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A COMPARISON OF SOLUBILITY COEFFICIENT VALUES DETERMINED BY GRAVIMETRIC AND ISOSTATIC PERMEABILITY TECHNIQUES

presented by

Christopher Donald Barr

has been accepted towards fulfillment
of the requirements for

MASTER degree in PACKAGING

Jack K. Giacin
Major professor

Date April 28, 1997

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A COMPARISON OF SOLUBILITY COEFFICIENT VALUES DETERMINED BY GRAVIMETRIC AND ISOSTATIC PERMEABILITY TECHNIQUES

By

Christopher Donald Barr

A THESIS

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

MASTER OF SCIENCE

School of Packaging

1997

ABSTRACT

A COMPARISON OF SOLUBILITY COEFFICIENT VALUES DETERMINED BY GRAVIMETRIC AND ISOSTATIC PERMEABILITY TECHNIQUES

By

Christopher Donald Barr

The solubility coefficient (S) values for ethyl acetate in three heat sealant polymer membranes (LDPE, LLDPE, and ionomer) were determined over a range of permeant vapor concentrations by a gravimetric procedure and an isostatic permeability technique. The respective solubility coefficient values obtained by the two methods were found to be in good agreement, with no statistically significant difference observed as a function of vapor activity. This agreement suggests that the solubility coefficient values obtained were independent of permeant vapor activity and the sorption process followed a Henry's law relationship over the vapor concentration range evaluated.

Comparison of the solubility coefficient values obtained by the gravimetric and isostatic permeability techniques showed reasonably good agreement over the vapor concentration range considered, with the S values obtained from permeability experiments being approximately 25 to 30% higher than those obtained from sorption measurements. Because of the procedural differences between the gravimetric and isostatic permeability techniques, this agreement is considered to be within acceptable limits. For the gravimetric technique, the solubility coefficient value is determined directly from the steady state portion of the sorption profile curve, while the solubility coefficient value obtained from the permeability experiment is derived from transient state data.

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I would like to begin by thanking God for giving me the ability to undertake and complete this project. All glory belongs to God, from whom all good things come.

I would also like to express my thanks to my major professor, Dr. Jack Giacin, for his guidance, support, and patience which enabled me to complete my research. I am also grateful to Dr. Ruben Hernandez and Dr. Krishnamurthy Jayaraman for serving on my graduate thesis committee. Without their guidance, this study could not have been completed.

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INTRODUCTION

The capability of a polymeric packaging material to serve as a barrier to organic vapor permeability can be characterized by its ability to minimize molecular exchange between the product and the outside environment. As this exchange is often responsible for product quality deterioration and shelf life reduction, a thorough understanding of organic vapor permeability characteristics is of great practical and commercial importance. Consequently, this topic has been and continues to be the subject of study by a number of investigators (Apostolopoulos and Winters, 1991; Doyon et al., 1995; Mannheim and Passy, 1990; Halek et al., 1989; Liu et al., 1991).

The permeability of a polymer membrane can be described by the following expression:

$$\overline{P} = D \times S \qquad (1)$$

where $\overline{P}$ is the permeability coefficient, D is the diffusion coefficient, and S represents the solubility coefficient. The permeability coefficient ($\overline{P}$) can be described as the steady state transport rate of permeant molecules through the polymer, while the diffusion coefficient (D) represents the rate of permeant molecular movement through the polymer bulk phase, and the solubility coefficient (S) is a measure of the quantity of molecules sorbed by the polymer.

Several methods have been described for measuring the mass transfer characteristics

of polymer films, including a gravimetric technique and an isostatic permeation procedure (Hernandez et al., 1986; Baner, 1987). Use of the former procedure allows one to calculate both S and D, from which $\bar{P}$ can be obtained by substitution into Equation 1. In contrast, the isostatic permeation procedure involves calculation of $\bar{P}$ at steady state, with D determined by substitution into Equation 2:

$$D = \frac{l^2}{7.199\ t_{0.5}} \qquad (2)$$

where D is the diffusion coefficient, l is the thickness of the polymer film, and $t_{0.5}$ represents the time required to reach half of the steady state rate of transmission. Once $\bar{P}$ and D have been determined, the solubility coefficient can then be obtained from substitution into Equation 1. Comparison of the solubility coefficient values determined by these two procedures, for the same polymer/penetrant system, may show a lack of agreement, particularly for organic penetrants where, to date, no such investigation has been conducted.

While it can be assumed that the solubility and diffusion coefficients are independent of concentration when dealing with non-interactive permeants, this assumption may not be valid in the case of organic vapors. For example, references can be cited where once an apparent steady state rate of diffusion had been obtained, continued exposure to the organic penetrant resulted in observed, concentration dependent phenomena such as long term chain relaxation, swelling of the polymer matrix, and additional sorption of permeant (Nielsen and Giacin, 1994; Berens, 1979; Mohney et al., 1988). In addition, researchers have demonstrated that prolonged time of polymer exposure to a permeating organic vapor can cause time dependent transfer processes to

occur which are non-Fickian in nature.

From sorption studies at low vapor activities of vinyl chloride monomer in polyvinyl chloride powder, Berens (Berens, 1977) proposed that above the glass transition temperature, the relaxation process is sufficiently rapid to be complete within the time scale of the Fickian diffusion process. However, for PVC polymer films, Berens (Berens, 1977) found that the separation of relaxation and diffusion phenomena is not possible. The results of Blackadder and Keniry (Blackadder and Keniry, 1972) support Berens observation of a longer time scale for the relaxation phenomena in polymer films. These investigators found that it took 8 to 24 hours for a true steady state rate of permeation of p-xylene through a 0.75 mil polyethylene film to be attained. Their conclusion was that there are long stress relaxation times occurring in the polyethylene film, which are longer than the time required for diffusion.

On the basis of the studies of Berens (Berens, 1977) and Blackadder and Keniry (Blackadder and Keniry, 1972), there is supportive evidence for long time period relaxation effects occurring in polymer films above their glass transition temperature. Thus, there may be relaxation effects occurring during the diffusion process. From the work of Berens (Berens, 1977), the relaxation effects are expected to be more severe at higher vapor activities. In addition to the proposed changing concentration gradient within the polymer bulk phase during the transient state, long time relaxation effects may also occur and contribute to possible differences in the magnitudes and concentration dependencies of the solubility coefficient values determined from transient state (permeability measurement) and steady state (sorption measurement) data.

The relaxation processes which occur over a longer time scale than diffusion may be related to a structural reordering or redistribution of the free volume elements in the polymer, thus providing additional sites of suitable size and accessibility to accommodate more penetrant molecules (Berens and Hopfenberg, 1978). Possible differences between the transient and steady state solubility coefficient values may therefore also be related to the change in the free volume of the polymer matrix.

A primary objective of this study involves developing a correlation between solubility coefficient values determined by a gravimetric procedure, which would reflect the steady state value, and solubility coefficient values obtained from a permeability experiment. In terms of theoretical importance, the results of this study will provide a better understanding of the sorption process and its concentration dependency. This study will also be of significant practical importance in terms of the relationship between the sorption process and "flavor scalping" of food product volatiles by a contacting polymeric structure.

In addition to comparing the solubility coefficient values, this study will provide a comparison of the diffusion coefficient values obtained by the gravimetric and isostatic permeability techniques. These results may provide a better understanding of the concentration dependency of the diffusion process as well as the different methods by which organic molecular diffusion can be measured for a particular polymer/penetrant system.

LITERATURE REVIEW

The Importance of Understanding Organic Molecular Mass Transfer in Polymeric Packaging Films

The increased use of semi-permeable packaging materials in recent years has caused molecular mass transfer through polymeric materials to become an important area of interest and study. This growth has also led to the development of two commercially available apparatus designed to measure organic molecular mass transfer in polymeric materials. Mass transfer of organic vapors can involve the loss of volatiles from a product to a packaging material and/or the external environment (sorption and/or permeation), the uptake of volatiles from the outside environment by the product/package system (permeation) or the transfer of volatiles from the packaging material to the product (migration). This organic molecular exchange can result in diminished product quality and a reduction in product shelf life. For example, research conducted by Charara et al. (1992) indicated that sorption of citrus oil components from a packaged orange juice product by various contacting polymer structures resulted in a substantial decrease in flavor quality. Similarly, in a study of the sorption of volatiles from an apple juice product into contacting heat sealant polymer membranes, Konczal et al. (1992) found that the loss of aroma components from the product was significant when low density polyethylene was the contacting polymer structure. In addition, Lin (1995) recently investigated the

permeability of toluene vapor through a product/package system and its impact on the quality of a packaged confectionery product. While the transport of non-interactive permeants, such as oxygen, carbon dioxide, and water vapor, through polymeric structures has been well studied, there is still a need to develop a more comprehensive understanding of the mechanism by which organic molecular mass transfer occurs in polymeric packaging materials.

According to Gillette (1988), the flux of an organic permeant through a polymeric film is the product of two variables: a thermodynamic parameter of solubility, and a kinetic parameter of diffusion. The diffusion coefficient, D, is a measure of the rate at which permeant molecules move through the polymer in the direction of the concentration gradient. The solubility coefficient, S, describes the number of molecules that dissolve into the polymer bulk phase. The present study will focus primarily on comparing the solubility coefficient values obtained from two experimental procedures: a gravimetric sorption experiment and an isostatic permeability technique. Therefore, a brief summary of permeation, sorption, and diffusion theory will be presented in this review. For a thorough mathematical treatment, the reader is referred to Crank (1975).

The Mechanism of Sorption, Diffusion and Permeation in Polymers

The phenomenon of molecular mass transfer through polymeric materials can be characterized as occurring in three steps: adsorption, diffusion, and desorption. Molecular adsorption can be described as the condensation of a penetrant molecule onto the high partial pressure surface of the polymer membrane. After condensing on the

membrane surface, the molecule can then dissolve, or solubilize, into the polymer matrix. The solution process is then followed by penetrant molecular diffusion through the polymer bulk phase. In polymers above their glass transition temperature (T_g), diffusivity can be characterized as molecular movement through a series of small microvoids, or "holes," being continuously formed and reformed as a result of the thermal vibrations between polymer chains. According to the commonly accepted "random jump theory," penetrant molecular movement takes place through a series of random "hops" or "jumps" from one fluctuation (hole formation) or void between the polymer chains (free volume) to another, within the polymer bulk phase (Van Krevelen, 1990; Rogers, 1985). Since these voids are usually smaller than the size of a permeating molecule, several jumps must be attempted in the same direction before the molecule moves a distance comparable to its length. The diffusion process is then followed by penetrant molecular desorption from the low partial pressure side of the polymer (Laine and Osburn, 1971).

Factors Affecting Sorption, Diffusion, and Permeation in Polymers

The Nature of the Permeant

1. Size and Shape

The size and shape of a penetrant molecule can directly affect its mass transport through a polymeric packaging material. An increase in penetrant size (area and volume) normally results in a decrease in the diffusion coefficient value (D), and an increase in the solubility coefficient value (S). However, because the permeability coefficient value ($\overline{P}$) is the product of these two parameters, its variation with penetrant size is often much less.

As a consequence of the increase in solubility, S, D, and $\bar{P}$ typically become more concentration dependent with increasing penetrant size (Rogers, 1985).

In a study conducted by Kosinowski (1986), n-alkanes of various carbon length were dissolved in methanol, and the effect of n-alkane penetrant size on molecular mass transfer was investigated using low density polyethylene film. When 12, 16 and 20-carbon alkane penetrants were employed, the observed diffusion coefficient values were: 27×10^{-10}, 15×10^{-10}, and 4.7×10^{-10} cm^2/sec, respectively. In the same study, relative solubility coefficients and relative permeation constants were obtained for the respective penetrant molecules in LDPE film.

Berens and Hopfenberg (1982) have also shown that the shape of an organic penetrant molecule can impact its diffusivity in polystyrene, polyvinyl chloride and polymethyl methacrylate. In their research, the investigators found that the diffusivities of n-alkanes and other linear-shaped molecules were higher than the diffusivities of more spherical molecules of similar volume or molecular weight.

2. Molecular Branching

It has also been shown that molecular branching in a penetrant molecule causes a greater decrease in diffusivity than does an increase in its carbon chain length. According to Laine and Osburn (1971), the diffusion coefficient at zero concentration, D(0), generally decreases as penetrant molecular volume increases, but branching has a much greater effect than does molecular size. For example, the addition of a methyl group on a given hydrocarbon reduces the value of D(0) more than does increasing the chain length by one carbon atom (Laine and Osburn, 1971). This suggests that permeant molecules

diffuse preferentially along the direction of their greatest length.

However, in the same study, the investigators observed an exponential increase in the solubility coefficient value, S, as a function of increasing penetrant molecular volume and cross-sectional area. As a result of this compensating dependence of D(0) and S(0) on penetrant size and shape, the zero concentration permeability coefficient, $\bar{P}(0)$, was much less dependent upon the geometry of the penetrant molecule than either term separately (Laine and Osburn, 1971).

3. Chemical Composition

Penetrant diffusion and permeation are generally higher when the polymer and penetrant are of similar chemical composition or polarity. For example, Laine and Osburn (1971) measured the permeation of 19 separate organic penetrants through polyethylene film and found that nonpolar penetrants, such as hydrocarbons, produced the highest permeability in polyethylene film, while the lowest permeability levels were observed for polar permeants. This difference can be attributed to the interactive nature of sorbed organic permeants, which can cause swelling and plasticization of the polymer structure. These interactions can result in greater mobility of both the polymer segments and the permeant molecules, thereby increasing polymer permeability and promoting the concentration dependence of the diffusion process.

4. Co-permeants

The presence of copermeants is another factor that has been shown to influence the mass transfer properties of polymer films. For example, studies conducted by Hensley (1991) on the permeation rate of an ethyl acetate (A_v = 0.1)/limonene (A_v = 0.21) binary

mixture through a biaxially oriented polypropylene film showed an ethyl acetate transmission rate 40 times greater than that observed for pure ethyl acetate vapor at the same vapor activity level. However, while the permeation rate was found to increase, the solubility of ethyl acetate seemed to be unaffected by the presence of limonene as a copermeant, and appeared to follow a Henry's law relationship over the vapor concentration range evaluated. This was shown by Nielsen and Giacin (1994), who reported that the presence of the copermeant (limonene) had no apparent effect on the sorption characteristics of ethyl acetate in oriented polypropylene, over the vapor concentration range evaluated.

Hensley (1991) stated that the observed increase in the permeation rate of ethyl acetate in the presence of limonene could be attributed to the copenetrant (limonene) acting to plasticize the polypropylene matrix, thereby increasing the mobility of the ethyl acetate vapor through the polymer bulk phase. Therefore, the observed copenetrant dependency of the diffusion process may have been the result of relaxation effects caused by the presence of limonene in the polymer bulk phase. As stated by Meares (1965), these configurational changes are not instantaneous, but are controlled by the retardation times of the polymer chains. If these times are long, stresses may be set up which relax slowly. Thus, organic molecular sorption and diffusion may be accompanied by concentration as well as time dependent processes within the polymer bulk phase, which are slower than the micro-Brownian motion of the polymer chain segments which promote diffusion (Meares, 1965).

The results obtained by Nielsen and Giacin (1994) support Hensley's proposed

explanation for the observed increase in the permeation rate of ethyl acetate in the presence of limonene as a copermeant. While the investigators observed that limonene had no apparent effect on ethyl acetate solubility in oriented polypropylene film, a significant change was observed in the inherent mobility of ethyl acetate (in the presence of limonene as a copermeant) within the polymer bulk phase, possibly accounting for the dramatic increase in the permeability of ethyl acetate through the OPP film (Nielsen and Giacin, 1994).

There is a precedence in the literature in support of long time period relaxation effects occurring in polymer membranes above their glass transition temperature (Berens, 1977; Blackadder and Keniry, 1972). Therefore, copenetrant induced relaxation effects may have occurred during the diffusion of ethyl acetate/limonene binary mixtures in the oriented polypropylene film investigated (Nielsen and Giacin, 1994). Such relaxation processes, which occur over a longer time scale than diffusion, may be related to a structural reordering or redistribution of the free volume elements in the polymer. Thus, providing additional sites of appropriate size and frequency of formation, which promote diffusion and account for the observed increase in the permeation rate of ethyl acetate in the presence of limonene as a copermeant.

The Nature of the Polymer

1. Glass Transition Temperature and Morphology

Published research on organic molecular mass transfer in polymers is divided between studies conducted using glassy polymers, and studies of polymers above their glass transition temperature. In the glassy state, a polymer lacks sufficient thermal energy

to allow micro-Brownian motion of the chain segments to occur. As a result, the polymer chains are fixed in the conformational orientation acquired during processing.

However, when a polymer passes from the glassy state, through its glass transition temperature (T_g) to a rubbery state, its chain segments become mobile and are able to assume different conformations. In the amorphous state, the vibrational and rotational motions of the polymer chain segments create microvoids within the polymer matrix through which penetrant molecules can diffuse. This enhanced molecular diffusivity in the rubbery state generally results in higher penetrant permeability.

Because of the great practical and commercial importance associated with the barrier characteristics of polymeric packaging materials, organic molecular mass transfer has been, and continues to be the subject of study by a number of investigators (Nielsen et al., 1992; Miltz et al., 1991; Sadler and Braddock, 1991; Yamada et al., 1991). Most polymer structures used in packaging applications are above their glass transition temperature (T_g), and their properties have been studied. In contrast, the more complex mechanism of organic molecular mass transfer through polymeric structures below their T_g is not very well understood at this time (Hernandez-Macias, 1984). According to Fujita (1961), anomalous, non-Fickian sorption and diffusion processes have been frequently observed in polymers below their glass transition temperature. Such glassy polymers are not readily penetrated by organic vapors because sorption of penetrant molecules is thought to occur almost exclusively within the amorphous domains of the polymer matrix (Sobelev et al., 1957). Therefore, the degree of polymer crystallinity is significant, not only because crystalline regions are excluded from the sorption process, but also because these

regions are impermeable barriers to diffusion (Rogers, 1985).

The presence of crosslinking can also affect the permeability characteristics of a polymer membrane. Crosslinking can effectively restrain segmental mobility, and thereby markedly decrease polymer permeability, primarily because of its influence on the diffusion coefficient (Rogers, 1964). In contrast, the presence of crosslinking has little effect on the solubility coefficient, except when the degree of crosslinking is high, or when the penetrant causes significant swelling of the polymer matrix (Rogers, 1985).

Orientation can also influence polymer barrier characteristics by allowing laterally bonding groups to approach each other and interact. For example, Shirakura (1987) investigated the effect of orientation temperature on the ethyl acetate permeability of biaxially oriented polyethylene terephthalate (PET) films of varying thermomechanical history. By changing the orientation temperature from 90 to 115 °C, the percent crystallinity of the obtained PET film increased from 22 to 31%. Further, by increasing the percent crystallinity of the PET film as described, Shirakura observed an ethyl acetate permeability level 4 times lower than that observed for the PET having 21% crystallinity.

2. Intermolecular Forces

According to Rogers (1985), a polymer membrane's barrier properties are a function of the structural symmetry of its polymer chains, as well as the intermolecular forces that exist between them. An increase in the structural symmetry and the cohesive energy of a polymer normally causes polymer permeability to decrease.

Chemical modification can also produce significant changes in a polymer's diffusion and permeability coefficient values. For example, addition of methyl or polar

side groups to rubber chains will increase the cohesive energy, thereby decreasing the polymer's permeability and diffusion coefficient values, but only slightly affecting its solubility coefficient value (Rogers, 1985).

3. Plasticizers and Additives

The incorporation of plasticizers and additives into the polymer bulk phase can significantly impact polymer properties. Plasticizers can effectively force the polymer chains farther apart, thereby increasing the free volume of the system. Based on the studies of Fujita (1961) and Duda and Zielinski (1996), it was concluded that the mobility of diffusant molecules is a function of the average free volume of the system. As the free volume within the polymer matrix increases, the cohesive energy is reduced and the polymer's glass transition temperature (T_g) is lowered. In contrast, the addition of impermeable or solid additives (such as fillers), may not significantly impact the free volume of the system, but instead create a more torturous path through which a permeant molecule must travel, resulting in a decrease in penetrant diffusivity (Duda and Zielinski, 1996).

