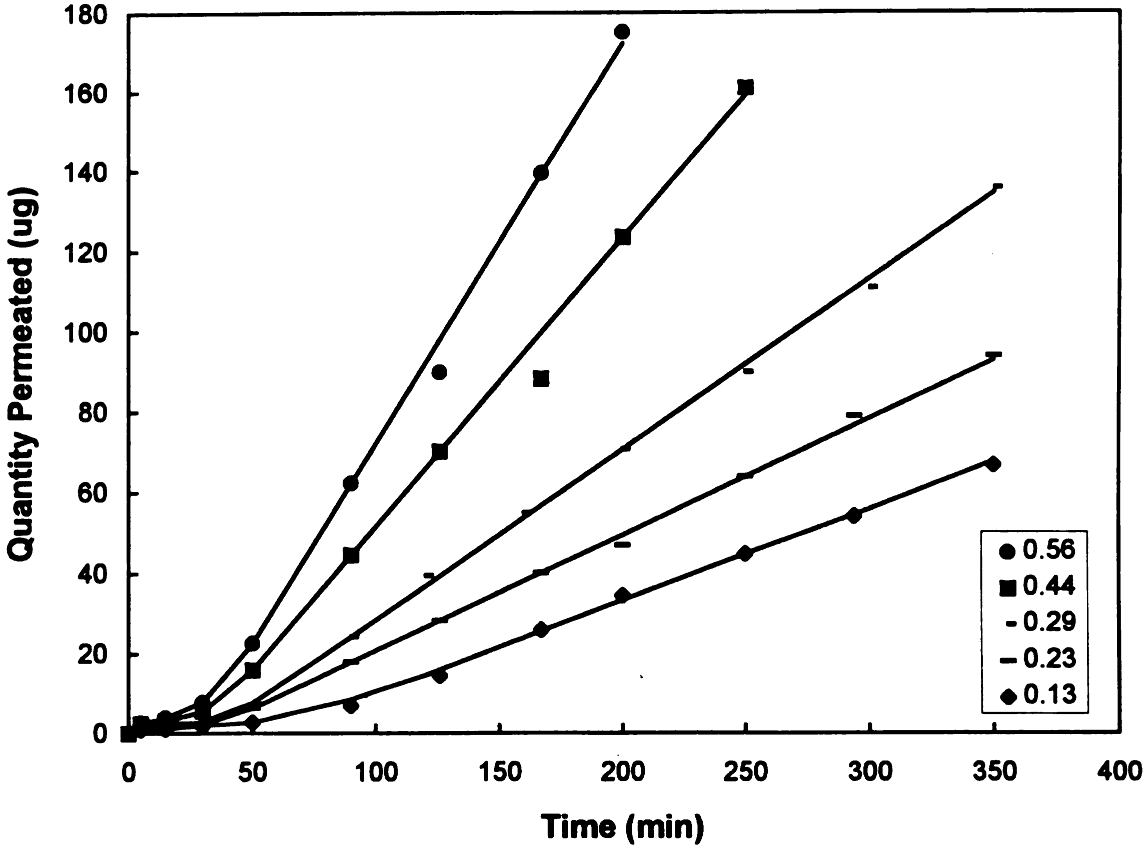


Figure 32. Transmission rate profile of 2-nonanone at 40°C and various vapor activities