Concentration

While it can be assumed that the permeability, solubility and diffusion coefficient values for a given polymer/penetrant system are independent of concentration when dealing with non-interactive permeants, this assumption may not be valid in the case of organic vapors. For example, references can be cited where once an apparent steady state rate of diffusion had been obtained, continued exposure to the organic penetrant resulted in observed, concentration dependent phenomena such as long term chain relaxation,

swelling of the polymer matrix, and additional sorption of permeant (Nielsen and Giacin, 1994; Berens 1979; Mohney et al., 1988). Researchers have also shown that prolonged exposure of a polymer membrane to organic penetrant vapors can cause time dependent transfer processes to occur which are non-Fickian in nature (Berens, 1977; Blackadder and Keniry, 1972; Rogers, 1985).

From a study investigating the sorption of vinyl chloride monomer in polyvinyl chloride powder, Berens (1977) proposed that above the glass transition temperature (T_g), the relaxation process is sufficiently rapid to be complete within the time scale of the Fickian diffusion process. However, for PVC polymer films, Berens (1977) found that the separation of relaxation and diffusion phenomena is not possible. The results of Blackadder and Keniry (1972) support Berens observation of a longer time scale for relaxation phenomena in polymer films. From permeability studies of p-xylene through a 0.75 mil polyethylene film, the investigators found that it took between 8 and 24 hours before a true steady state rate of permeation was attained. They concluded that long stress relaxation times had occurred in the polyethylene film, which were longer than the time required for diffusion.

Based on the research of Berens (1977) and Blackadder and Keniry (1972), there is supportive evidence of long time period relaxation effects occurring in polymer films above their glass transition temperature (T_g). Therefore, there may be relaxation effects occurring during the diffusion process. From studies conducted by Berens (1977), the relaxation effects were shown to be more severe at higher vapor activities. Relaxation processes which occur over a longer time scale than diffusion may be related to a structural

reordering or redistribution of the free volume elements in the polymer. Thus, providing additional sites of suitable size and accessibility to accommodate more penetrant molecules (Berens and Hopfenberg, 1978).

Temperature

The effect of temperature on the mass transfer properties of polymer membranes has been and continues to be the subject of study for a number of researchers (DeLassus and Strandburg, 1991; Michaels and Parker, 1959; Sajiki and Giacin, 1993). For example, research conducted by Wahid (1996) showed temperature dependency for the obtained diffusion and permeability coefficient values for 2-nonanone vapor in LLDPE film, over a range of permeant vapor concentration levels. Similarly, in a study conducted by Matur (1993), the mass transport of a number of organic volatiles was shown to be directly correlated with temperature for the polymeric test films investigated.

As stated earlier, mass transfer of penetrant molecules in polymer membranes occurs by a diffusion mechanism through the polymer matrix. This mechanism can be characterized as a process in which a penetrant molecule moves or "jumps" from one "hole" to another within the polymer bulk phase, proceeding from a domain of higher penetrant concentration to a region of lower penetrant concentration. The formation of these "holes" in the amorphous phase, or the free volume of the polymer, is the result of the rotational, vibrational, and translational motions of the polymer chain segments. Diffusion of permeant vapors can occur only if the free volume, or void volume, is greater than the size required to accommodate the permeant molecule. As the temperature of a polymer above its T_g increases, greater molecular motion takes place. Consequently, this

can lead to an increase in the size and frequency of hole formation within the polymer bulk phase, thus increasing permeability and diffusion.

Theory of Permeation Through Polymer Films

According to Crank (1975), the process of molecular diffusion through a polymer membrane can be described by Fick's first and second laws of diffusion. Fick's first law is presented in Equation 3 and describes the flux (F), or penetrant transfer rate per unit area, as being proportional to the concentration gradient dc/dx.

$$F = -D \frac{\partial c}{\partial x} \tag{3}$$

where c represents the permeant concentration in the polymer film, D is the diffusion coefficient, and x is the length of direction in which penetrant molecular transport occurs. Fick's second law is presented in Equation 4:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial c}{\partial x}\right) \tag{4}$$

where t represents time. Taking into account the concentration dependency of the diffusion coefficient, Fick's second law states that the total concentration change across the polymer bulk phase as a function of time is directly proportional to the change in concentration gradient as a function of permeant penetration depth. When the diffusion coefficient (D) varies with time, the diffusion process is often described as being non-Fickian in nature.

By integrating Fick's first law, the following expression can be obtained:

$$F = \frac{1}{x} \int_{c_1}^{c_2} D \cdot \partial c = D\,(c_2 - c_1)\,\frac{1}{x} \tag{5}$$

where F represents the flux or penetrant transfer rate per unit area; D is the diffusion coefficient; c_1 and c_2 are the high and low penetrant concentration levels being separated by the polymer membrane, respectively; and x represents the thickness of the polymer film sample.

For a given polymer membrane at equilibrium, the steady state rate of permeation can be described by:

$$F = \frac{1}{x} \int_{p_1}^{p_2} \overline{P} \cdot \partial p = \overline{P}\,(p_2 - p_1)\,\frac{1}{x} \tag{6}$$

where p_1 and p_2 represent the partial pressure on either side of the polymer film, and $\overline{P}$ is the permeability coefficient. From Equations 5 and 6, the total quantity of permeating substance (Q) passing through a polymer can be determined using the following expression:

$$Q = D\,A\,t\,\frac{(c_2 - c_1)}{l} = \overline{P}\,A\,t\,\frac{(p_2 - p_1)}{l} \tag{7}$$

where A represents area, t is time, and l is the polymer thickness. The concentration of the permeating substance (c) within the polymer membrane can then be related to the permeant concentration in the vapor phase by assuming Henry's law:

$$c = S\,p \tag{8}$$

where S represents the solubility coefficient for the polymer/penetrant system. Therefore, the permeability of a polymeric packaging material can be expressed by:

$$\overline{P} = D \times S \tag{9}$$

where $\bar{P}$ is the permeability coefficient, D is the diffusion coefficient, and S is the solubility coefficient.

Techniques for Measuring Organic Molecular Mass Transfer in Polymeric Packaging Materials

Electrobalance Sorption Measurements

Gravimetric measurements have been used by a number of researchers to investigate the mass transfer characteristics of polymer membranes (Hernandez et al., 1986; Baner, 1987; Sfirakis and Rogers, 1980). The preferred apparatus for conducting sorption experiments is an electrobalance, as this system continually records the weight gain or loss of the sample as a function of time. In addition, this system is often interfaced with a vapor generator system, allowing sorption measurements to be conducted over a range of penetrant vapor concentration levels.

Using the gravimetric electrobalance technique, the solubility coefficient value can be obtained by first suspending a film sample weighing approximately 30 mg in the electrobalance hangdown tube. After sufficient time has passed, such that the air in the hangdown tube has been displaced with nitrogen, the organic vapor stream is then diverted into the hangdown tube, where it surrounds the polymer sample. The weight change of the sample is continuously recorded as a function of time, using either a strip chart recorder or a computer. Once a steady state level of sorption has been obtained, the solubility coefficient value can be determined from the following expression:

$$S = \frac{M_\infty}{w \cdot b} \tag{10}$$

where S is the solubility coefficient value, expressed as mass of vapor sorbed at equilibrium per mass of polymer per driving force. M_∞ represents the total mass of vapor sorbed by the polymer at equilibrium at a given temperature, w is the initial weight of the polymer test sample, and b is the value of the permeant driving force.

Experimental sorption data is usually presented graphically as a plot of M_t/M_∞ as a function of the square root of time, with the initial portion of the curve being linear (Meares, 1965). The diffusion equation appropriate for the sorption of penetrant by a polymer sample in film or sheet form was described by Crank (1975) as:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\left[\exp\left(\frac{-D \cdot \pi^2 \cdot t}{l^2}\right) + \frac{1}{9}\exp\left(\frac{-9D \cdot \pi^2 \cdot t}{l^2}\right)\right] \qquad (11)$$

where M_t and M_∞ are the amount of penetrant sorbed by the polymer film sample at time t and the equilibrium sorption after infinite time, respectively; t is the time required to reach M_t, and l represents the film thickness. If the experimental and calculated curves are in good agreement, the diffusion process is usually considered Fickian, and an accurate estimation of D can be made (Nielsen and Giacin, 1994). This is achieved by setting $M_t/M_\infty = 0.5$ and calculating the sorption diffusion coefficient as follows:

$$D_s = \frac{0.049\ l^2}{t_{0.5}} \qquad (12)$$

where D_s is the sorption diffusion coefficient, and $t_{0.5}$ is the time required to attain half of the sorption level at steady state. Once the solubility and diffusion coefficient values have been determined, the permeability coefficient value, $\bar{P}$, can be obtained from Equation 13:

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

where $\bar{P}$ is the permeability coefficient value, and D is the diffusion coefficient value, and S represents the solubility coefficient value.

Isostatic Permeability Measurements

Several test methods have been described in the literature for measuring the permeability characteristics of polymer membranes, most notably the isostatic technique and the quasi-isostatic technique. While both techniques provide equivalent information regarding the organic vapor barrier properties of a polymer film, the present study focuses on the isostatic procedure. The reader is referred to Hernandez, et al. (1986) for a thorough discussion of both the isostatic and quasi-isostatic permeability techniques.

Use of the isostatic permeability procedure involves continuous collection of permeant flux data from the initial time zero to the time at which a steady state rate of permeation is attained. This is achieved by employing a permeability cell, consisting of two chambers with the film sample mounted between them. Throughout the experiment, a constant concentration of organic vapor is continuously flowed through the upstream chamber of the permeability cell, enabling a consistent vapor concentration to be maintained. Simultaneously, pure dry grade nitrogen gas is continuously flowed through the low concentration chamber, and molecules that have permeated through the film sample are conveyed to a detector for quantification. In this way, a constant concentration gradient is maintained throughout the experiment. The permeability coefficient value is obtained directly from the steady state value of the isostatic experiment using Equation 14:

$$\bar{P} = \frac{F_\infty \, l}{A \, \Delta p} \qquad (14)$$

where F_∞ is the steady state rate of permeant flux (quantity per time), l represents the polymer film thickness, A is area of film exposed to the permeant vapor, and Δp is the driving force. By plotting the permeant flux ratio as a function of time, the diffusion coefficient, D, can be obtained from the following expression (Ziegel et al., 1969):

$$D = \frac{l^2}{7.199\, t_{0.5}} \tag{15}$$

where l is the thickness of the polymer film, and $t_{0.5}$ represents the time required to reach half of the steady state rate of transmission.

The permeation rate at any time F_t, during the transient state portion of the permeability experiment, varies from zero at time zero, up to the value F_∞, reached at steady state. This is described by the following expression (Pasternak et al., 1970):

$$\frac{F_t}{F_\infty} = \left(\frac{4}{\sqrt{\pi}}\right)\left(\sqrt{\frac{l^2}{4Dt}}\right)\sum_{n=1,3,5}^{\infty}\left(\frac{-n^2 l^2}{4Dt}\right) \tag{16}$$

where F_t/F_∞ is the permeant flux ratio, F_t is the permeant flux at time t, and F_∞ is the permeant flux at steady state. If good agreement is observed between the experimental and theoretical flux rate profiles, it can be assumed that the diffusion process followed Fickian behavior. Once $\bar{P}$ and D have been determined, the solubility coefficient value, S, can be obtained from Equation 17:

$$S = \frac{\bar{P}}{D} \tag{17}$$

where S represents the solubility coefficient value, $\bar{P}$ is the permeability coefficient value, and D is the diffusion coefficient value.

Cahn 2000 Electrobalance

Sorption experiments conducted using the gravimetric technique are usually carried out at equilibrium vapor pressure and employ an apparatus that continuously records the weight gain or loss of a polymer sample as a function of time. A recording electrobalance, such as the Cahn 2000, is commonly used for such studies.

The Cahn 2000 is a very sensitive weighing instrument, and is designed to measure weights up to 3.5 g, and is sensitive to weight changes as small as 0.1 μg. The electrobalance can be described as a torque-to-current converter. The apparatus consists of a balance beam mounted to, supported by, and pivoting about the center of a taut ribbon; a torque motor coil, located in a permanent magnetic field and also mounted to the taut ribbon; sample suspension fixtures; a beam position sensor system; and controls, circuitry and indicators.

When conducting a sorption measurement by the continuous flow method, the polymer sample is suspended from the arm of the electrobalance, and a sorbate of constant concentration is continuously flowed through the sample hangdown tube. The sorbate vapor is produced by bubbling pure nitrogen gas through the liquid sorbate. This can be achieved by constructing a vapor generator system, consisting of a gas washing bottle with a fritted dispersion tube, containing the organic liquid. As the weight of the polymer test sample changes, a torque is produced about the axis of rotation. The electrobalance effectively measures the amount of electric current needed by the torque converter to maintain the balance beam in a level position. By calibrating the electrobalance using calibration weights, the change in electric current can be related to weight change of the

polymer sample. By interfacing the electrobalance control unit with a strip chart recorder or a computer, the polymer sample's change in weight can be continuously recorded as a function of time (Cahn Instruments, Inc., 1987).

MAS 2000 Organic Vapor Permeation Test System

As previously stated, organic molecular mass transfer in polymeric materials has become a significant area of interest and study. This has led to the development of two commercially available apparatus: the MAS 2000 Organic Vapor Permeation Test System (MAS Technologies Inc., Zumbrota, MN), and the Aromatran (Modern Controls Inc., Minneapolis, MN). The MAS 2000 system, used in this study, is an isostatic permeability test apparatus, designed to continuously collect permeant flux data from the initial time zero, to the time at which a steady state rate of permeation is attained. Experimentally obtained data is recorded by the system's computer, which is equipped with the MAS 2000 software package. The MAS 2000 system and software package are based on Henry's law and Fick's first and second laws of diffusion, and can be used to obtain the steady state permeability coefficient value, $\overline{P}$. This permeability coefficient value is assumed to be directly proportional to the solubility coefficient, S, and the diffusion coefficient, D, as described by Equation 18.

$$\overline{P} = D \times S \tag{18}$$

The solution to the differential equations which describe the mass transport rate through a planar surface is:

$$R_t = R\, C^{1/2} \sum_{k = 1, 3, 5\ldots} \exp\,(-k^2 C) \tag{19}$$

where R_t represents the mass transport rate at time t, R is a constant related to the

permeability coefficient, and C is a constant associated with the diffusion coefficient.

When substituting experimental data into Equation 19, the initial baseline value, B, should also be considered. The baseline value represents the system's resultant FID response to the release of any organic volatiles which may have been trapped within the polymer membrane, and driven off at the time of test initiation. In addition, the time of experiment initiation, t_0, must be recorded. However, because of instrumental lag time, this t_0 value is generally an approximation of the true initiation time. A more accurate determination of R_t can be obtained from:

$$R_t = B + RC^{1/2} \sum_{k = 1, 3, 5...} \exp(-k^2 C) \qquad (20)$$

where $C = 1/(4D(t - t_0))$, and $R = 4\overline{P}/\sqrt{\pi}$.

The experimental temperature of the MAS 2000 is controlled by the system's computer, and is based on the following expression:

$$H = H_o + c_1 + c_2 \qquad (21)$$

where H represents the system's heater operation time, H_0 is the previous time cycle value, c_1 is a time correction factor related to the current temperature value, and c_2 is a time correction factor describing the current temperature value as a function of time. Values for c_1 and c_2 can be calculated from Equations 22 and 23, respectively.

$$c_1 = A \times \left(\frac{c_r}{r_t}\right) \times (t_s - (T + r_t \times D)) \qquad (22)$$

$$c_2 = B \times \left(\frac{c_r}{r_t}\right) \times D \qquad (23)$$

where c_r represents the set cycle rate, r_t is the controlled temperature time response (set by the system's program), t_s is the temperature set point value, T is the specified system temperature, D is a slope value describing the current temperature value as a function of time, A is a constant which describes the relationship between the heater setting (H) and temperature, and B is a constant which describes the relationship between heater setting (H) and the derivative of temperature with respect to time (MAS Technologies, Inc., 1994).

MATERIALS AND METHODS

Materials

Film Samples

Three typical, heat-sealing polymers were investigated, namely:

(1) Low density polyethylene (LDPE)
Trade name: Petrothene NA 940000
Density: 918 kg/m^3
Thickness: 50.8 μm

(2) Linear low density polyethylene (LLDPE)
Trade name: Sclairfilm
Density: 920 kg/m^3
Thickness: 50.8 μm

(3) Ionomer
Trade name: Surlyn 1601
Density: 940 kg/m^3
Thickness: 50.8 μm

These polymer membranes were selected because of their range of barrier property values, as well as their various cost, processibility, and use in food packaging. All polymer test films were provided by E.I. duPont de Nemours and Company (Wilmington, DE).

Permeant

Ethyl acetate of 99.8% purity was obtained from Aldrich Chemical Company (Milwaukee, WI) and used as the permeant in this study because it is present in many food flavor profiles, and therefore commonly comes in contact with heat-sealing membranes.

Acetonitrile

Used as a solvent when preparing standard solutions for construction of an ethyl acetate calibration curve (EM Science, Gibbstown, NJ).

Nitrogen Gas

Used as the carrier of the sorbate vapor. High purity, dry grade nitrogen (99.98%) was employed throughout the study (AGA Gas, Inc., Cleveland OH).

Methods

Analysis of permeant sorption into the test films was determined by two procedures.

Gravimetric Method

Sorption studies were conducted on a Cahn 2000 electrobalance (Cahn Instruments, Inc., Cerritos, CA) by the continuous flow method. A polymer sample weighing approximately 30 mg was suspended from the arm of the electrobalance. A sorbate of constant concentration was produced by bubbling pure nitrogen gas through the liquid sorbate. This was achieved by constructing a vapor generator system, consisting of a gas washing bottle with a fritted dispersion tube, containing the organic liquid.

To provide insight into the concentration dependency of the mass transfer process, four vapor activity levels were evaluated: 0.05, 0.1, 0.2, 0.4. To achieve this range of concentration levels, the sorbate stream was mixed with a second stream of pure nitrogen gas. Flow meters (Cole Parmer, Chicago, IL) and needle valves (Nupro 'M' series, Nupro Co., Willoughby, OH) were used to regulate the gas flow and indicate a constant flow rate. The sorbate uptake was continuously recorded on a Linseis Model L6512 flat bed recorder (Linseis, Inc., Princeton Junction, NJ) until steady state was reached.

Composition of the vapor stream was determined by using a high performance, gas tight syringe (Hamilton 1750, Supelco Inc., Bellefonte, PA) to take samples from a sampling port located on the hangdown tube and performing gas chromatographic (GC) analysis. The gravimetric sorption studies were conducted at a temperature of 22 ± 1 °C.

Isostatic Permeability Technique

For the polymers tested, the solubility coefficient was obtained using the MAS 2000 Organic Vapor Permeation Test System (MAS Technologies Inc., Zumbrota, MN). Polymer samples tested were cut to measure approximately 6 × 6-1/2 in for mounting in the test cell. A permeant vapor of constant concentration was produced by bubbling pure nitrogen gas through the liquid sorbate. This was achieved by constructing a vapor generator system, as described above.

To produce a range of vapor activity levels, the sorbate stream was mixed with a second stream of pure nitrogen gas. Experimental temperature and flow rate was regulated by a control system incorporated into the MAS 2000 apparatus design. Permeant molecule detection was carried out by a flame ionization detector (FID) that is integrated into the MAS 2000 system. Experimental results were recorded on the system's 486SX computer equipped with the MAS 2000 software package (MAS Technologies Inc., Zumbrota, MN).

The vapor stream concentration was determined by taking samples with a high performance, gas-tight syringe (Hamilton 1750, Supelco Inc., Bellefonte, PA) through a sampling port and performing gas chromatographic (GC) analysis. Isostatic permeability measurements were made at a temperature of 22 ± 1 °C.