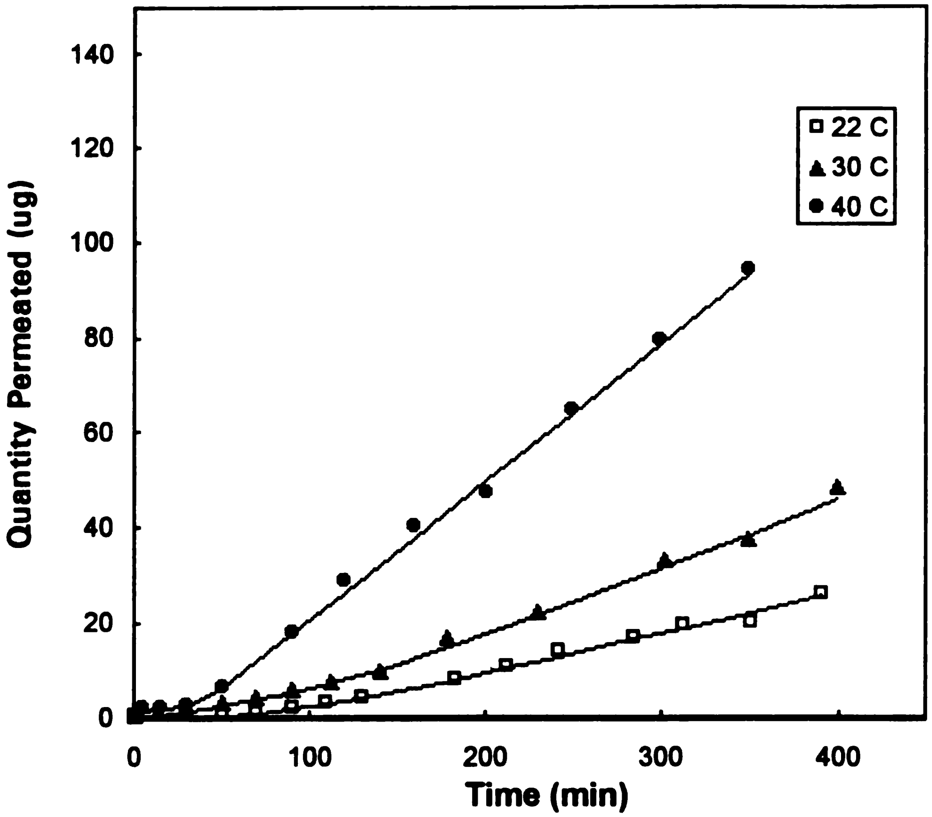


Figure 33. Transmission rate profile of 2-nonanone at vapor activity = 0.23

Figure 34 demostrates that the permeability coefficient (P) is exponentially dependent on the penetrant concentration as found in the literature (Zobel, 1982,1985; Baner et al., 1986; Hernandez et al., 1986). The observed concentration dependency of the permeability coefficient shows penetrant/polymer interaction occurred during the experiment resulting in swelling of the polymer matrix by 2-nonanone vapor and corresponding changes in polymer chain conformations, leading to an increase in penetrant diffusivity, and therefore permeability. The diffusion coefficient values of 2-nonanone were determined from the permeability data based on Equation (13). As shown in Figure 35, there is an increase in diffusion coefficient with an increase in vapor activity of 2-nonanone over the vapor activity range studied. The diffusion coefficient values are calculated from the transient state region of the transmission rate profile curve because at the steady state penetrant/polymer interaction may lead in a gradual relaxation of the polymer structure, resulting in a change in the free volume of the polymer. In addition to molecular size, another possible explanation for the strong dependence of 2-nonanone diffusion through polyethylene film is the swelling effect by the sorbed permeant. In Figure 35, as the temperature increases, the diffusion coefficient increases. The polymer segmental mobility is greater and it is easier to increase the free volume. The magnitude of the dependence of the diffusion coefficient on the concentration is influenced by the temperature prevailing during the transport process and the molecular size of the penetrant.

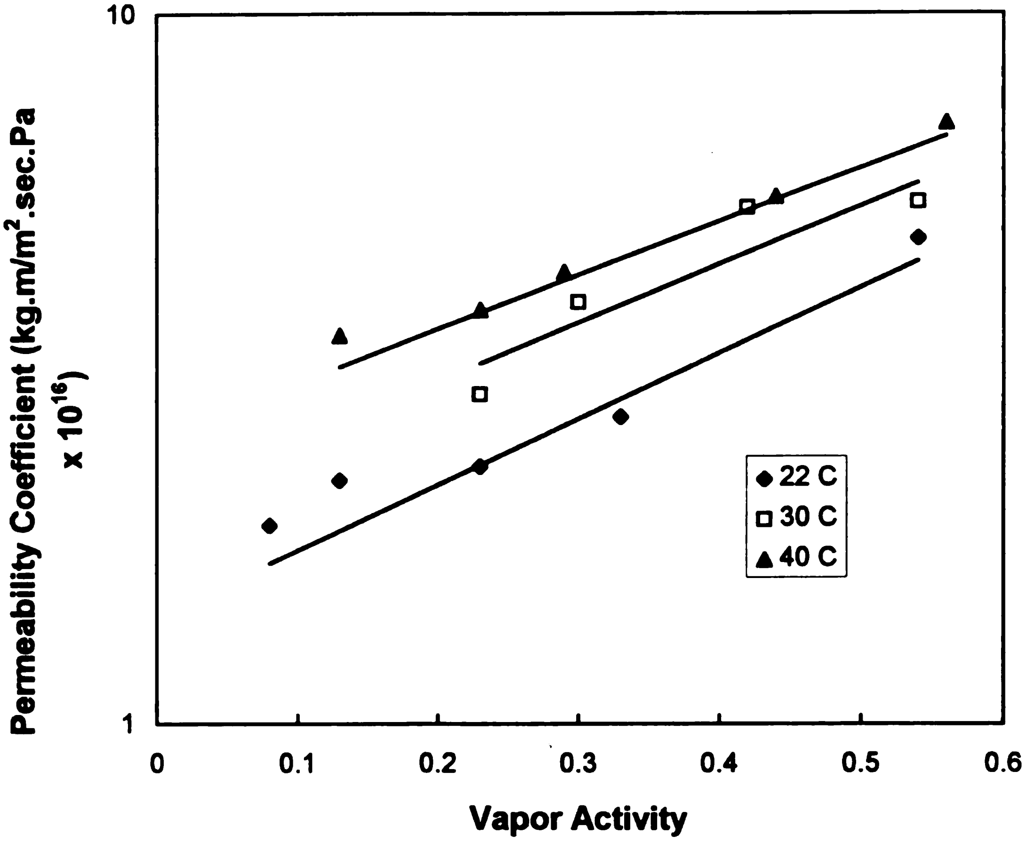


Figure 34. The effect of 2-nonanone vapor activity on Log P at different temperatures

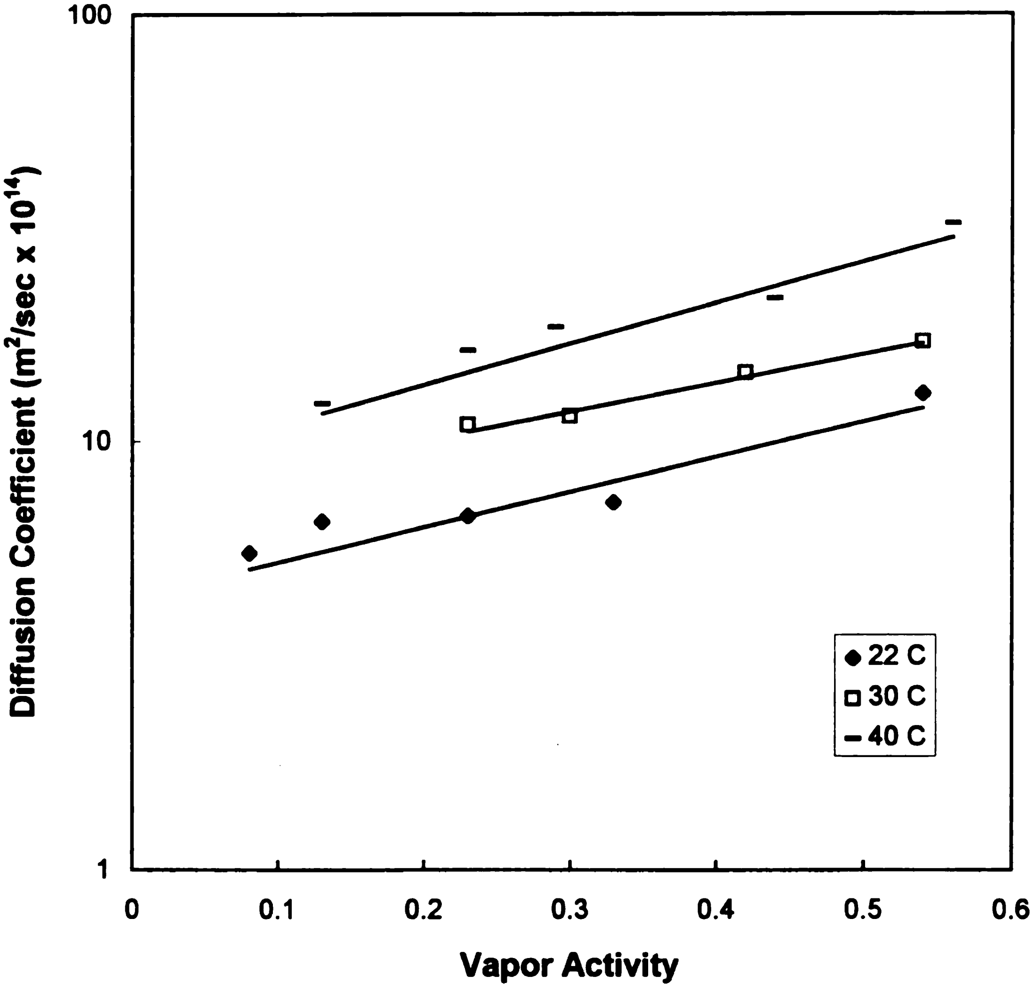


Figure 35. The effect of 2-nonanone vapor activity on Log D at different temperatures

Package Design for the Release of 2-Nonanone in the Headspace of the Package

2-Nonanone is one of several promising antifungal natural volatiles that has been used to prevent decay in packaged fruit (Vaughn et al., 1993). To develop a model that can predict the package headspace concentration after flushing the package with antifungal volatile or by adding it into the polymer material itself, requires knowledge of fungi response, product's toxicity, mass transport and solubility parameters of the antifungal volatile compounds in the polymer material. The optimum concentration level of 2-nonanone in the headspace of the package that can prevent decay in fruit should be investigate in order to develop the actual product/package system (Leepipattanawit, 1996). The permeability and solubility characteristics of 2-nonanone have been studied in this work and for relatively high concentration it produces some swelling of the polyethylene. We assume the 2-nonanone desorbed into the headspace of the package is half of the 2-nonanone initial content in the polymeric film. The concentration level of 2-nonanone in the headspace can be expressed as,

$$C_{2N} = M_{2N}/V_{HS} \qquad (18)$$

where C_{2N} is the concentration of 2-nonanone in the headspace, M_{2N} is the amount of 2-nonanone desorb into the headspace of the package and V_{HS} is the volume of the headspace. V_{HS} is related to the total package volume by,

$$V_{HS} = V_{PKG} - V_{PRT} \tag{19}$$

where V_{PKG} is the total package volume and V_{PRT} is the product volume.