Gas Chromatographic Analysis

Gas chromatographic analyses were performed using a Hewlett-Packard 5890A gas chromatograph, equipped with a dual flame ionization detector and interfaced with a Hewlett-Packard 3395 integrator for quantification (Avondale, PA). The column used in this study was a Supelcowax 10 fused silica capillary column (60 m, 0.25 mm ID, 0.25 μm film thickness) (Supelco Inc., Bellefonte, PA). A detailed summary of the GC conditions employed in this study is presented in Appendix A.

A calibration curve was constructed to determine the relationship between area response and ethyl acetate quantity injected. The standard curve and the procedure used for its construction are presented in Appendix A. Retention times for ethyl acetate and acetonitrile were found to be 7.2 and 8.4 minutes, respectively.

In addition, the saturation vapor pressure of ethyl acetate at 22 °C was experimentally determined using gas chromatographic analysis. A detailed summary of this procedure is presented in Appendix B. Based on GC analysis, the saturation vapor pressure was estimated to be 10.97 kPa, which was in close agreement with the reported literature value of approximately 10.77 kPa (Lide, 1997). Also discussed in Appendix B is the method used to calculate the ethyl acetate vapor activity levels employed in this study.

RESULTS AND DISCUSSION

Solubility and Diffusivity of Ethyl Acetate in LDPE, LLDPE and Ionomer Films Determined by the Gravimetric Technique

In this study, the solubility and diffusion coefficients for ethyl acetate in LDPE, LLDPE and ionomer films were determined using two experimental methods: the gravimetric and isostatic permeability techniques. Gravimetric sorption experiments were conducted at ambient temperature (22 ℃), over a range of permeant vapor concentrations. LDPE and LLDPE film samples were tested at vapor activities of: 0.05, 0.1, 0.2 and 0.4, while the ionomer film samples were tested at vapor activities of 0.1, 0.2 and 0.4, respectively. Under these experimental conditions, equilibrium sorption times of less than 30 hours were observed.

The solubility coefficient, S, for permeant vapor in a polymer can be calculated from Equation 24:

$$S = \frac{M_\infty}{w \cdot b} \tag{24}$$

where S is the solubility coefficient value, expressed as mass of vapor sorbed at equilibrium per mass of polymer per unit driving force. M_∞ is the total mass of vapor absorbed by the polymer sample at equilibrium, w is the initial weight of the polymer sample under test, and b is a value of the permeant driving force. Solubility coefficient

values obtained from gravimetric experiments are presented in Table 1. As shown, for the respective test films, good agreement between the solubility coefficient values was obtained over the range of vapor activities evaluated. The relationship between ethyl acetate equilibrium solubility in the polymer films evaluated and penetrant partial pressure is presented graphically in Figure 1. In Figures 2, 3 and 4, the solubility coefficient values are plotted as a function of permeant vapor activity for the LDPE, LLDPE and ionomer films, respectively. As shown, good agreement was obtained over the permeant concentration range evaluated in this study.

Table 1. Solubility coefficient values obtained from gravimetric experiments for ethyl acetate in LDPE, LLDPE and ionomer films at 22 °C [a]

Vapor activity	Solubility coefficient [kg/kg·Pa (× 10^{-6})]		
	LDPE	LLDPE	Ionomer
0.05	2.2	2.3	
0.1	2.2	2.1	4.0
0.2	2.4	2.5	4.4
0.4	2.3	2.2	3.9
Mean value ± standard deviation	2.3 ± 0.1	2.3 ± 0.2	4.1 ± 0.2

[a] Average of replicate runs, with a confidence limit of 7%, 5% and 12%, respectively (maximum)

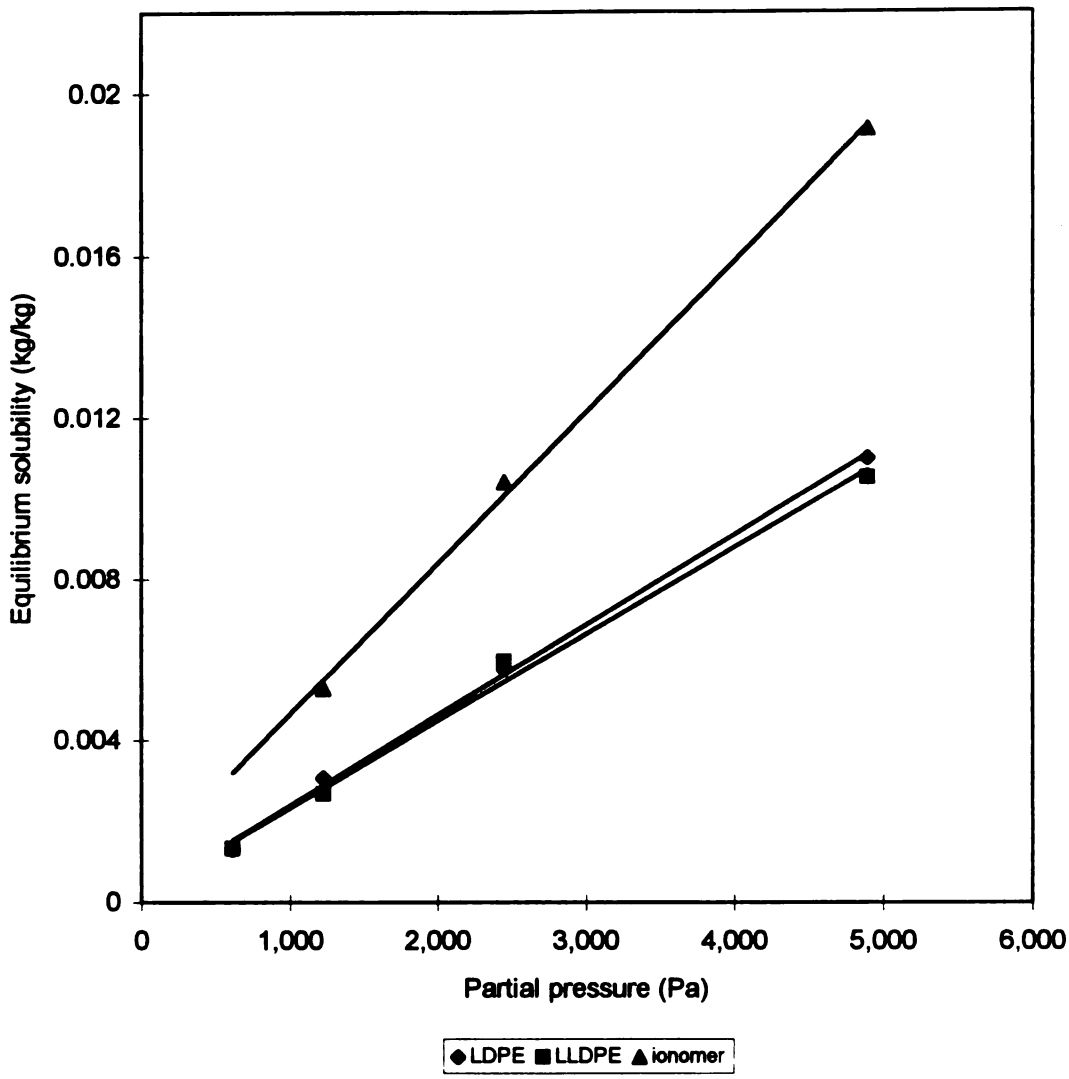

Figure 1. Equilibrium solubility as a function of partial pressure for ethyl acetate in LDPE, LLDPE and ionomer films at 22 °C

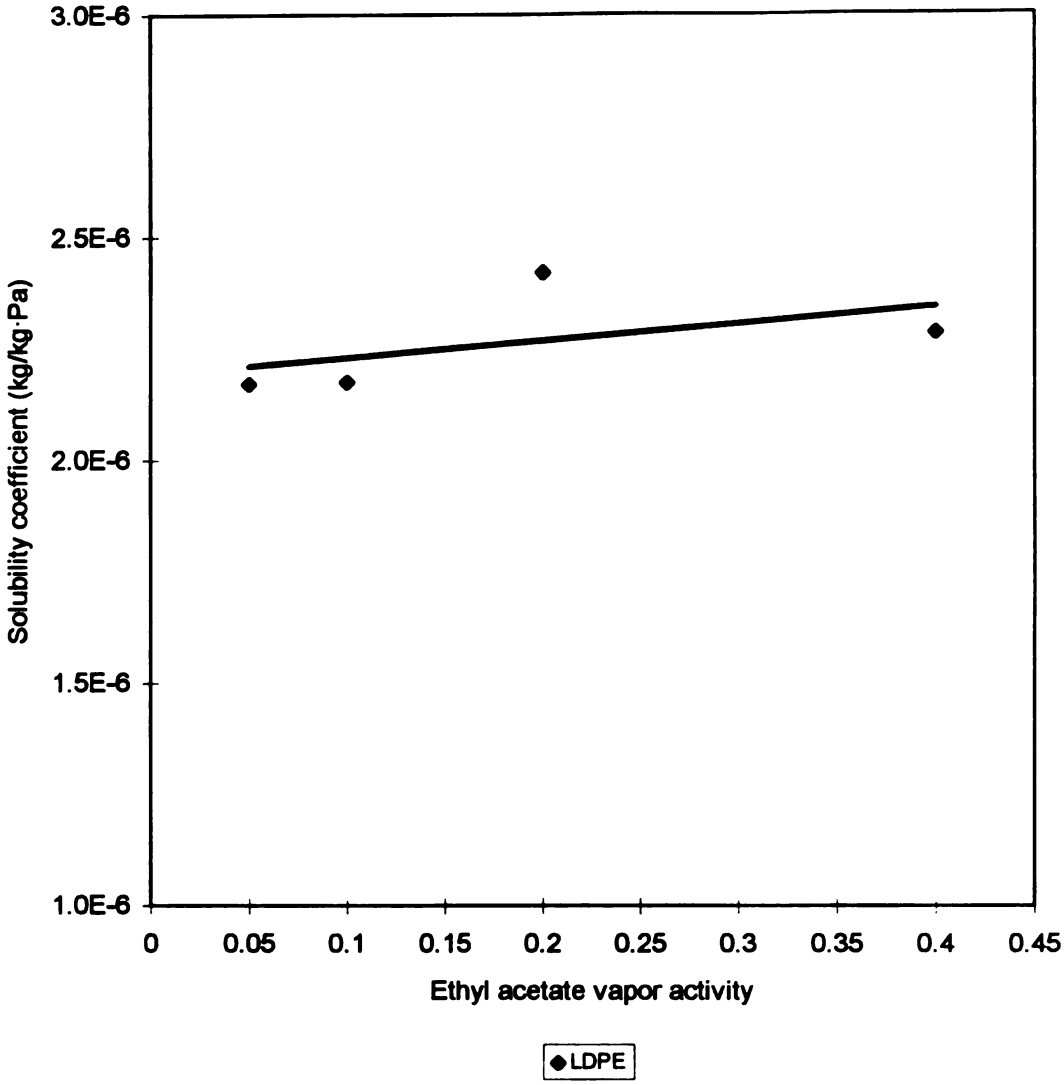

Figure 2. Equilibrium solubility coefficient as a function of sorbate vapor activity for ethyl acetate in LDPE film at 22 °C

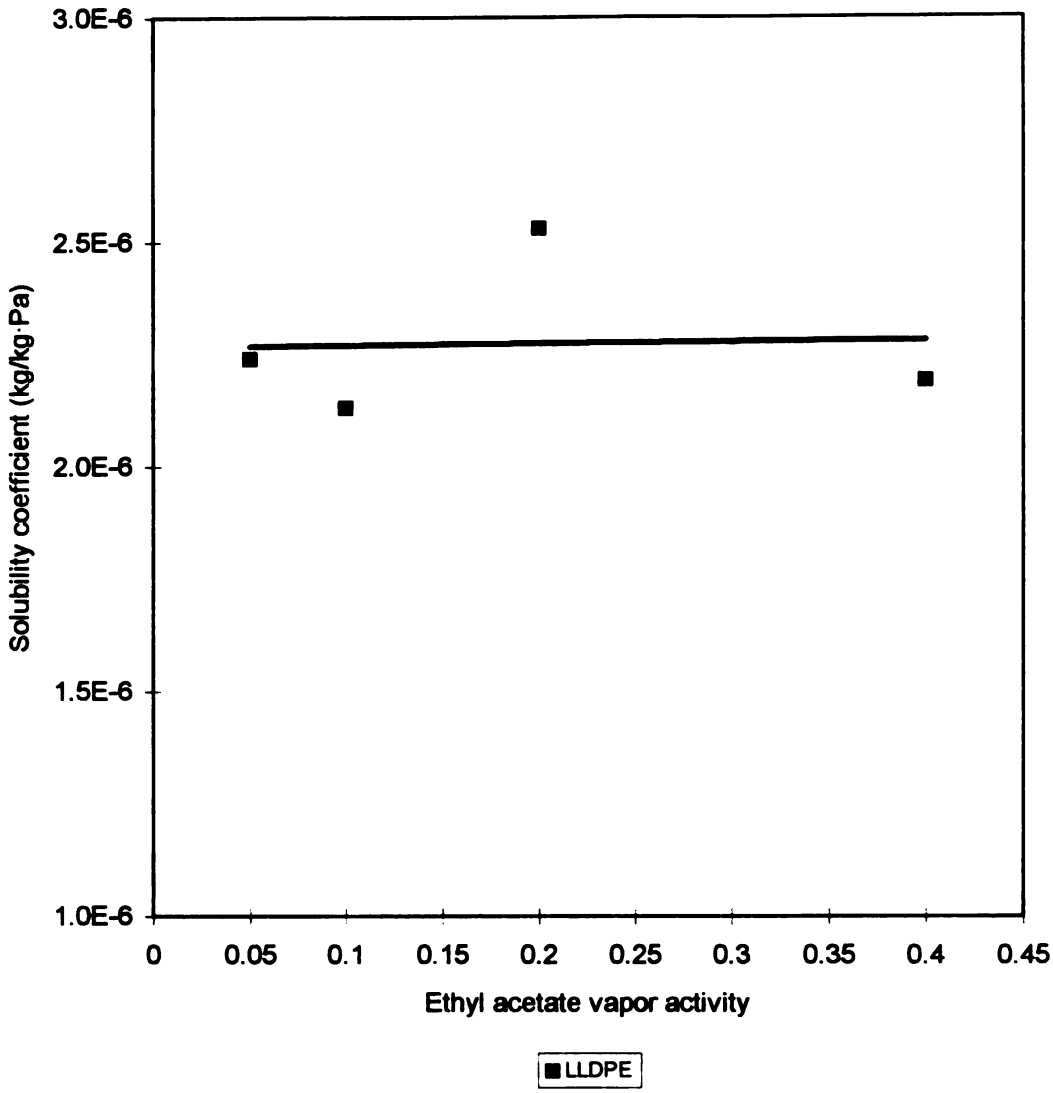

Figure 3. Equilibrium solubility coefficient as a function of sorbate vapor activity for ethyl acetate in LLDPE film at 22 °C

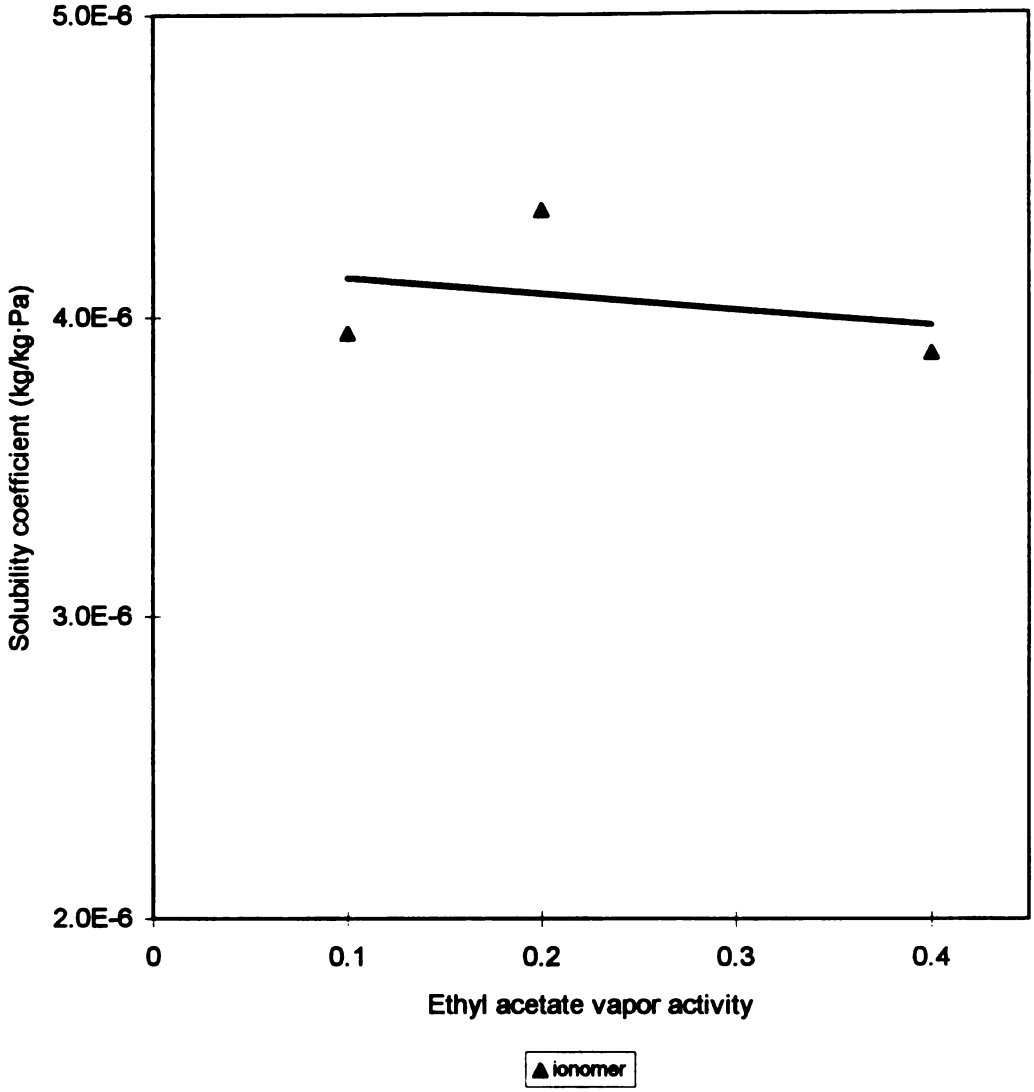

Figure 4. Equilibrium solubility coefficient as a function of sorbate vapor activity for ethyl acetate in ionomer film at 22 °C

Statistical analysis was conducted to determine whether the solubility coefficient values obtained from the gravimetric sorption experiments differed as a function of vapor activity, for the polymer test films considered. This analysis was performed using the MSTAT-C Statistical Analysis Program's Least Significant Difference test, which can be described as a comparison of paired means which uses a pooled variance, or as a Student's T-test which uses a pooled error variance. Results of this treatment are presented in detail in Appendix C. As shown, nearly all of the solubility coefficient values obtained showed no significant difference as a function of vapor activity, when an alpha level of 0.05 was used. In addition, at an alpha level of 0.01, it was found that the difference between the remaining S values was nonsignificant as a function of vapor activity. The results of the statistical analysis strongly suggest that the solubility coefficient values obtained are independent of ethyl acetate vapor concentration, and that the sorption process followed a Henry's law relationship over the range of vapor activities evaluated.

Representative plots of M_t/M_∞ as a function of the square root of time, for the sorption of ethyl acetate by the test films, are presented in Figures 5 through 15, respectively. Superimposed on the experimental sorption profile plots are the theoretical sorption curves obtained by solution of Equation 25 for comparison. The theoretical curves were derived using the data-fitting equation for the sorption of a penetrant by a polymer sample in film or sheet form as described by Crank (1975):

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\left[\exp\left(\frac{-D\cdot\pi^2\cdot t}{l^2}\right) + \frac{1}{9}\exp\left(\frac{-9D\cdot\pi^2\cdot t}{l^2}\right)\right] \qquad (25)$$

where M_t and M_∞ represent the amount of penetrant sorbed by the polymer film sample at

time t and the equilibrium sorption after infinite time, respectively. D is the diffusion coefficient, t is the time required to attain M_t, and l is the thickness of the film. It can be seen that the theoretical curves fit the experimental data well, and the initial portion is approximated by a straight line. This agreement suggests that over the penetrant concentration range evaluated, mass transport followed Fickian type behavior.