According to Leepipattanawit (1996), 300 x 10^{-6} liter of liquid 2-nonanone per liter of air in the headspace is needed in the headspace of the packaging system to control the fungi growth of sliced apple at room temperature. The first method that can be applied to maintain the concentration of 2-nonanone in the headspace of the package is by assuming that 2-nonanone will be initially sorbed in the film of area, A, and it will be desorbed into the headspace after the package is formed. Table 10 summarizes the package area needed to control the microbial growth in the package at vapor activity ranging from 0.13 to 0.58 by assuming that 50% of the organic vapor desorbed into the headspace from the film which is given by the following equation,

$$Y = 55.695X^{-1.1018} \tag{20}$$

where,

Y = package area (cm^2)
X = vapor activity of 2-nonanone

Figure 36 illustrates the relationship between the vapor activity and the package area. As the vapor activity increased, the equilibrium solubility, C*, in the polymer increased, which will reduce the area needed to develop the packaging system for sliced apple. A typical package can be a pouch or a covered tray as shown in Figure 37.

Vapor Activity	Partial Pressure (Pa)	Equilibrium Solubility ($mg_{2N}/100mg_p$)	Weight Polymer (mg)	Area Package (cm^2) (t=1.9mil)
0.13	7.96	0.0017	2231	512
0.15	9.2	0.0019	2002	460
0.18	11.03	0.0025	1527	351
0.23	14.09	0.0029	1291	297
0.38	23.28	0.0051	751	172
0.48	29.41	0.0071	535	122
0.58	35.54	0.0089	427	98

Table 10. Package design in relation with equilibrium solubility of 2-nonanone at 22 °C

Another method that can be applied to maintain the concentration of 2-nonanone in the headspace of the package is by including a small pouch with 2-nonanone liquid in the package as illustrated in Figure 38. By assuming that the transmission rate of 2-nonanone from the small pouch is equal to the transmission rate of 2-nonanone through the package, we can get the ratio between the area of the small pouch and the package at various material thicknesses and vapor activities. In this method, we want to maintain in the headspace a target concentration of 300 ul/l during 3 weeks. We also need to calculate the thicknesses of the small pouch, A, that will give the same rate of permeation through package, B.

Transmission rate across A,

$$Q_1/t_1 = P_1A\,(p_s - p_1)\,/\,l_1 \tag{21}$$

Transmission rate across B,

$$Q_2/t_2 = P_2B\,(p_1 - p_2)\,/\,l_2 \tag{22}$$

where,

A and B = area of the small pouch and package respectively
P_1 and P_2 = permeability coefficient
Q_1 and Q_2 = quantity permeated
t_1 and t_2 = time
p_s = saturated partial pressure
p_1 and p_2 = partial pressure
l_1 and l_2 = thickness

$$Q_1/t_1 = Q_2/t_2 = P_1A\,(p_s-p_1)\,/\,l_1 = P_2B\,(p_1 - p_2)\,/\,l_2 \qquad (23)$$

Assuming that $P_1 = P_2$

$$A\,(p_s - p_1)\,l_2 = B\,(p_1)l_1$$

$$A\,/\,B = (p_1)\,l_1\,/\,(p_s - p_1)\,l_2 \qquad (24)$$

Assuming that the area of the small pouch is 8 cm^2, Figure 39 gives the area of the package B as a function of 2-nonanone activity in the headspace, for three values of l_1/l_2. Table 11 summarizes the total quantity of 2-nonanone to be placed into the small pouch to produce a headspace concentration of 2-nonanone as a function of l_1/l_2. Calculation of the amount of 2-nonanone needed in the small pouch to keep the 2-nonanone concentration in the headspace of the package B during 21 days from Equation (21),.

For a specific activity value,

at vapor activity = 0.33
partial pressure, p_1 = 20.2 Pa.
partial presure, $p_2 = 0$
saturated partial pressure, p_s = 61.3 Pa
permeability coefficient = 2.7×10^{-16} kg.m/m^2.sec.Pa
thickness = 2 mil
pouch area = 8 cm^2

$$Q = (2.7 \times 10^{-16})(8 \times 10^{-4})(61.3-20.2)(21 \times 86400)\,/\,(2 \times 25.4 \times 10^{-6})$$

$$= 3.17 \times 10^{-7}\ \text{kg}$$

$$= 0.317\ \text{mg}$$

	Ratio of Thickness (l_1/l_2)	0.25	0.30	0.50
Vapor Activity	Concentration (mg/L)	Amount of 2-Nonanone (mg)		
0.08	0.27	0.30	0.18	0.15
0.23	0.8	0.31	0.19	0.15
0.33	1.15	0.32	0.19	0.16
0.54	1.88	0.38	0.23	0.19

Table 11. Total quantity of liquid 2-nonanone to be place into the small pouch to produce a headspace concentration of vapor activity as a function of l_1/l_2