The sorption diffusion coefficient (D_s) can be calculated from Equation 25 by setting M_t/M_∞ equal to 0.5 and solving for D_s.

$$D_s = \frac{0.049\, l^2}{t_{0.5}} \tag{26}$$

where $t_{0.5}$ is the 'half sorption time' or the time required to attain a value of $M_t/M_\infty = 0.5$. By plotting M_t/M_∞ as a function of the square root of time as described, values of $t_{0.5}$ can be obtained graphically and substituted into Equation 26 for calculation of an accurate estimation of the diffusion coefficient. The half-time diffusion coefficient (D_s) values determined from sorption experiments are summarized in Table 2. As shown, good agreement was obtained between D_s values for the penetrant concentration range considered in this investigation.

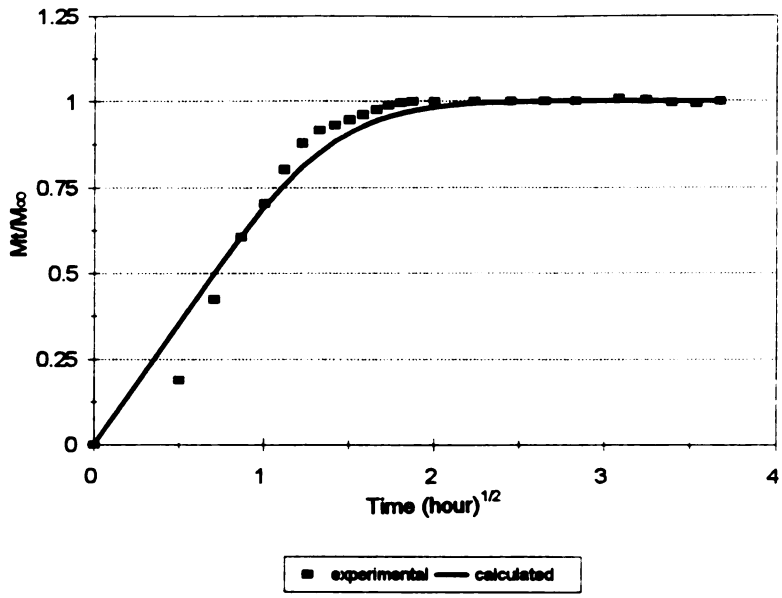

Figure 5. Sorption profile for ethyl acetate in LDPE at 22 °C, Av = 0.05

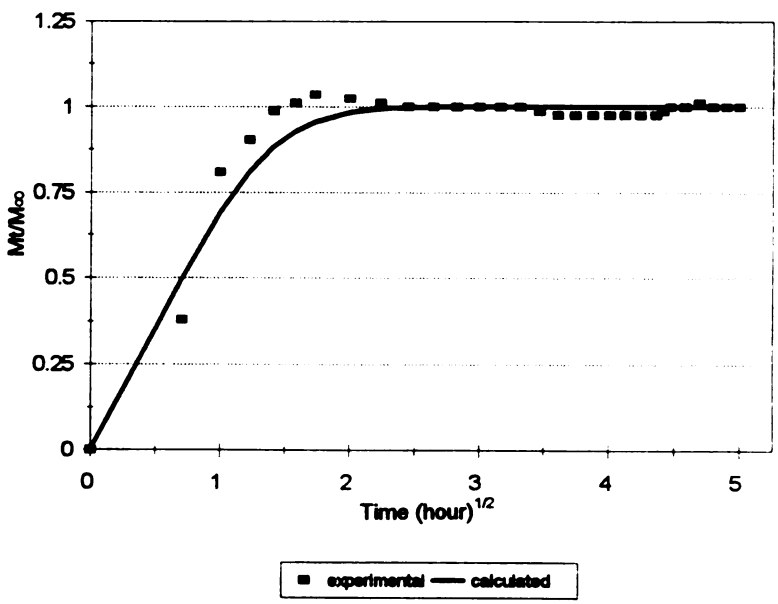

Figure 6. Sorption profile for ethyl acetate in LDPE at 22 °C, Av = 0.1

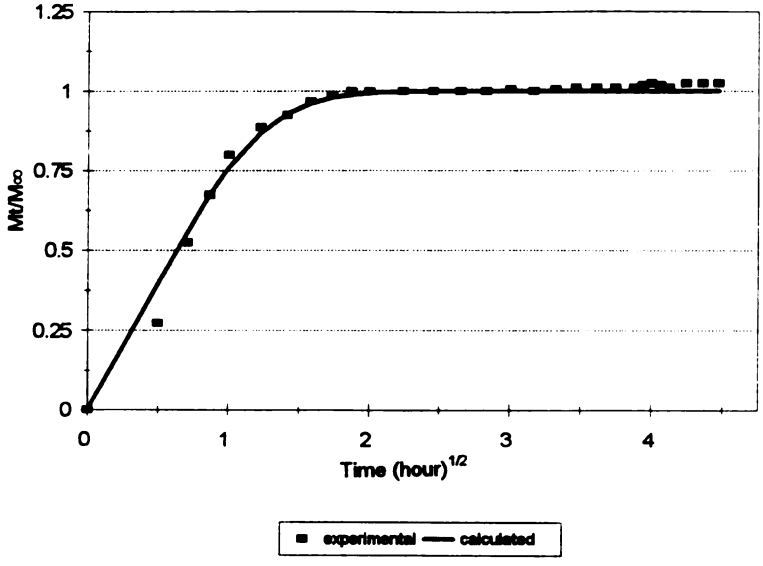

Figure 7. Sorption profile for ethyl acetate in LDPE at 22 °C, Av = 0.2

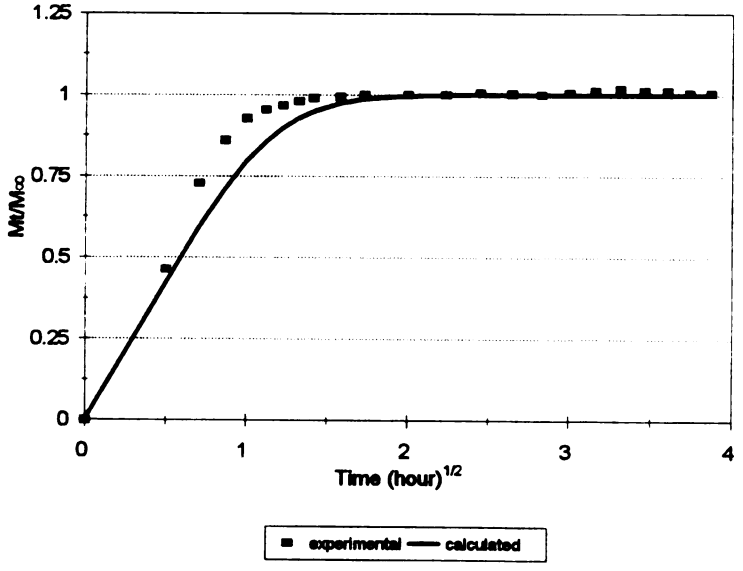

Figure 8. Sorption profile for ethyl acetate in LDPE at 22 °C, Av = 0.4

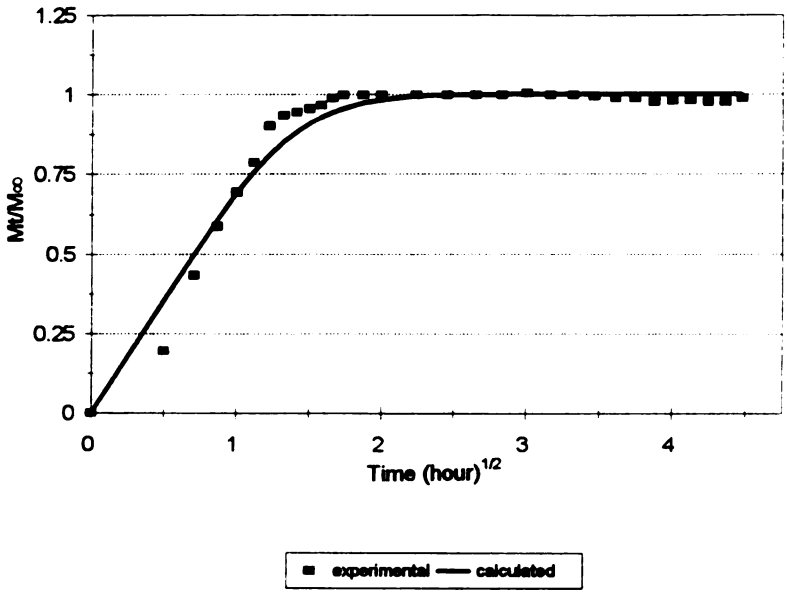

Figure 9. Sorption profile for ethyl acetate in LLDPE at 22 °C, Av = 0.05

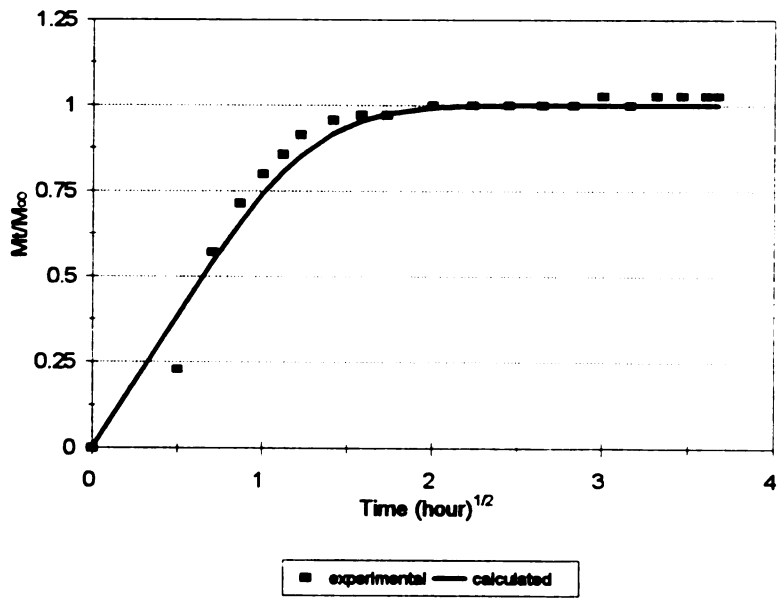

Figure 10. Sorption profile for ethyl acetate in LLDPE at 22 °C, Av = 0.1

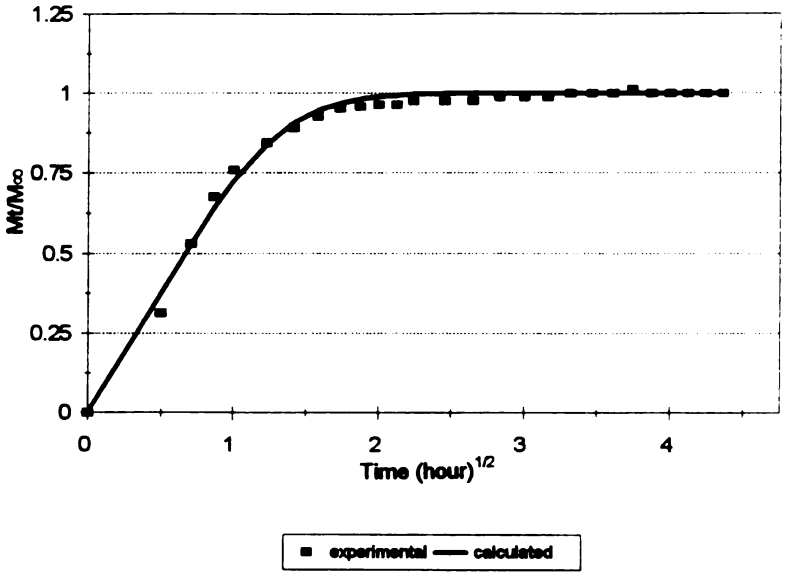

Figure 11. Sorption profile for ethyl acetate in LLDPE at 22 °C, Av = 0.2

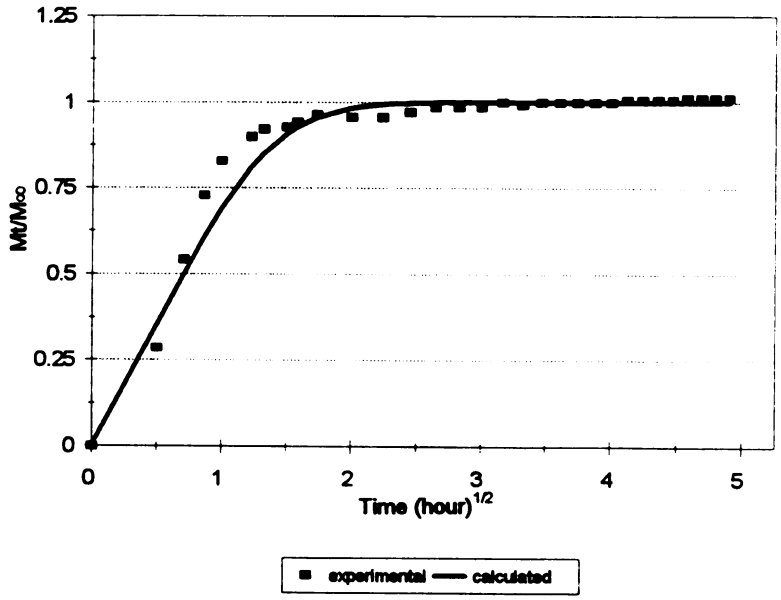

Figure 12. Sorption profile for ethyl acetate in LLDPE at 22 °C, Av = 0.4

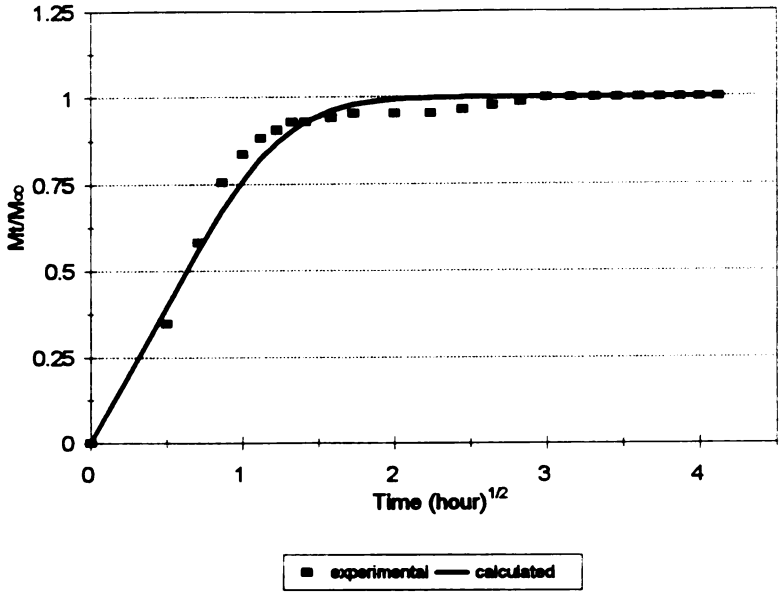

Figure 13. Sorption profile for ethyl acetate in ionomer at 22 °C, Av = 0.1

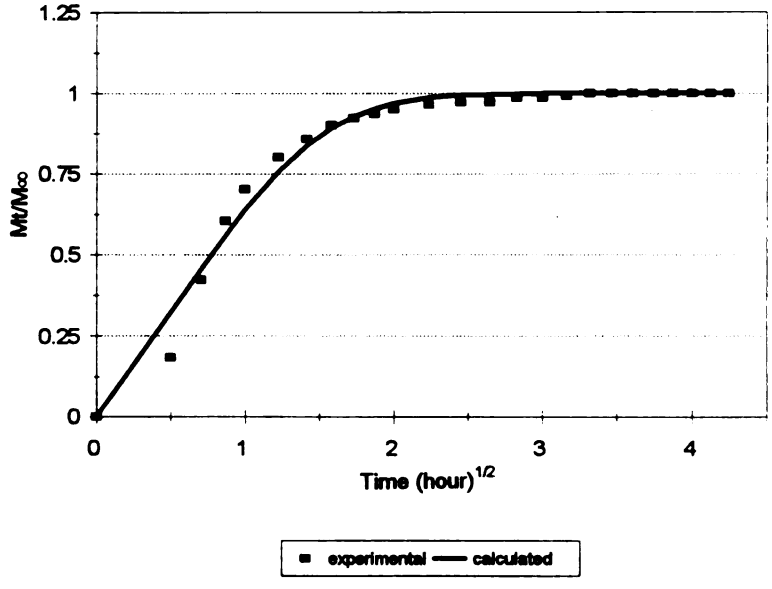

Figure 14. Sorption profile for ethyl acetate in ionomer at 22 °C, Av = 0.2

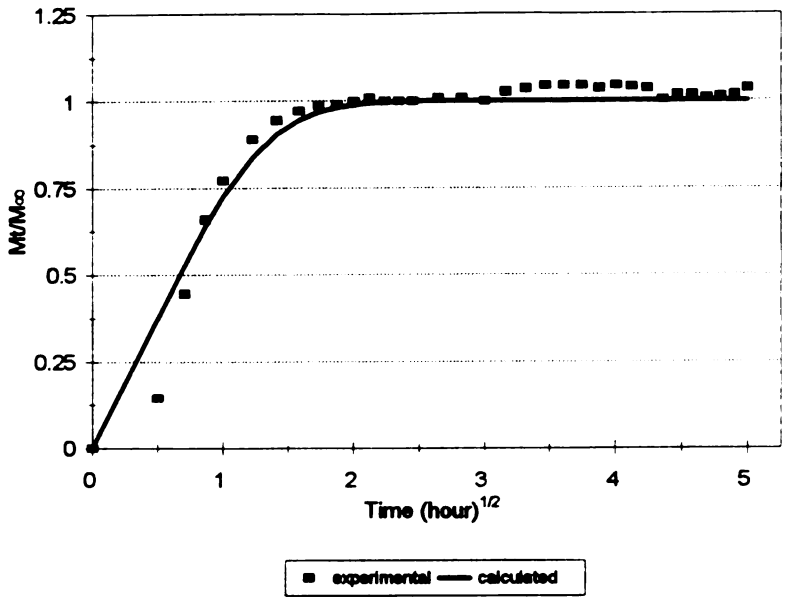

Figure 15. Sorption profile for ethyl acetate in ionomer at 22 °C, Av = 0.4

Table 2. Sorption diffusion coefficient (D_s) values obtained from gravimetric experiments for ethyl acetate in LDPE, LLDPE and ionomer films at 22 °C [a]

Vapor activity	Diffusion coefficient [m^2/sec (× 10^{-14})]		
	LDPE	LLDPE	Ionomer
0.05	7.0	6.5	
0.1	7.9	8.3	7.9
0.2	8.8	8.1	6.1
0.4	10.0	6.7	7.4
Mean value ± standard deviation	8.4 ± 1.1	7.4 ± 0.8	7.2 ± 0.8

[a] Average of replicate runs, with a confidence limit of 11%, 9% and 11%, respectively (maximum)

Statistical analysis was performed by using the Least Significant Difference test, as described above, to determine whether the diffusion coefficient values obtained by the gravimetric technique differed significantly over the vapor activity range evaluated. A detailed summary of these test results is presented in Appendix D. As shown, a nonsignificant level of difference was found to exist between nearly all of the diffusion coefficient values when an alpha level of 0.05 was employed. When an alpha level 0.01 was applied, the difference between the remaining D values obtained from sorption experiments was found to be nonsignificant as a function of penetrant vapor concentration. This statistical agreement indicates that for the polymer/permeant systems considered, the diffusion coefficient remained constant over the vapor concentration range evaluated.