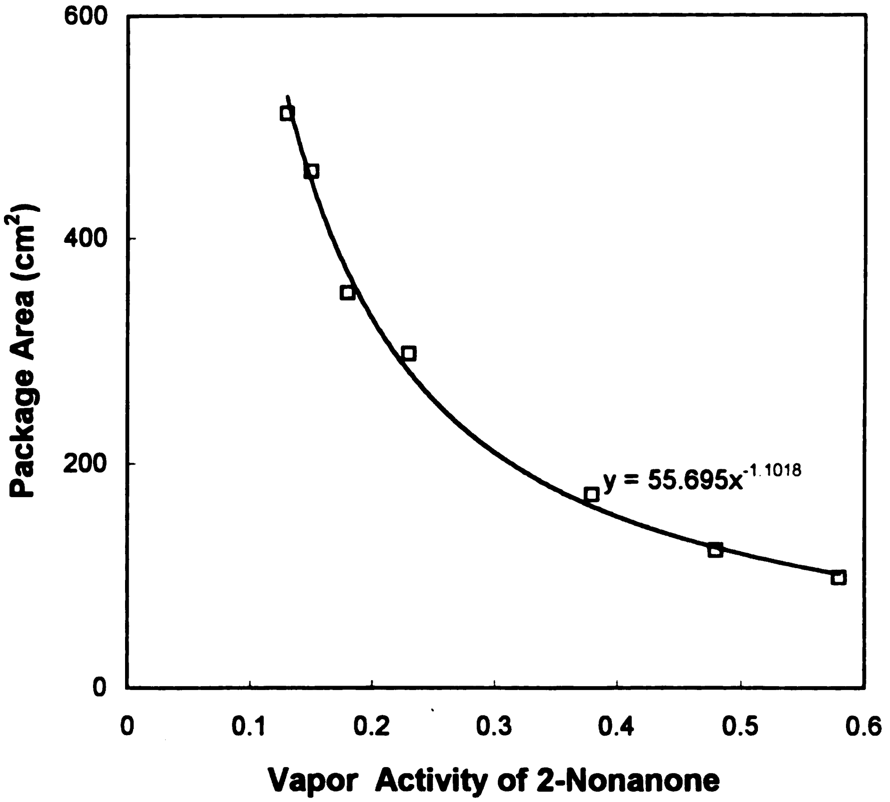


Figure 36. The vapor activity of 2-nonanone vs package area using desorption process from the polymer film

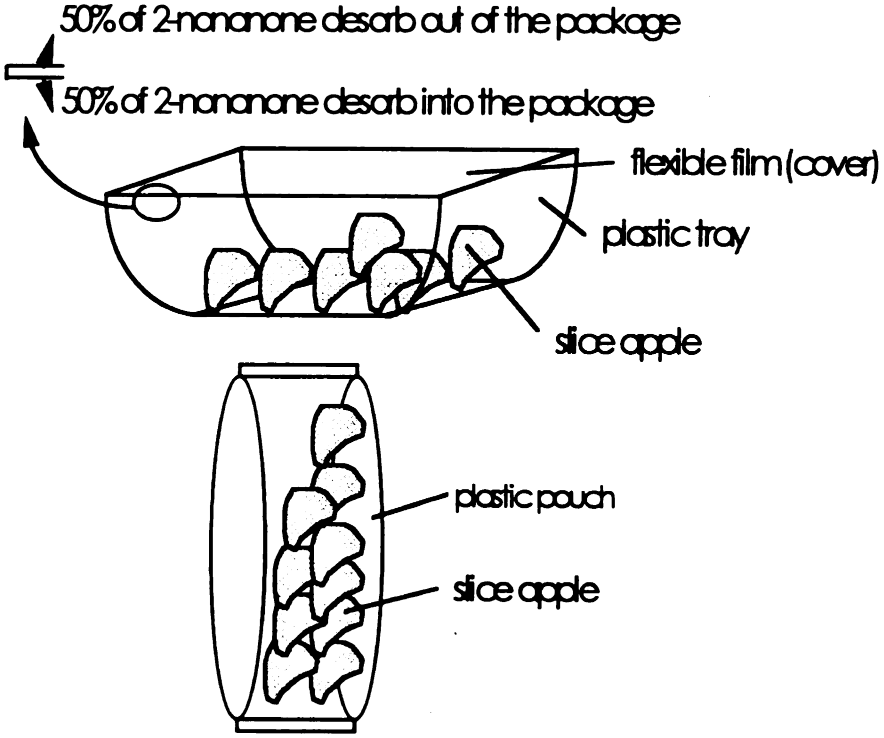


Figure 37. A typical package of slice apples to maintain 2-Nonanone concentration in the headspace of A package through desorption process

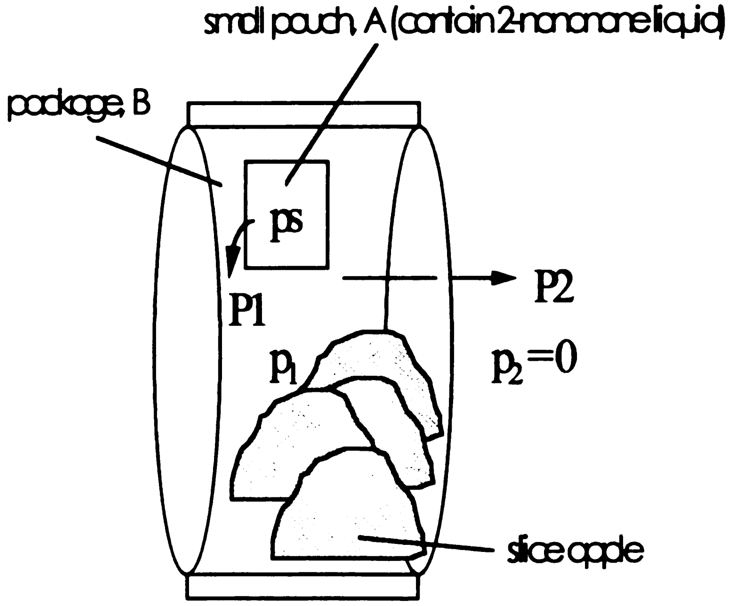


Figure 38. A small pouch with 2-nonanone liquid in the package to maintain the concentration of 2-nonanone in the headspace of the package

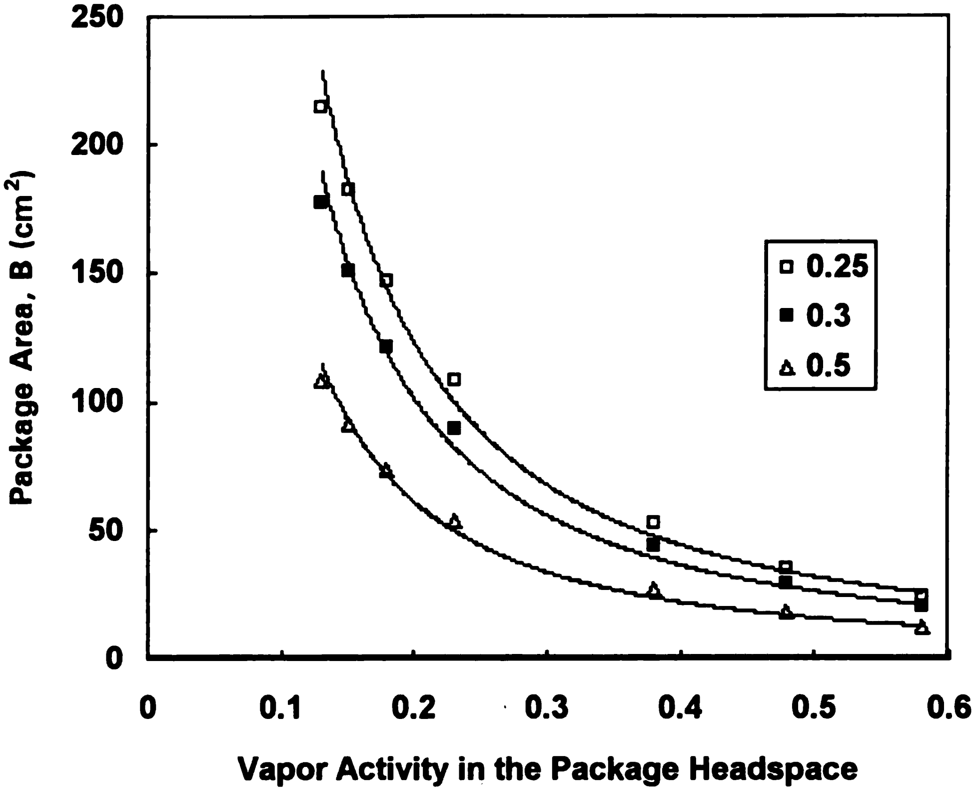


Figure 39. The vapor activity of 2-nonanone vs. package area using small pouch in package system at different ratio of thickness, l_1/l_2 between small pouch and package

CONCLUSIONS

The results of this study showed concentration and temperature dependencies for permeation, diffusion, and solubility characteristic of 2-nonanone through polyethylene Affinity PL 1880 over the temperatures and concentration investigated. The sorption of 2-nonanone followed the simple Fickian kinetics at low vapor activity. However at higher vapor activity levels a relaxation-controlled swelling process associated with penetrant sorption may result in the rearrangement of free volume, and thus provide additional sites to accommodate more penetrant molecules. From the observed vapor activity dependence of the diffusion and permeability coefficients, it appears that the plasticizing effect of the sorbed vapor resulted in an exponential increase in these coefficients. An increase in temperature contribute energy to increase the segmental motion of the polymer chains, which increased the permeability of 2-nonanone through low density polyethylene samples.

In terms of practical importance, the studies develop a better understanding of the mechanism of transport process of 2-nonanone through polymer film over a range of concentration and temperature. The study also provide a method for estimating the barrier properties of the test film at lower temperature, by extrapolation of the Arrhenius plot obtained from higher temperature data.

The development of a package design can be established with the relationship of the permeant transport process. The sorption/desorption process of 2-nonanone from the packaging material into the headspace of the package has a potential for controlling the microbial growth in modified atmosphere packaging of minimally processed fruits.

In terms of theoretical importance, this study was viewed as a method to describe the phenomena of diffusion in polymeric films, for the case of changing concentrations of permeant and changing temperature.

RECOMMENDATIONS

A number of studies can be proposed for future investigation which could lead to an increased understanding of the mass transport properties of organic vapor.

1. Evaluate the extent of swelling of the polymer as a result of sorption over a wide range of penetrant concentration.
2. Study the effect of co-permeants which include organic and water vapors on the diffusivity of the respective individual penetrants through the test barrier polymer structure.
3. Determine the effect of the permeant concentration and temperature on various type of polyethylene homopolymer and copolymer.
4. Determine the crystallinity and glass transition temperature (Tg) of the polymer following equilibrium sorption studies.