Permeability, Solubility and Diffusivity of Ethyl Acetate in LDPE, LLDPE and Ionomer Films Determined from Isostatic Permeability Experiments

Isostatic permeability experiments were conducted to determine the permeability coefficient, $\bar{P}$, the diffusion coefficient, D, and the solubility coefficient, S, for ethyl acetate through LDPE, LLDPE and ionomer films. Permeability tests were conducted at ambient temperature (22 °C) and over a range of vapor activities, including: 0.1, 0.2 and 0.4. Under these experimental conditions, a steady state rate of permeation was achieved in times of less than 1 hour.

The permeation rate at any time F_t, during the transient state portion of the permeability experiment, varies from zero at time zero, up to the value F_∞ reached at steady state. This is described by the following expression (Pasternak et al., 1970):

$$\frac{F_t}{F_\infty} = \left(\frac{4}{\sqrt{\pi}}\right)\left(\sqrt{\frac{l^2}{4Dt}}\right)\sum_{n=1,3,5}^{\infty}\left(\frac{-n^2 l^2}{4Dt}\right) \qquad (27)$$

where F_t/F_∞ is the permeant flux ratio, F_t is the permeant flux at time t, and F_∞ is the permeant flux at steady state. Equation 27 can be simplified to:

$$\phi = \left(\frac{4}{\sqrt{\pi}}\right) X^{1/2} \exp(-X) \qquad (28)$$

where ϕ is the permeant flux ratio (represented by F_t/F_∞ in Equation 27), and $X = l^2/4Dt$. Representative plots of permeant flux as a function of time are presented in Figures 16 through 24. The calculated transmission rate profile curves obtained using the data-fitting expression (Equation 27) are superimposed for comparison. As shown, good agreement was obtained between the experimental and theoretical flux rate profiles, supporting the assumption that the diffusion process followed Fickian type behavior.

Using the value of permeant flux at steady state (F_∞), the permeability coefficient, $\bar{P}$, can be determined by substitution into Equation 29:

$$\bar{P} = \frac{F_\infty\, l}{A\, \Delta p} \qquad (29)$$

where l represents the film thickness, A is the area of the film exposed to the permeant and Δp is the partial pressure gradient across the polymer membrane. From the flux rate profile, the half-time diffusion coefficient, D, can be estimated using the following expression derived by Ziegel, et al. (1969):

$$D = \frac{l^2}{7.199\, t_{0.5}} \qquad (30)$$

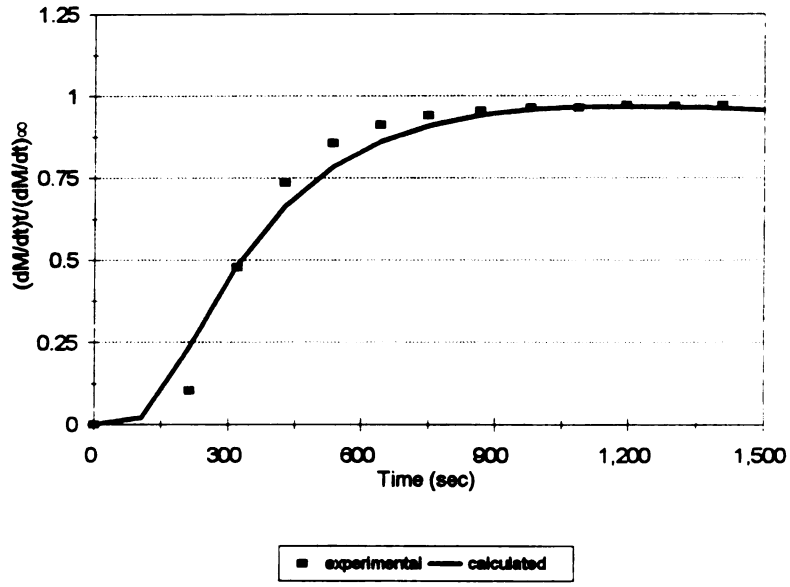

Figure 16. Permeant flux ratio versus time for the system ethyl acetate/LDPE at 22 °C, Av = 0.1

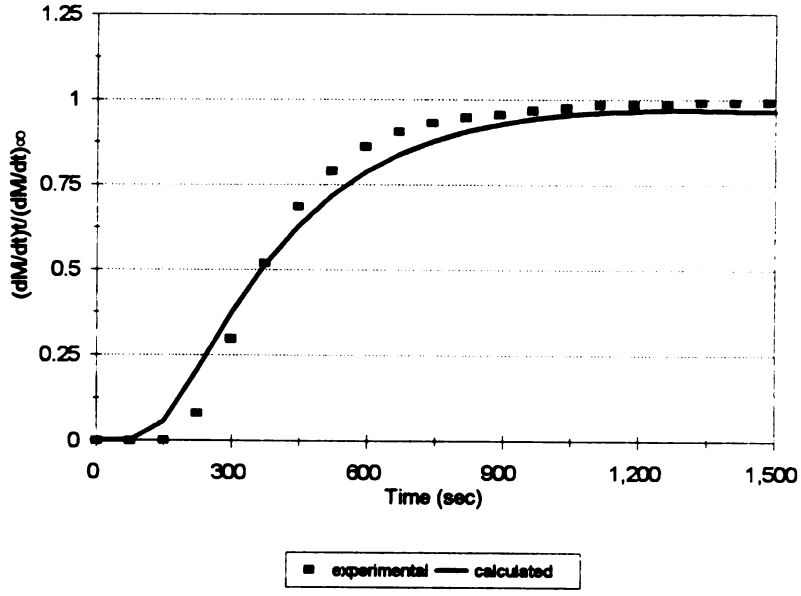

Figure 17. Permeant flux ratio versus time for the system ethyl acetate/LLDPE at 22 °C, Av = 0.1

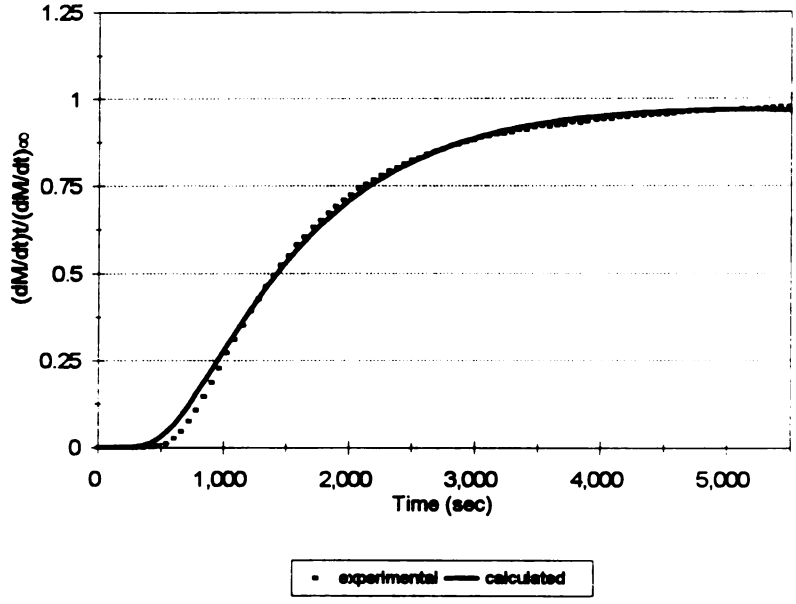

Figure 18. Permeant flux ratio versus time for the system ethyl acetate/ionomer at 22 °C, Av = 0.1

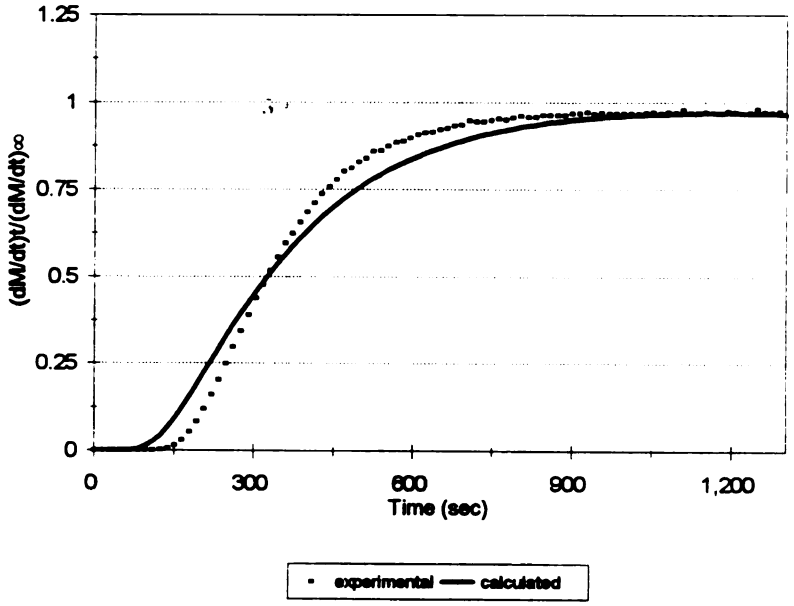

Figure 19. Permeant flux ratio versus time for the system ethyl acetate/LDPE at 22 °C, Av = 0.2

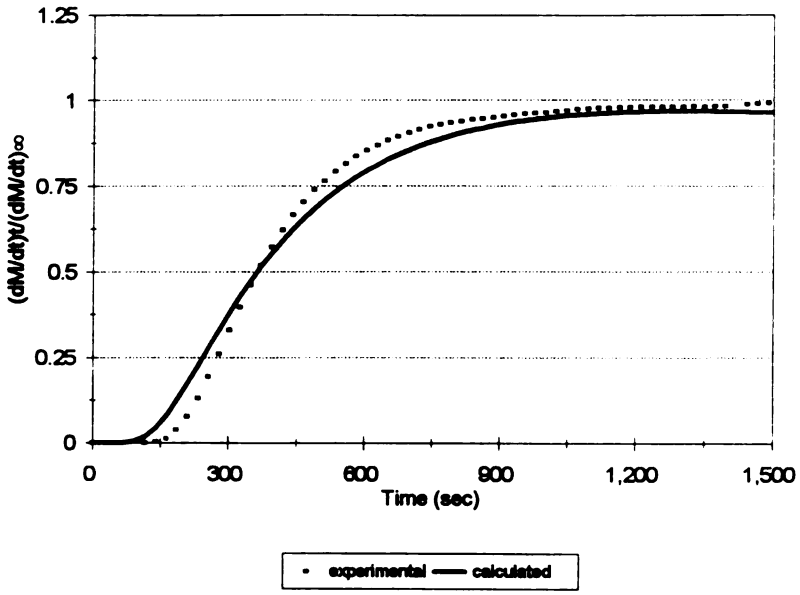

Figure 20. Permeant flux ratio versus time for the system ethyl acetate/LLDPE at 22 °C, Av = 0.2

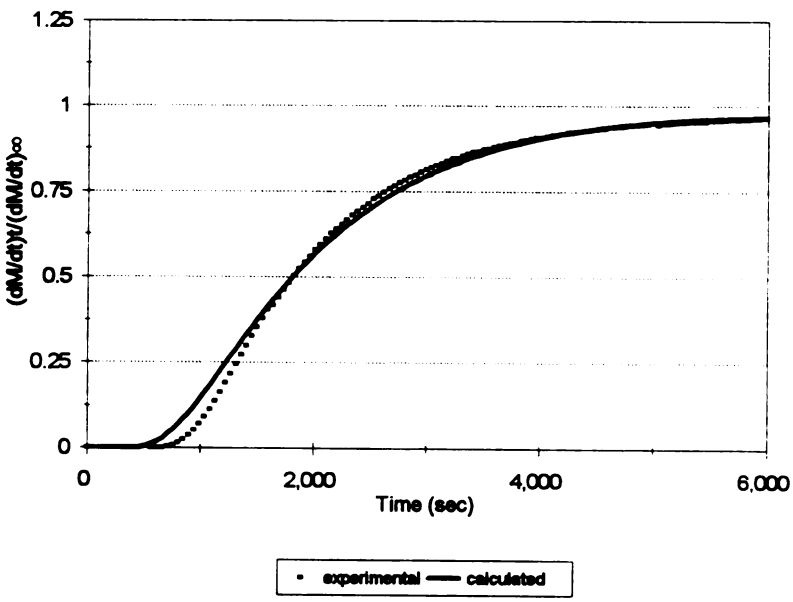

Figure 21. Permeant flux ratio versus time for the system ethyl acetate/ionomer at 22 °C, Av = 0.2

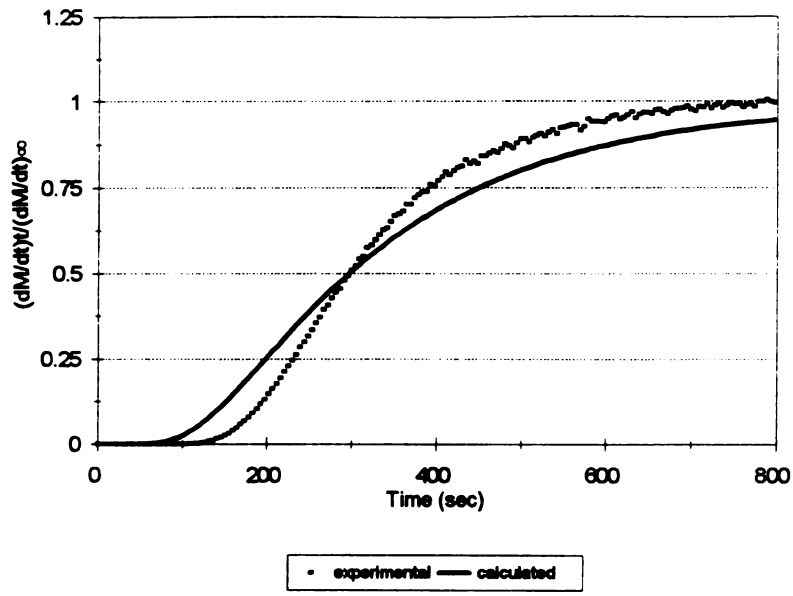

Figure 22. Permeant flux ratio versus time for the system ethyl acetate/LDPE at 22 °C, Av = 0.4

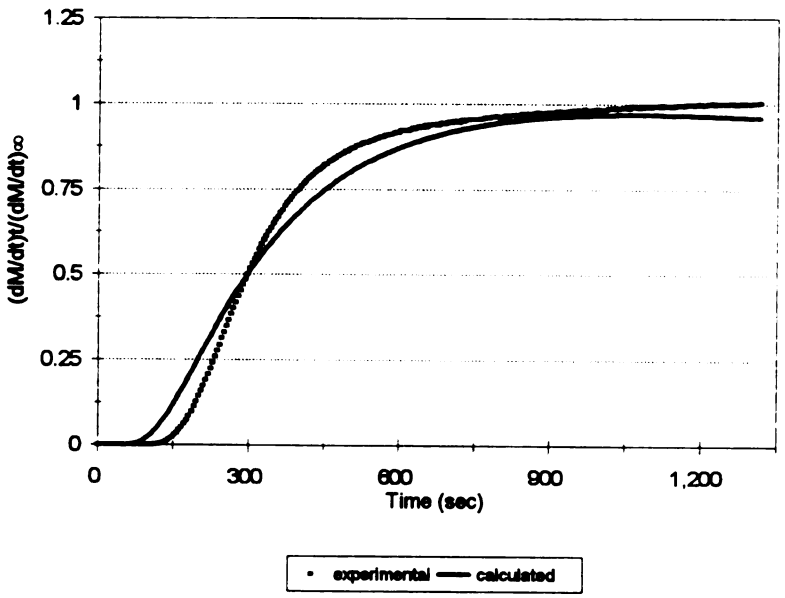

Figure 23. Permeant flux ratio versus time for the system ethyl acetate/LLDPE at 22 °C, Av = 0.4

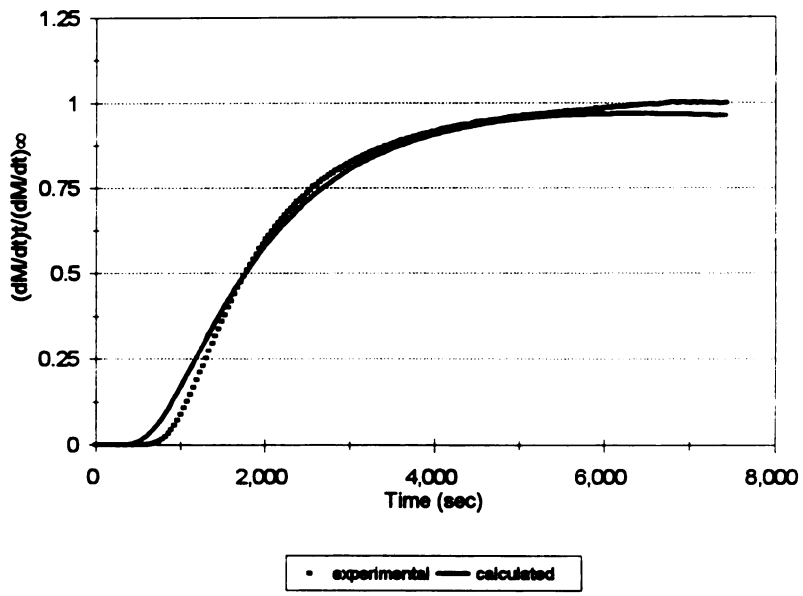

Figure 24. Permeant flux ratio versus time for the system ethyl acetate/ionomer at 22 °C, Av = 0.4

where $t_{0.5}$ represents the time required to reach half of the steady state rate of transmission. Once $\overline{P}$ and D have been determined, the solubility coefficient, S, can be calculated using Equation 31:

$$S = \frac{\overline{P}}{D} \tag{31}$$

Permeability, diffusion and solubility coefficient values obtained from the isostatic permeation experiments are summarized in Tables 3, 4, and 5, respectively. The relationship between the permeability parameters and vapor activity is shown graphically in Figures 25, 26 and 27, where the respective constants are plotted as a function of vapor activity. As shown, the obtained values for $\overline{P}$, D, and S agree well over the range of vapor activities evaluated.

Table 3. Permeability coefficient values obtained from isostatic permeability experiments for ethyl acetate in LDPE, LLDPE and ionomer films at 22 °C [a]

Vapor activity	Permeability coefficient [kg·m/m²·sec·Pa (× 10^{-15})]		
	LDPE	LLDPE	Ionomer
0.1	3.4	3.6	1.1
0.2	3.5	3.2	1.3
0.4	3.7	3.1	1.2
Mean value ± standard deviation	3.5 ± 0.1	3.3 ± 0.2	1.2 ± 0.1

[a] Average of replicate runs, with a confidence limit of 10%, 13% and 5%, respectively (maximum)

Table 4. Diffusion coefficient values obtained from isostatic permeability experiments for ethyl acetate in LDPE, LLDPE and ionomer films at 22 °C [a]

Vapor activity	Diffusion coefficient [m^2/sec (× 10^{-13})]		
	LDPE	LLDPE	Ionomer
0.1	12.2	10.5	2.5
0.2	11.6	10.3	2.1
0.4	11.6	11.4	2.2
Mean value ± standard deviation	11.8 ± 0.3	10.7 ± 0.5	2.3 ± 0.2

[a] Average of replicate runs, with a confidence limit of 12%, 6% and 7%, respectively (maximum)

Table 5. Solubility coefficient values obtained from isostatic permeability experiments for ethyl acetate in LDPE, LLDPE and ionomer films at 22 °C [a]

Vapor activity	Solubility coefficient [kg/kg·Pa (× 10^{-6})]		
	LDPE	LLDPE	Ionomer
0.1	3.1	3.7	4.6
0.2	3.3	3.4	6.4
0.4	3.4	3.0	5.8
Mean value ± standard deviation	3.3 ± 0.1	3.4 ± 0.3	5.6 ± 0.8

[a] Average of replicate runs, with a confidence limit of 12%, 6% and 7%, respectively (maximum)

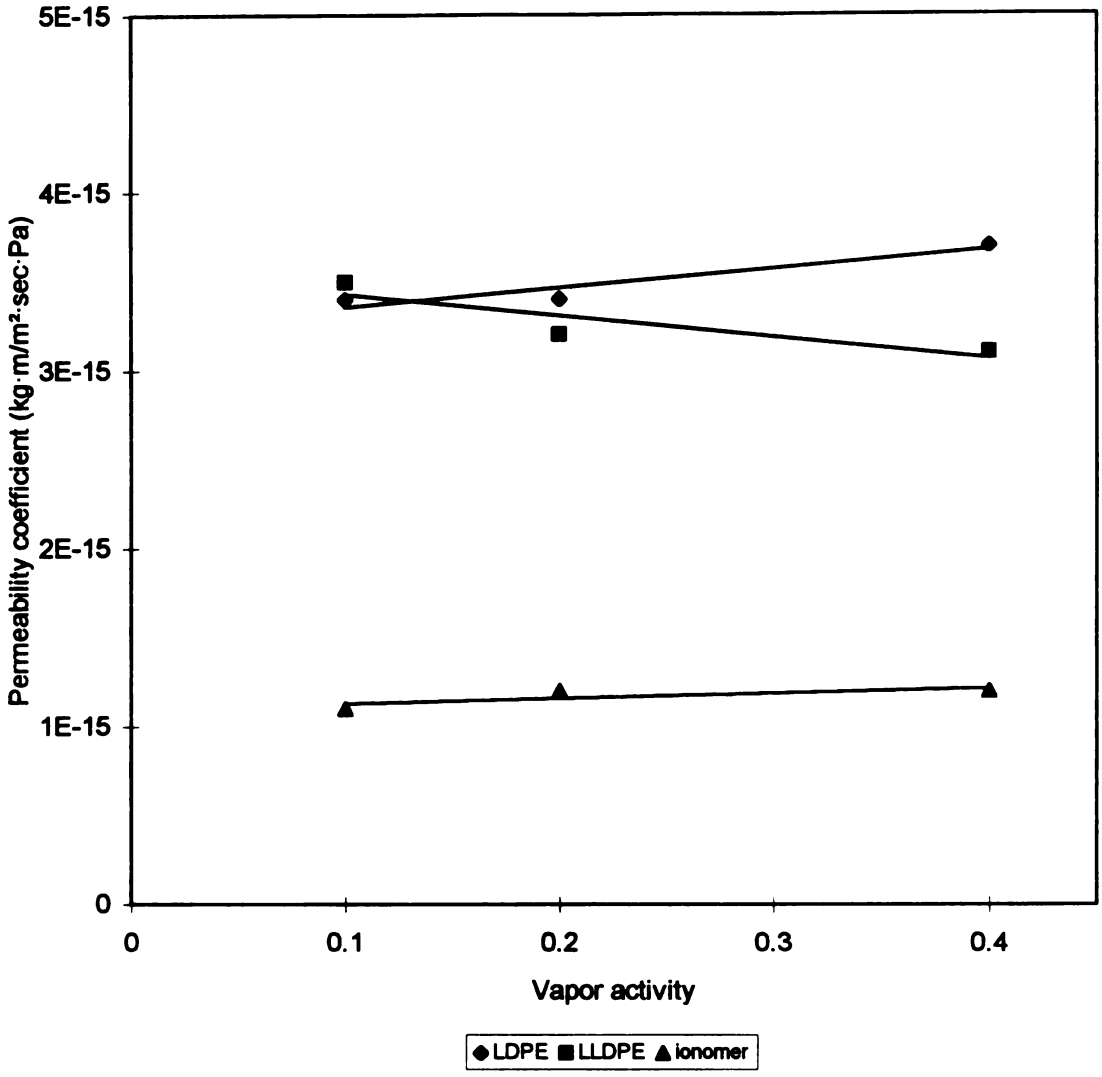

Figure 25. Permeability coefficient as a function of sorbate vapor activity for ethyl acetate in LDPE, LLDPE and ionomer films at 22 °C

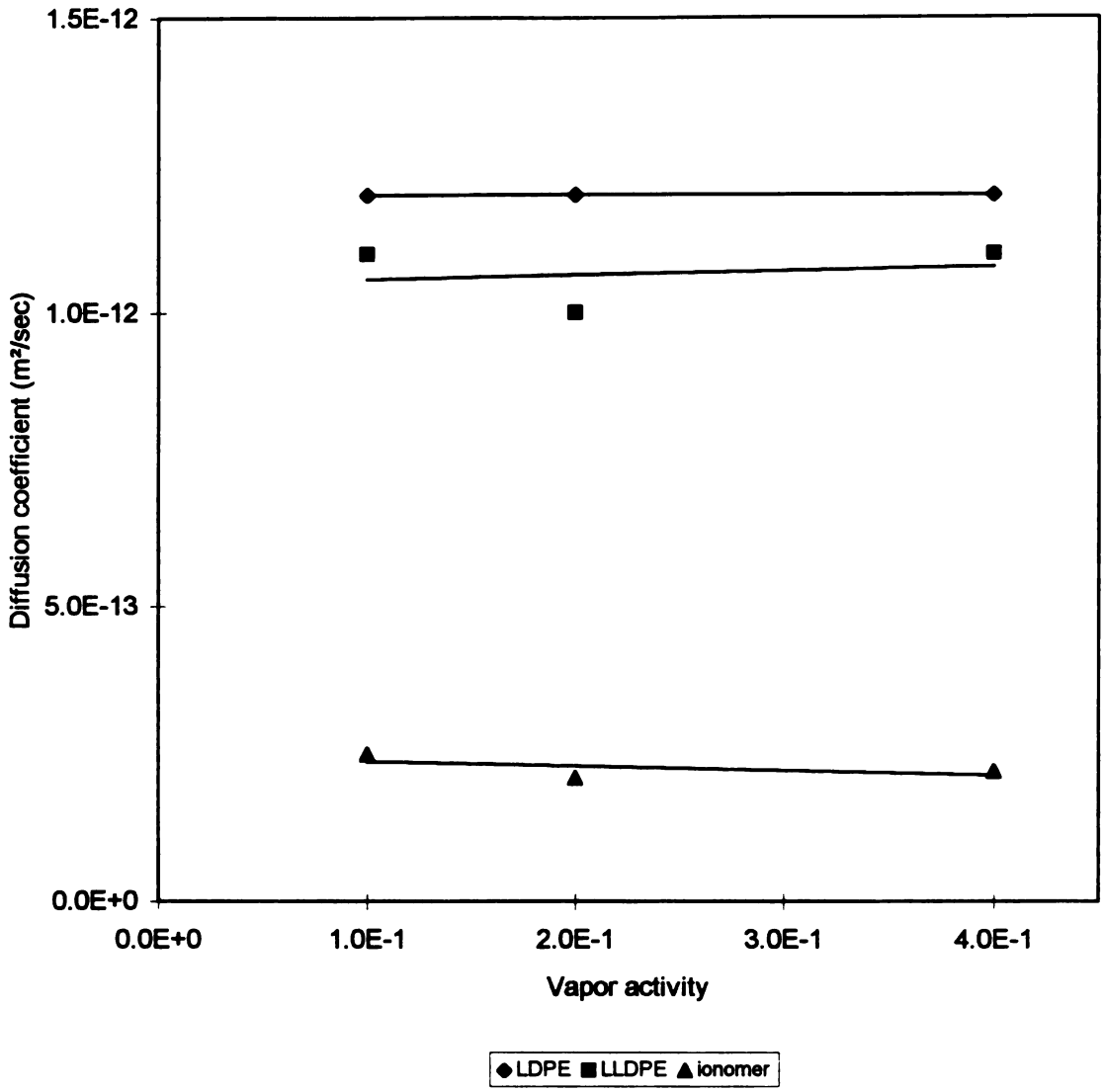

Figure 26. Diffusion coefficient as a function of sorbate vapor activity for ethyl acetate in LDPE, LLDPE and ionomer films at 22 °C

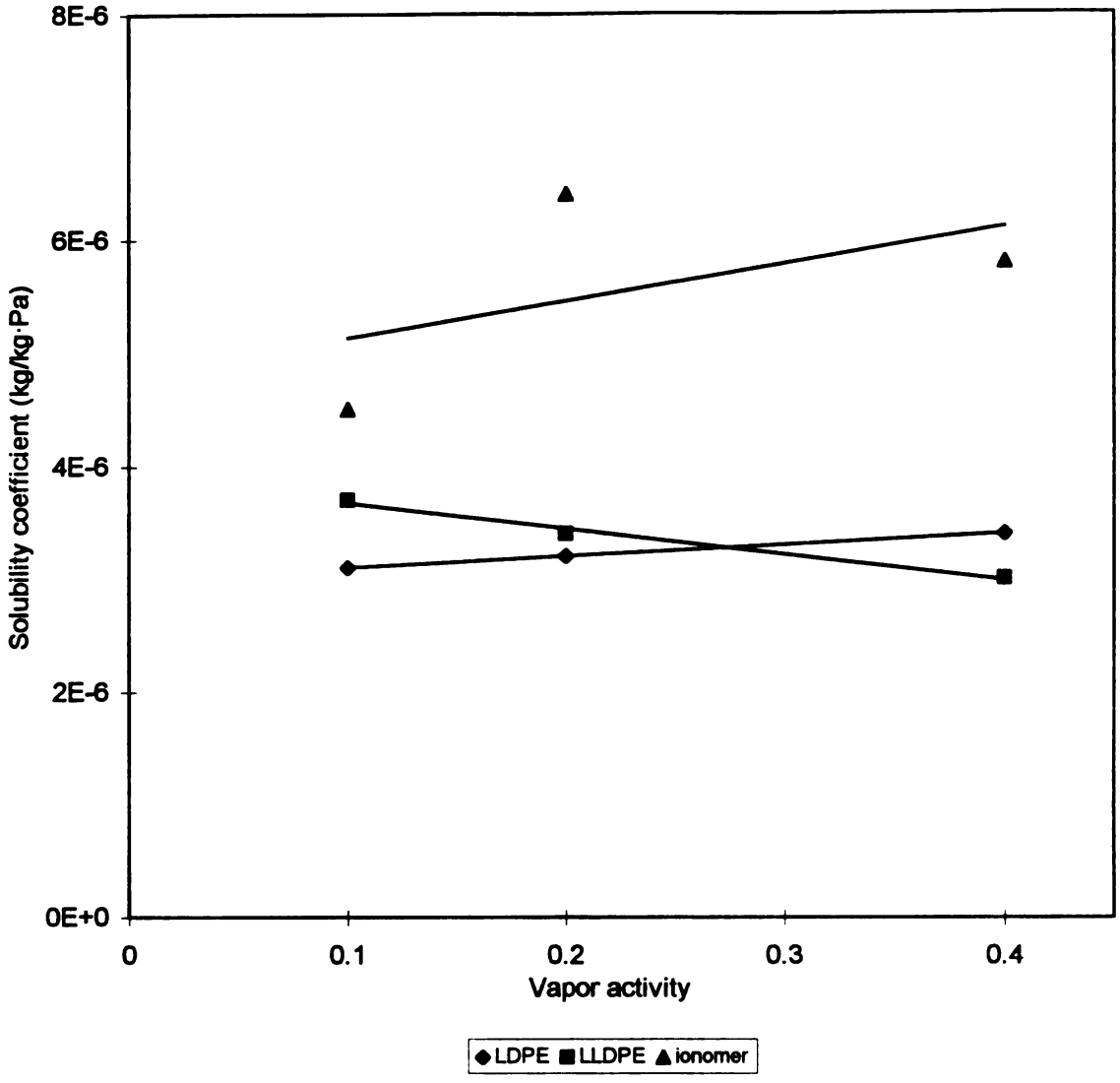

Figure 27. Solubility coefficient as a function of sorbate vapor activity for ethyl acetate in LDPE, LLDPE and ionomer films at 22 °C

The consistency of the permeability test results was evaluated using the procedure described by Gavara and Hernandez (1993). In this procedure, the authors describe a method for analyzing the consistency of experimental permeation data, based on the calculation of two constants, K_1 and K_2, and evaluation of the linear relationship between permeant flux ratio and time.

By letting $X_{1/4}$, $X_{1/2}$, and $X_{3/4}$ represent the numerical values of X when the permeability experiment has reached $\phi = 0.25$, $\phi = 0.50$, and $\phi = 0.75$, respectively, Equation 28 can be used to obtain the following expressions:

$$X_{1/4} = \frac{l^2}{4D}\frac{1}{t_{1/4}} \tag{32}$$

$$X_{1/2} = \frac{l^2}{4D}\frac{1}{t_{1/2}} \tag{33}$$

$$X_{3/4} = \frac{l^2}{4D}\frac{1}{t_{3/4}} \tag{34}$$

where $t_{1/4}$, $t_{1/2}$, and $t_{3/4}$ are the times when the permeability experiment has reached $\phi = 0.25$, $\phi = 0.50$, and $\phi = 0.75$, respectively. By dividing Equations 33 and 34 by Equation 32, two dimensionless constants, K_1 and K_2, are obtained. If an error level of 5% is considered acceptable, the range for the allowable experimental values of K are as follows: $0.42 \leq K_1 \leq 0.46$ and $0.65 \leq K_2 \leq 0.69$. As shown in Table 6, the K values obtained from the experimental permeation test data were found to be within 5% of the theoretical values for K_1 and K_2, suggesting that the permeability data can be considered consistent.

Table 6. K_1 and K_2 values obtained from isostatic permeability data for ethyl acetate in LDPE, LLDPE and ionomer films at 22 °C

Vapor activity	LDPE		LLDPE		Ionomer	
	K_1	K_2	K_1	K_2	K_1	K_2
0.1	0.4388	0.6649	0.4405	0.6681	0.4404	0.6680
	0.4371	0.6663	0.4390	0.6679	0.4403	0.6681
0.2	0.4404	0.6680	0.4403	0.6678	0.4404	0.6681
	0.4404	0.6681	0.4404	0.6681	0.4405	0.6681
0.4	0.4405	0.6681	0.4405	0.6681	0.4405	0.6681
	0.4405	0.6681	0.4405	0.6681	0.4405	0.6681

According to Hernandez, et al., (1986), plotting 1/X as a function of time should produce a straight line which intercepts the ordinate axis at zero. Representative plots of 1/X versus time for the respective penetrant/polymer combinations are presented in Figures 28 through 36. Based on linear regression analysis, the correlation coefficients (R^2) for the plotted data were determined, and the results are summarized in Table 7. As shown, high correlation coefficient values (> 0.99) and y-intercept values approaching zero were obtained for all plots evaluated. These results, combined with the agreement between the experimental and theoretical K_1 and K_2 values, suggest that temperature and vapor concentration remained constant throughout the permeation experiments conducted in this investigation. From the results of the consistency analysis, it can be concluded that the diffusion processes followed Fickian behavior and the parameters of the experiment were well controlled.

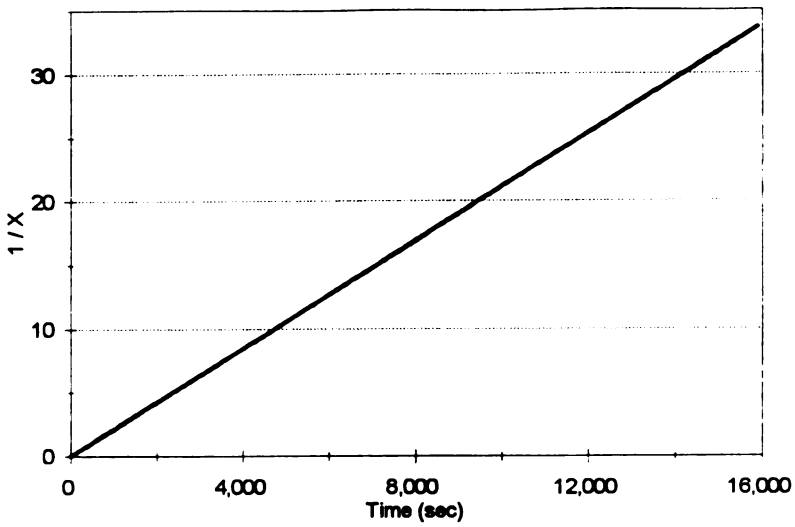

Figure 28. 1/X as a function of time for the system ethyl acetate/LDPE at 22 °C, Av = 0.1

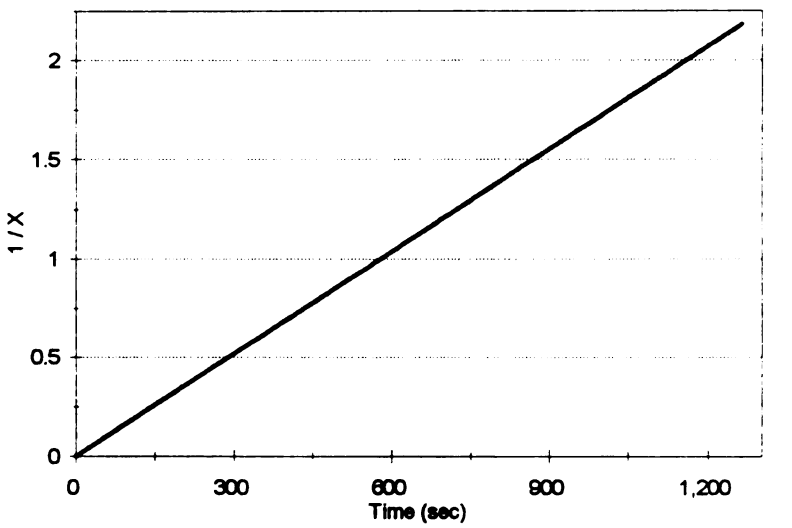

Figure 29. 1/X as a function of time for the system ethyl acetate/LLDPE at 22 °C, Av = 0.1

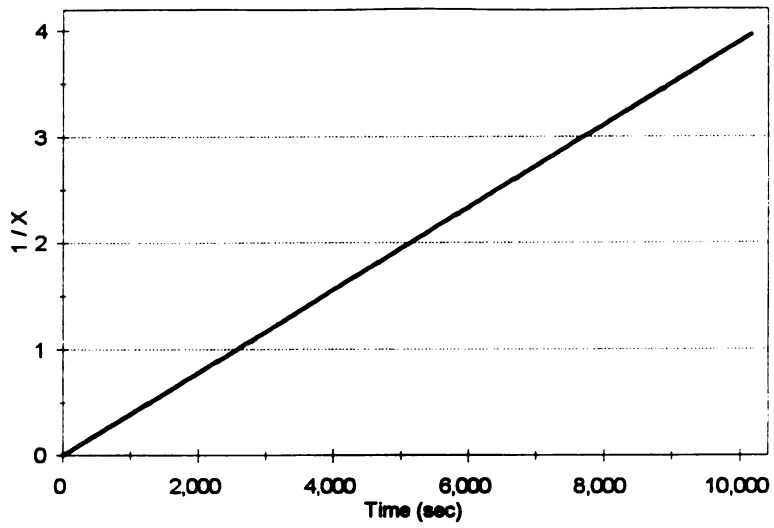

Figure 30. 1/X as a function of time for the system ethyl acetate/ionomer at 22 °C, Av = 0.1

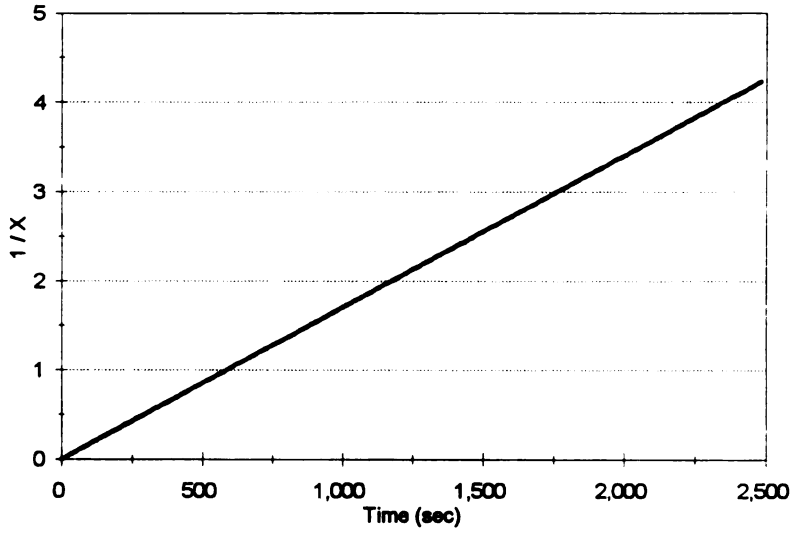

Figure 31. 1/X as a function of time for the system ethyl acetate/LDPE at 22 °C, Av = 0.2