APPENDIX

Appendix A

Procedure of Standard Calibration Curve Construction

A standard curve of response vs penetrant concentration was constructed from standard solution of known concentration. Calibration solutions were prepared by dissolution of known quantities of 2-nonanone in acrylonitrile. The detailed procedure are as follows.

1. Prepare dilute solutions for the permeant standard by the following procedure. Fill up 10 ml volumetric flask with 5 ml of acrylonitrile. Put the flask on the balance. By using a syringe inject 0.6 mg of 2-nonanone. Transfer this solution into 25 ml volumetric flask and dilute with acrylonitrile. This becomes 24 ng standard solution.

2. Make up similar standard solution with acrylonitrile. Make 3 more different concentration solutions by using the same method. From the lowest concentration solution, inject 1μl sample solution directly into the gas chromatography and area response was recorded. Triplicate the run and calculate the average.

3. Plot the gas chromatography area unit response vs the number of grams injected per sample. The slope of this curve equals the calibration factor. Injected quantity can be calculated as follows;

w = concentration (w/v) x 1 μl x 1 ml/1000 μl
  = weight (g)

Appendix B

Calculation of the Saturated Vapor Pressure of 2-Nonanone.

Temperature (°C)	Saturated Vapor Pressure, (experiment) (mmHg)	Saturated Vapor Pressure, (Perry Handook) (mmHg)
3	0.08	-
22	0.46	-
38	1.12	1.45
50	2.36	2.9

Table 11 : Saturated Vapor Pressure of 2-Nonanone

Sample Calculation:

The molecular weight of 2-Nonanone = 142 g/mol

From the gas law, the vapor activity at 22 °C is;

$$PV = nRT = mRT/M$$

$$P = \frac{(AU)(CF)(R)(T)}{MV}$$

$$= \frac{(1999219\ \text{AU})(1.7772 \times 10^{-13}\ \text{g/AU})(82\ \text{cc.atm/mol.K})(295\text{K})(760\ \text{mmHg})}{(0.1\ \text{cc})(142\ \text{g/mol})(\text{atm})}$$

= 0.46 mmHg at 22 °C

where,

P = partial pressure

V = volume

R = gas constant

T = temperature

M = molecular weight

AU = area unit

CF = calibration factor

BIBLIOGRAPHY

BIBLIOGRAPHY

Baner, A. L, 1987. The Measurement and Analysis of the Diffusion of Toluene in Polymeric Films. MS. Thesis. Michigan State University, East Lansing, MI.

Baner, A. L., R. J. Hernandez, K. Jayaraman, and J. R. Giacin, 1986. Isostatic and Quasi-Isostatic Methods for Determining the Permeability of Organc Vapors Through Barrier Membranes. In Current Technologies in Flexible Packaging, ASTM STP 912.

Barrer, R. M, 1939. Permeation, Diffusion, and Solubility of Gases in Organic Polymer. Trans Faraday Soc. 35:628.

Berens, A. R, 1975. Angew. Macromol. Chem., 47:97

Billmeyer, F.W, 1984. Ionic and Coordination Chain Polymerization. In Textbook of Polymer Science, 3rd Ed. John Wiley and Sons, Inc.

Brown, R.P, 1981. Permeability. In Handbook of Plastics Test Methods, 2nd Edn., George Godwin Ltd., Essex, England, chap.18.

Crank, J, 1975. The Mathematics of Diffusion, 2nd ed., Oxford University Press, London.

Davis, P.L. and J.J. Smoot, 1972. Germination of Penicilium Digitatum Spores as Affected by Solutions of Volatile Components of Citrus Fruits. Phytopathology 62:488

DeLassus, P.T. and G. Strandburg, 1991. Flavor and Aroma Permeability in Plastics. Food Packaging Technology. ASTM. STP 1113:64

Ding, W., T.R. Hamilton-Kemp, W.S. Grayburn, G.B. Collins and D.F.Hildebrand, 1992. Effects of Six-carbon Aldehydes and Alcohols on Bacterial Proliferation. J. Agric. Food Chem. 41:506

Edney, K.L, 1983. Top Fruit. In Postharvest Pathology of Fruits and Vegetables, Colin Dennis Ed., Academic Press, 43

Fujita, H., 1961. Fortschr. Hochpolymer. Forsch., 3:1.

Gillete, P.C, 1988. Measurement of Organic Vapor Migration in Thin Films. Adv. Converting Packaging Technology 4(1):193

Hamilton-Kemp, T.R., C.T. McCracken, J.H. Laughlin, R.A. Andersen and D.F. Hildebrand, 1992. Effects of Some Natural Volatile Compounds on the Pathogenic Fungi Alternaria Alternata and Botrytis Cinerea. J. Chem. Ecol. 18:1083

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

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

Holland, R. and R. Santangelo, 1988. `Laminate Film' Method for Measuring Odor Transmission Rates Through Food Packaging Films. CSIRO Food Research Quarterly 48:40

Hopfenberg, H.B, 1978. Molecular Factors Affecting Transport of Small Molecules in Polymers. Short Course PIA-18. North Carolina State University-Raleigh.