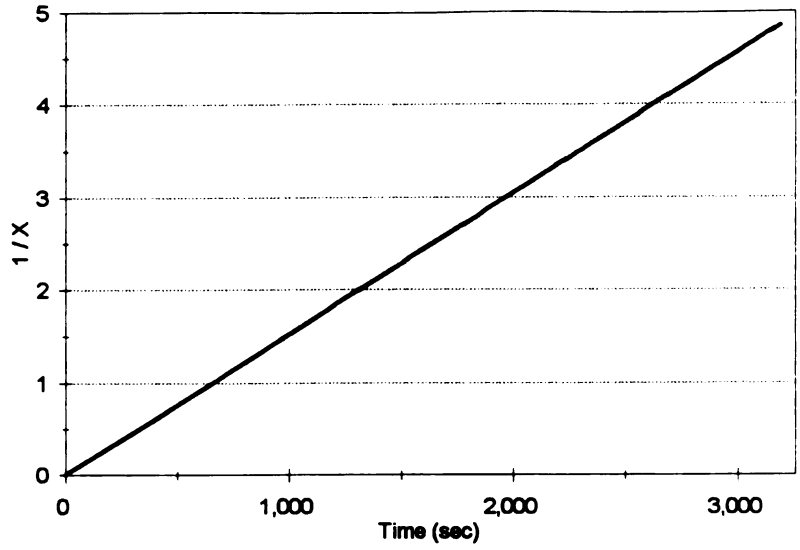

Figure 32. 1/X as a function of time for the system ethyl acetate/LLDPE at 22 °C, Av = 0.2

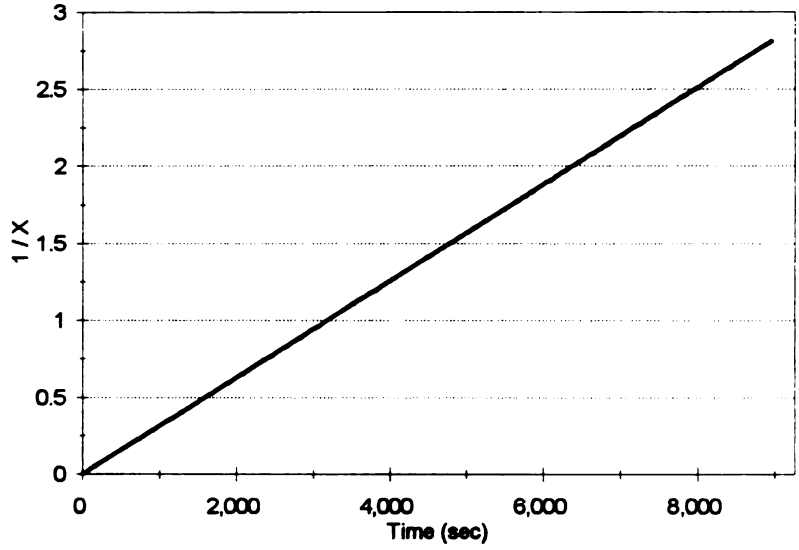

Figure 33. 1/X as a function of time for the system ethyl acetate/ionomer at 22 °C, Av = 0.2

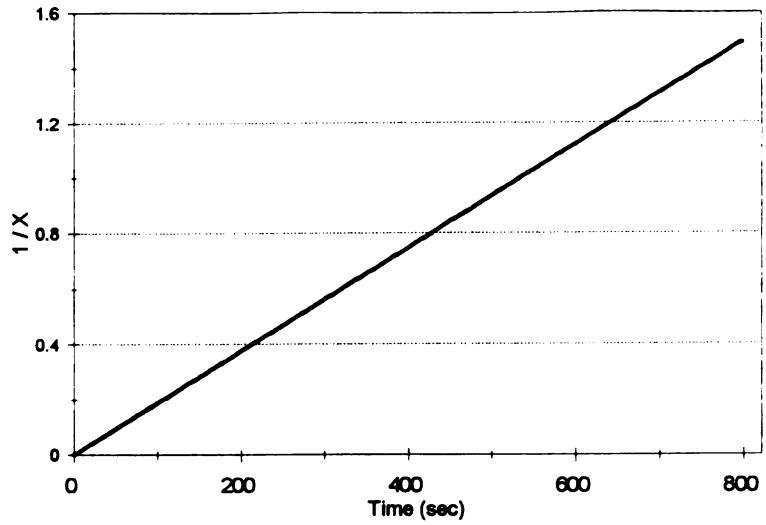

Figure 34. 1/X as a function of time for the system ethyl acetate/LDPE at 22 °C, Av = 0.4

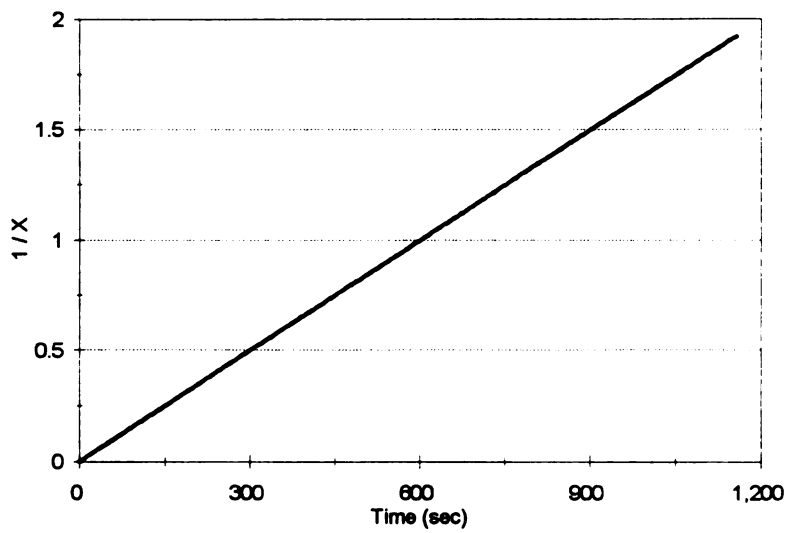

Figure 35. 1/X as a function of time for the system ethyl acetate/LLDPE at 22 °C, Av = 0.4

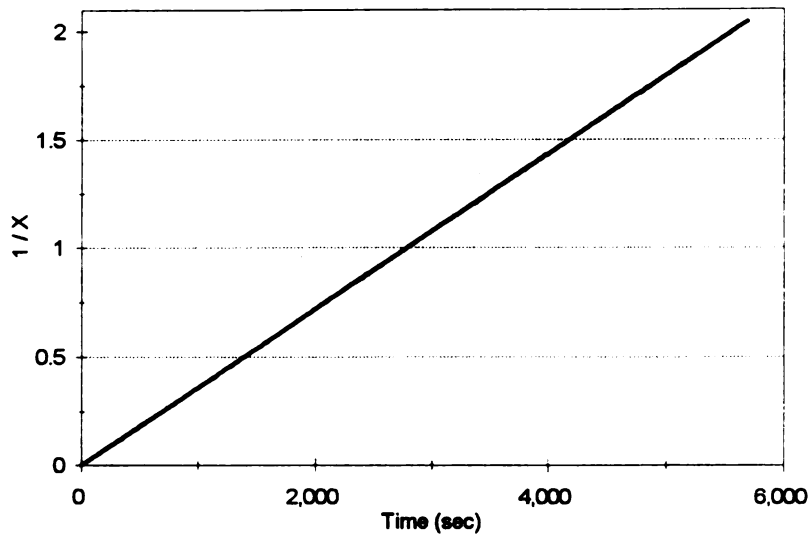

Figure 36. 1/X as a function of time for the system ethyl acetate/ionomer at 22 °C, Av = 0.4

Table 7. Correlation coefficient and y-intercept values obtained from linear regression of isostatic permeability data for ethyl acetate in LDPE, LLDPE and ionomer films at 22 °C [a]

Vapor activity	LDPE		LLDPE		Ionomer	
	Correlation coefficient (R^2) value	y-intercept	Correlation coefficient (R^2) value	y-intercept	Correlation coefficient (R^2) value	y-intercept
0.1	1.00	~0	1.00	~0	1.00	~0
0.2	1.00	~0	1.00	~0	1.00	~0
0.4	1.00	~0	1.00	~0	1.00	~0

[a] Based on duplicate analyses

A procedure based on the sum of the squares technique was also applied to determine the best estimated diffusion coefficient value (D_{est}). Representative plots of the sum of the squares value obtained as a function of the estimated D value are presented in Figures 37 through 45, from which the best estimated diffusion coefficient value can be determined from the minimum sum of the squares value. As shown in Tables 8 through 10, excellent agreement between the half-time and best estimated diffusion coefficient values was observed for all polymer/penetrant systems evaluated.

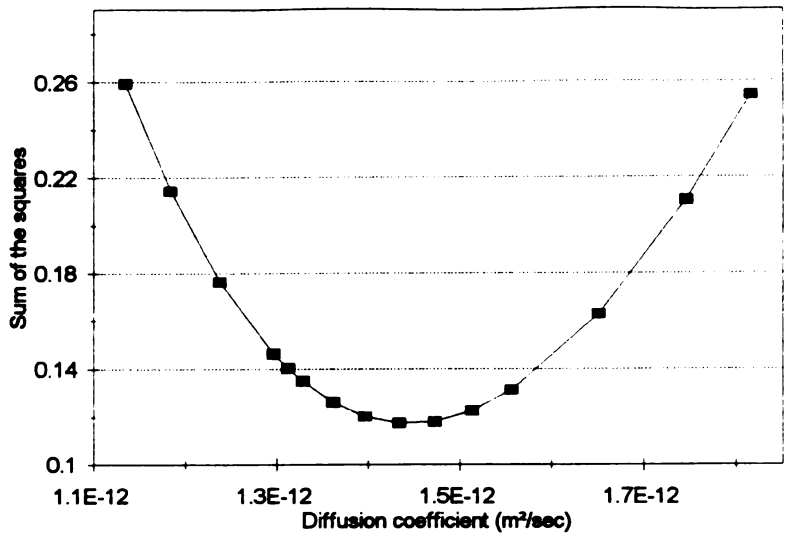

Figure 37. Sum of the squares profile as a function of the best estimated diffusion coefficient value for the system ethyl acetate/LDPE at 22 °C, Av = 0.1

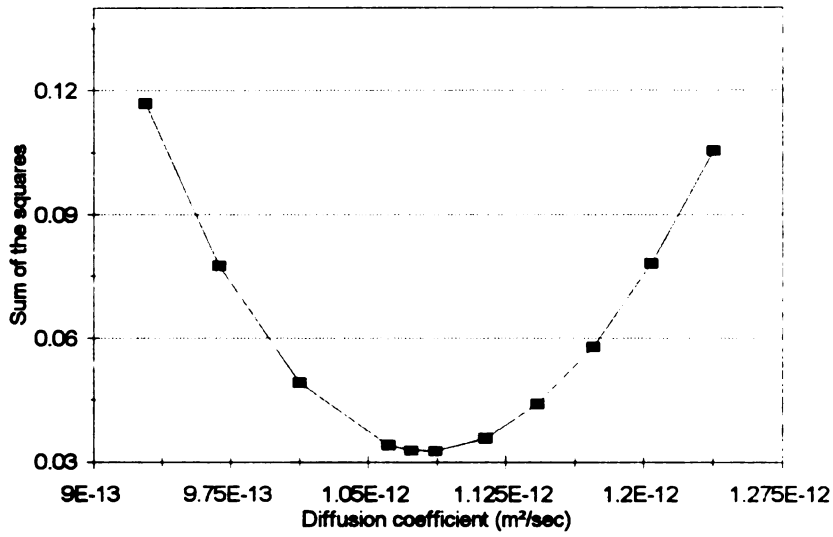

Figure 38. Sum of the squares profile as a function of the best estimated diffusion coefficient value for the system ethyl acetate/LLDPE at 22 °C, Av = 0.1

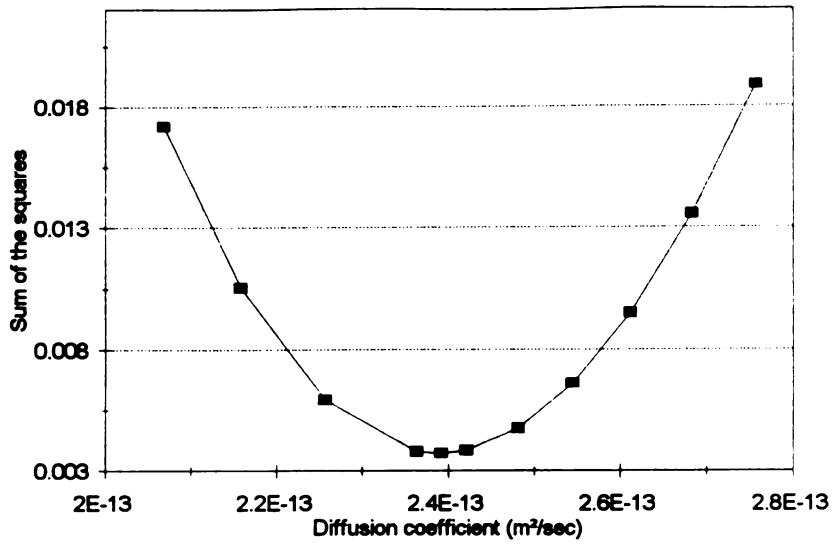

Figure 39. Sum of the squares profile as a function of the best estimated diffusion coefficient value for the system ethyl acetate/ionomer at 22 °C, Av = 0.1

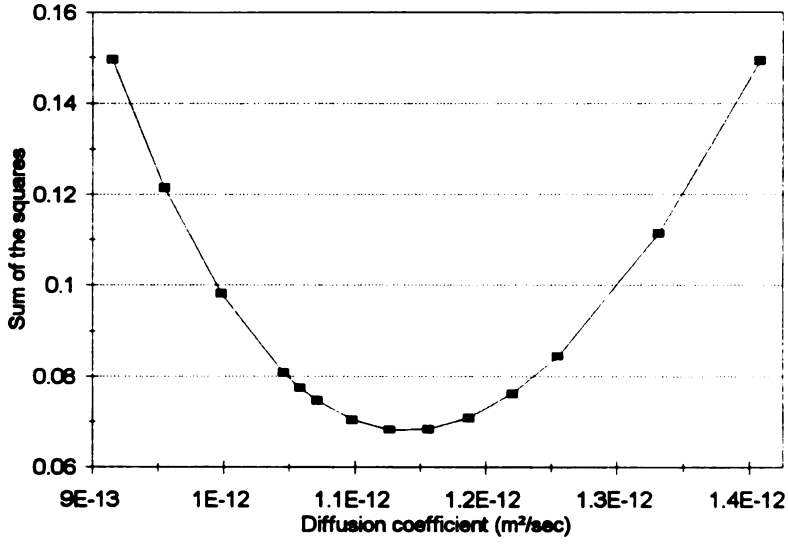

Figure 40. Sum of the squares profile as a function of the best estimated diffusion coefficient value for the system ethyl acetate/LDPE at 22 °C, Av = 0.2

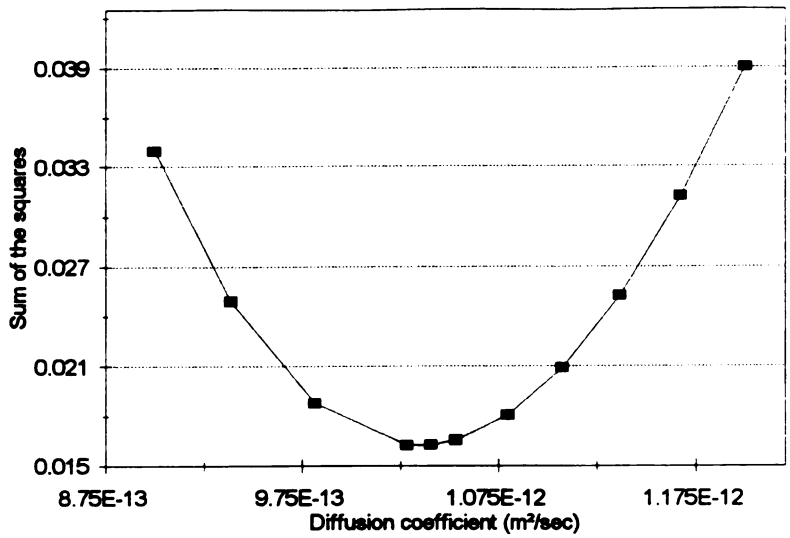

Figure 41. Sum of the squares profile as a function of the best estimated diffusion coefficient value for the system ethyl acetate/LLDPE at 22 °C, Av = 0.2

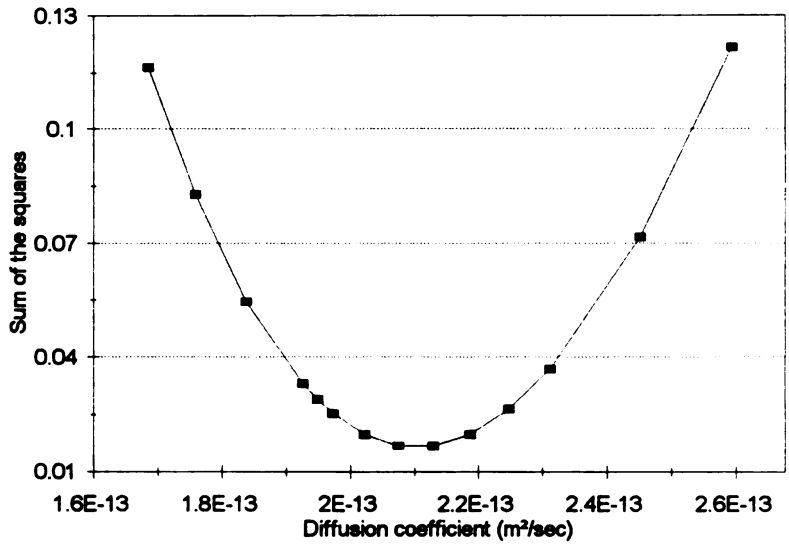

Figure 42. Sum of the squares profile as a function of the best estimated diffusion coefficient value for the system ethyl acetate/ionomer at 22 °C, Av = 0.2

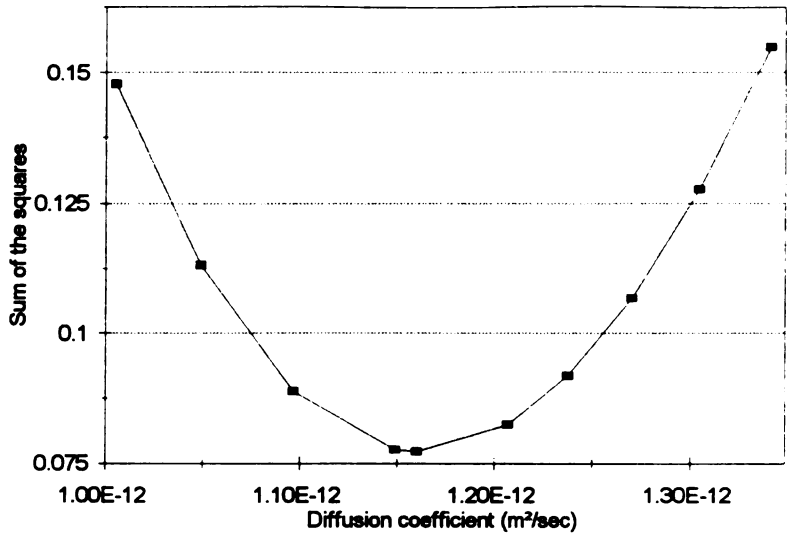

Figure 43. Sum of the squares profile as a function of the best estimated diffusion coefficient value for the system ethyl acetate/LDPE at 22 °C, Av = 0.4