Jost, W, 1960. Diffusion in Solids, Liquids, and Gases. Academic Press, New York.

Kader, A.A., 1985. Postharvest and Biology. In Postharvest Technology of Horticultural Crops, Cooperative Extension University of California Division of Agriculture and Natural Resources Special Publication 3311:2.

King, A.D. and H.R. Bolin, 1989. Food Technology 43:132

Koszinowski, J, 1986. J. Appl. Polymer Sci. 31:1805

Laine, R, 1971. Permeability of Polyethylene Film to Organic Vapors. J. of Applied Polymer Science 15:327.

Leaversuch, R.D, 1995. Fresh-cut Produce Market Ripe for Innovation. Modern Plastic. McGraw Hill Pub, 17

Leepipattanawit, R., 1995. Communication. School of Packaging, Michigan State University, East Lansing, Michigan.

Liu, K.J., R.J. Hernandez and J.R. Giacin, 1991. J.of Plastic Film and Sheeting 7:56

Mannapperuma, J. D., D. Zagory, R. P. Singh and A. A. Kader, 1989. Proc. 5th Int. Cont. Atmos. Res. Conf., Wenatchee, Washington, 2:225.

McCall, D.W. and W.P. Slichter, 1958. J. Am. Chem. Soc 80:1861.

Meares, P, 1953. Trans Faraday Soc. 49:1133

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

Michaels, A.S. and R.B. Parker, J.R, 1959. Sorption and Flow of Gases in Polyethylene. Journal of Polymer Science 41:53

Mohney, S.M., R.J. Hernandez, J.R. Giacin, B.R. Harte and J. Miltz, 1988. Permeability and Solubility of d-Limonene Vapor in Cereal Package Liners, Journal of Food Science 53:253

Murray, L.J, 1985. An Organic Vapor Permeation Rate Determination for Flexible Packaging Materials. Journal of Plastic Film and Sheeting 1:104

Naylor, T, deV, 1989. Permeation Properties. In Comprehensive Polymer Science, C. Booth and C. Price (Eds.), Pergamon Press, Oxford, England 2:20.

Ng, H.C, 1985. J. Polym. Sci (Phys. Ed.). 23:973

NIOSH, 1979. Registry of Toxic Effects of Chemical Substances, 1978 ed. R.J. Lewis (Ed.). National Institute for Occupational Safety and Health, US. Government Printing Office, Washington, DC.

Ono, K, 1990. Preservation and Distribution of Foods. Packaging Engineering Course. Japan Packaging Institute, Japan.

Paine, F.A. and H.Y. Paine, 1983. A Handbook of Food Packaging. Leonard Hill, London, England.

Pascat, B, 1986. Study of Some Factors Affecting Permeability. In Food Packaging and Preservation Theory and Practice, M. Mathlouthi (Ed.), Elsevier Applied Science Publishers Ltd., Essex, England, chap. 2.

Pinsky, J, 1957. Modern Plastic 34:145.

Robertson G.L, 1993. Principle and Practice. Food Packaging. Marcel Dekker, Inc. chap.4:90.

Rogers, C.E, 1965. Physics and Chemistry of the Organic Solid State. New York, NY, J. Wiley and Sons.

Rogers, C.E, 1965. Physics and Chemistry of the Organic Solid State. J.Wiley and Sons. New York, NY.

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

Rogers, C.E.., V. Stannett and M. Szwarc, 1956. The Sorption, Diffusion, and Permeation of Organic Vapors in Polyethylene. J. of Polymer Sci. 45:61

Sfirakis, A. and C.E. Rogers, 1980. Polymer Eng. Sci. 20:294.

Stannett, V. and H. Yasuda, 1965. The Measurement of Gas and Vapor Permeation and Diffusion in Polymers. In Testing of Polymers 1. Schmitz, J.Z. Interscience Publishers 13:393.

Stepek, J., V. Duchacek, D. Curda, and M. Sipek, 1987. Polymers as Materials for Packaging. Ellis Horwood Ltd. Chichester, UK, 83

Swogger, K.M, 1992. The Material Properties of Polymers Made From Constrained Geometry Catalysts. The Dow Chemical Company, Texas, 155

Van Amerongen, G.J, 1950. Journal Polymer Science 5:307.

Vaughn, S.F. and H.W. Gardner, 1993. Lipoxygenase-derived Aldehydes Inhibit Fungi Pathogenic on Soybean. J. Chem. Ecol. 19:2337

Vaughn, S.F., G.F. Spencer and B.S. Shasha, 1993. Volatile Compounds from Raspberry and Strawberry Fruit Inhibit Postharvest Decay Fungi. J. Food Science 58:793

Zagory, D. and Kader, A.A. (1988). Modified Atmosphere Packaging of Fresh Produce. Food Technology, 42:9, 70

Ziegler, K, 1955. Angew. Chem. 67: 541

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

Zobel, M.G.R, 1988. The Odor Barrier Performance of Packaging Films-coextruded Oriented Polyproylene. Packaging 12:22