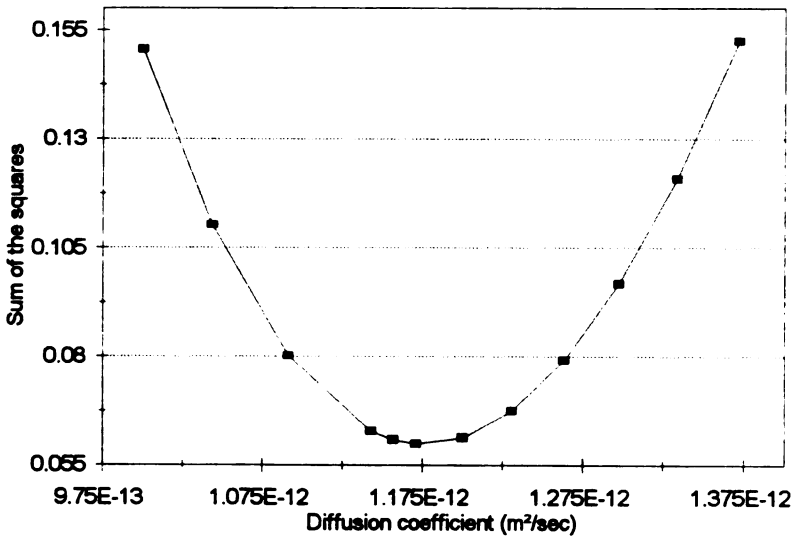

Figure 44. Sum of the squares profile as a function of the best estimated diffusion coefficient value for the system ethyl acetate/LLDPE at 22 °C, Av = 0.4

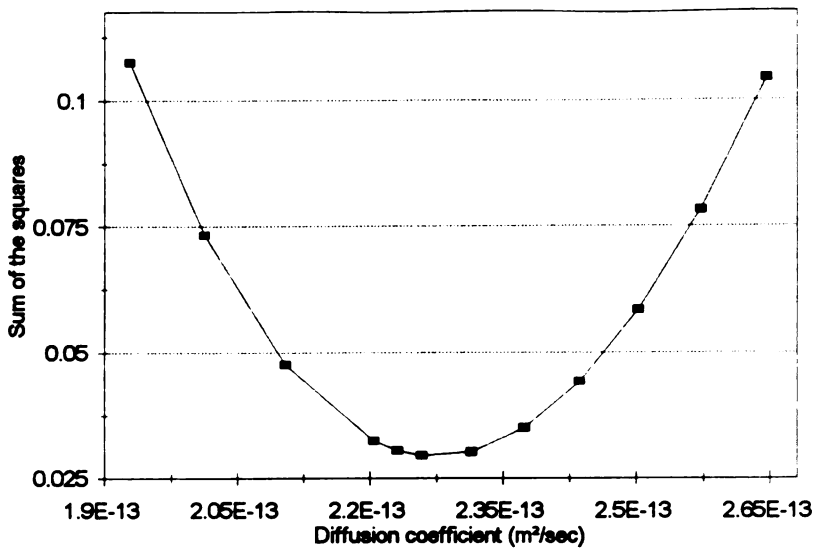

Figure 45. Sum of the squares profile as a function of the best estimated diffusion coefficient value for the system ethyl acetate/ionomer at 22 °C, Av = 0.4

Table 8. Half-time and best estimated (D_{est}) [a] diffusion coefficient values obtained from isostatic permeability experiments for ethyl acetate in LDPE film at 22 °C

Vapor activity	Diffusion coefficient [m^2/sec ($\times 10^{-13}$)]	
	D	D_{est}
0.1	12.2	12.5
0.2	11.6	11.5
0.4	11.6	11.2
Average ± standard deviation	11.8 ± 0.3	11.7 ± 0.6

[a] Average of replicate runs, with a confidence limit of 12% (maximum)

Table 9. Half-time and best estimated (D_{est}) [a] diffusion coefficient values obtained from isostatic permeability experiments for ethyl acetate in LLDPE film at 22 °C

Vapor activity	Diffusion coefficient [m^2/sec ($\times 10^{-13}$)]	
	D	D_{est}
0.1	10.5	10.2
0.2	10.3	10.1
0.4	11.4	11.0
Average ± standard deviation	10.7 ± 0.5	10.4 ± 0.4

[a] Average of replicate runs, with a confidence limit of 10% (maximum)

Table 10. Half-time and best estimated (D_{est}) [a] diffusion coefficient values obtained from isostatic permeability experiments for ethyl acetate in ionomer film at 22 °C

Vapor activity	Diffusion coefficient [m^2/sec ($\times 10^{-13}$)]	
	D	D_{est}
0.1	2.5	2.5
0.2	2.1	2.1
0.4	2.2	2.1
Average ± standard deviation	2.3 ± 0.2	2.2 ± 0.2

[a] Average of replicate runs, with a confidence limit of 7% (maximum)

In addition to performing the consistency treatment described by Gavara and Hernandez, statistical analysis was performed to determine whether the experimentally obtained permeability, diffusion and solubility coefficient values differed significantly over the vapor concentration range considered. As described above, the Least Significant Difference test was applied, using an alpha level of 0.05. Detailed results of this treatment are presented in Appendix E. As shown, the results indicate that when an alpha level of 0.05 was specified, all but one of the cases showed no significant difference over the permeant vapor concentration range evaluated. However, when an alpha level of 0.01 was designated, the outstanding difference was found to be nonsignificant as a function of vapor activity.

Comparison of the Solubility Coefficient Values Obtained by the Gravimetric and Isostatic Permeability Techniques

A primary objective of this study was to investigate the relationship between the solubility coefficient values obtained from gravimetric and isostatic permeability experiments. Solubility coefficient values obtained by the two procedures are compared in Tables 11 through 13, for the respective test films, over the vapor activity range considered. As shown, reasonably good agreement was obtained between the solubility coefficient values determined by the two procedures, with the solubility coefficient values derived from the permeability experiments being approximately 25 to 30% higher than those obtained from sorption studies.

Table 11. Solubility and diffusion coefficient values obtained from gravimetric and isostatic permeability experiments for ethyl acetate in LDPE film at 22 °C [a]

Vapor activity	Solubility coefficient [kg/kg·Pa (× 10^{-6})]		Diffusion coefficient [m^2/sec (× 10^{-13})]	
	Gravimetric procedure	Isostatic permeability technique	Gravimetric procedure	Isostatic permeability technique
0.05	2.2		0.70	
0.1	2.2	3.1	0.79	12.2
0.2	2.4	3.3	0.88	11.6
0.4	2.3	3.4	1.00	11.6
Average ± standard deviation	2.2 ± 0.1	3.3 ± 0.1	0.84 ± 0.11	11.8 ± 0.3

[a] Based on duplicate analyses

Table 12. Solubility and diffusion coefficient values obtained from gravimetric and isostatic permeability experiments for ethyl acetate in LLDPE film at 22 °C [a]

Vapor activity	Solubility coefficient [kg/kg·Pa (× 10^{-6})]		Diffusion coefficient [m^2/sec (× 10^{-13})]	
	Gravimetric procedure	Isostatic permeability technique	Gravimetric procedure	Isostatic permeability technique
0.05	2.3		0.65	
0.1	2.1	3.7	0.83	10.5
0.2	2.5	3.4	0.81	10.3
0.4	2.2	3.0	0.67	11.4
Average ± standard deviation	2.3 ± 0.2	3.33 ± 0.346	0.74 ± 0.08	10.7 ± 0.5

[a] Based on duplicate analyses

Table 13. Solubility and diffusion coefficient values obtained from gravimetric and isostatic permeability experiments for ethyl acetate in ionomer film at 22 °C [a]

Vapor activity	Solubility coefficient [kg/kg·Pa (× 10^{-6})]		Diffusion coefficient [m^2/sec (× 10^{-13})]	
	Gravimetric procedure	Isostatic permeability technique	Gravimetric procedure	Isostatic permeability technique
0.1	4.0	4.6	0.79	2.5
0.2	4.4	6.4	0.62	2.1
0.4	3.9	5.8	0.74	2.2
Average ± standard deviation	4.1 ± 0.22	5.6 ± 0.75	0.72 ± 0.07	2.3 ± 0.2

[a] Based on duplicate analyses

Deviation between the two sets of solubility coefficient values may be due to the inherently different methods by which the respective S values are determined. As discussed earlier, use of the gravimetric technique allows one to calculate the solubility coefficient value directly from the M_∞ value obtained when the polymer sample has reached steady state, as described in Equation 24. In contrast, determination of the S value from the isostatic permeability experiment involves calculation of $\overline{P}$ at steady-state, with D determined by substitution into Equation 30. Once $\overline{P}$ and D have been determined, S can then be obtained from Equation 31. In this latter case, calculation of the solubility coefficient value is directly dependent on the D value obtained from the transient state portion of the permeability experiment's flux rate profile curve.

Since the solubility coefficient determined by the gravimetric procedure is obtained at steady state, it is reasonable to assume that the value obtained is a very accurate measure of the solubility coefficient, for the polymer/penetrant systems studied. If this assumption is correct, the agreement between the S values obtained by these two procedures (for these polymer/penetrant systems) is considered to be within acceptable limits, given the different procedural methods by which the respective solubility coefficient values are determined. This agreement also suggests that, in the case of the polymer/penetrant systems considered in the present study, the solubility coefficient values obtained from the permeability procedure provide an accurate indication of the degree of ethyl acetate "flavor scalping" that could be expected from these polymer structures.

Comparison of the Diffusion Coefficient Values Obtained by the Gravimetric and Isostatic Permeability Techniques

In addition to the gravimetric and isostatic permeability techniques providing two independent procedures for determining solubility coefficient values, these procedures also allow determination of diffusion coefficient values, namely D_s determined from the sorption technique, and D determined from the permeability method. The diffusion coefficient values determined by the two procedures for the three test films are summarized in Tables 11 through 13. As shown, unlike the solubility coefficient values, there was a significant lack of agreement between the diffusion coefficient values determined by the two procedures. For the polymer/permeant systems considered in this present study, it was found that the D values obtained from the permeability experiments were at least an

order of magnitude larger than the D_s values obtained by the gravimetric technique.

While this lack of agreement is not fully understood, one possible explanation that may account, in part, for the disparity between the diffusion coefficient values determined by the two procedures is the differences in the physical design of the respective test apparatus used in this investigation. The MAS 2000 Organic Vapor Permeation Test System employs an isostatic permeability cell with an upstream cell volume of 6 cm^3 (total cell volume of 12 cm^3). In contrast, the hangdown tube of the Cahn 2000 electrobalance, in which a polymer sample is suspended during sorption testing, has a volume of approximately 500 cm^3.

The cell and hangdown tube volumes are significant, since they can directly impact the $t_{0.5}$ value used in calculating the diffusion coefficient. At the start of both the sorption and permeability experiments, these volumes are void of permeant vapor. While in an ideal test situation, the volume in the electrobalance hangdown tube and the upstream cell chamber of the permeability cell should instantaneously be filled with the desired vapor concentration at the time of experiment initiation, the physical designs of both apparatus do not make this possible.

The time required for the MAS 2000's upstream cell volume to reach 95% of the desired concentration level can be estimated using the following expression (Hernandez, 1997):

$$t_r = \frac{v}{r_f} \ln 20 \qquad (35)$$

where t_r is the time required, v is the volume of the upstream cell, and r_f is the flow rate of the incoming permeant vapor. If the incoming flow rate of ethyl acetate vapor into the

upstream cell is approximately 30 cm^3/min, the resulting time required to reach 95% of the desired vapor activity level would be approximately 0.6 minutes.

In contrast, a much longer time period is required for the electrobalance hangdown tube to reach 95% of the desired concentration level. This period of time can also be estimated using Equation 35, where t_r represents the time required, v is the volume of the hangdown tube, and r_f is the flow rate of the incoming permeant vapor. At an operating flow rate of 15 cm^3/min, the time required to attain a 95% concentration level would be approximately 100 minutes. Due to the time required for the vapor concentration in the hangdown tube to attain a constant concentration, and the strong affinity for the permeant vapor exhibited by the test films, it is reasonable to assume that a significant level of sorption may have taken place before the vapor concentration in the hangdown tube reached a constant level. To test the validity of this assumption, the following treatment was applied.

The ethyl acetate concentration level within the lower portion of the electrobalance hangdown tube was measured using gas chromatographic analysis from time zero, to the time at which an equilibrium concentration level of sorbate was attained. By plotting the ethyl acetate vapor concentration as a function of time, as shown in Figure 46, it was determined that the permeant vapor concentration within the lower portion of the hangdown tube increased exponentially as a function of time. Sorption data from a selected gravimetric experiment (ethyl acetate/LDPE, A_v: 0.1) was then substituted into the following expression, which describes exponential sorptive uptake by a polymer in film or sheet form (Crank and Park, 1968):

$$C = C_0 \, (1 - \exp(-\beta \, t)) \tag{36}$$

where C is the vapor concentration at time t, C_0 is the equilibrium vapor concentration level, t represents time, and β is a constant which can be obtained from the expression:

$$\beta = \frac{r_f}{v_0} \tag{37}$$

where r_f is the flow rate of the incoming permeant vapor, and v_0 is the volume of the lower portion of the electrobalance hangdown tube (Hernandez, 1997). The optimum β value for the selected experiment was then determined by using a sum of the squares technique, as shown in Figure 47, and was found to be in close agreement with the experimentally determined β value. The optimum β value was then substituted into the following data-fitting expression, and the amount of permeant sorbed by the polymer sample was plotted as a function of the square root of time:

$$\frac{M_t}{2 l C_0} = 1 - \exp(-\beta t) \, (D/\beta l^2)^{1/2} \tan (\beta l^2/D)^{1/2}$$

$$- \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp(-(2n+1)^2 \pi^2 D t/4 l^2)}{(2n+1)^2 [1 - (2n+1)^2 (D\pi^2/(4 b l^2))]} \tag{38}$$

where M_t is the total quantity of sorbed penetrant in the polymer sample at time t, l is half of the polymer membrane thickness, D is the sorption diffusion coefficient, and t represents time (Crank and Park, 1968). A representative plot of M_t/M_∞ as a function of the square root of time for the sorption of ethyl acetate into low density polyethylene is presented in Figure 48. Superimposed on the experimental data is the calculated curve obtained from Equation 38. It can be seen that the theoretical curve fits the experimental data well, with the initial portion of both sorption profile curves being approximately linear.

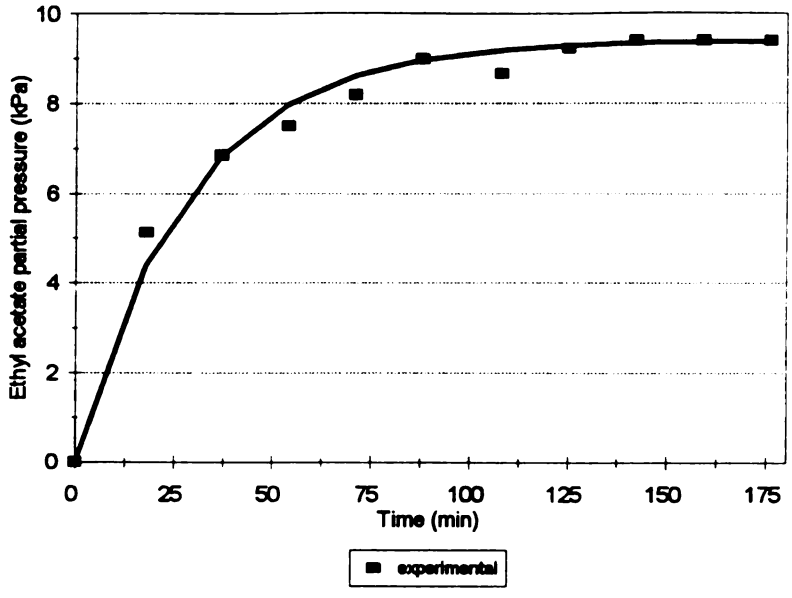

Figure 46. Ethyl acetate partial pressure in the lower portion of the electrobalance hangdown tube as a function of time

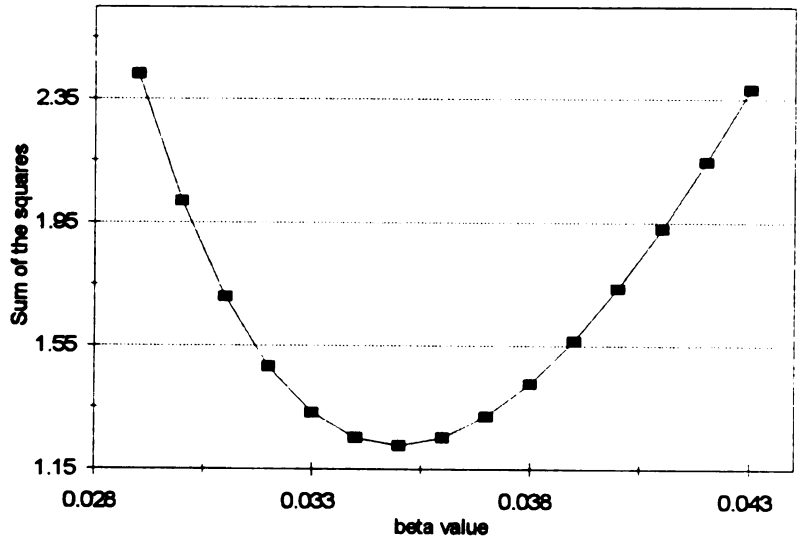

Figure 47. Sum of the squares profile as a function of the best estimated beta value for the system ethyl acetate/LDPE at 22 °C, Av = 0.1

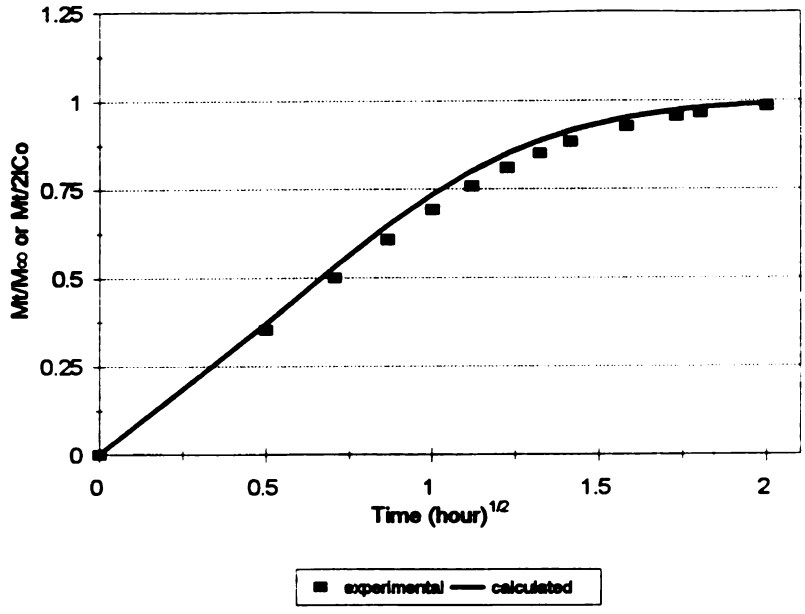

Figure 48. Sorption profile for ethyl acetate in LDPE at 22 °C, Av = 0.1

To determine whether the time required for displacement of the electrobalance hangdown tube volume by the penetrant vapor had introduced significant error into the diffusion coefficient calculation by the gravimetric technique, a range of permeant flow rate values were substituted into Equation 37. The resultant β values obtained were then substituted into Equation 38, and sorption profile curves were constructed. Presented in Figure 49 is the experimental sorption profile curve, with the theoretical sorption curves obtained by solution of Equation 38 superimposed for comparison. As shown, substitution of different permeant flow rate values appeared to produce no appreciable change in the agreement between the theoretical and experimental sorption profile curves.

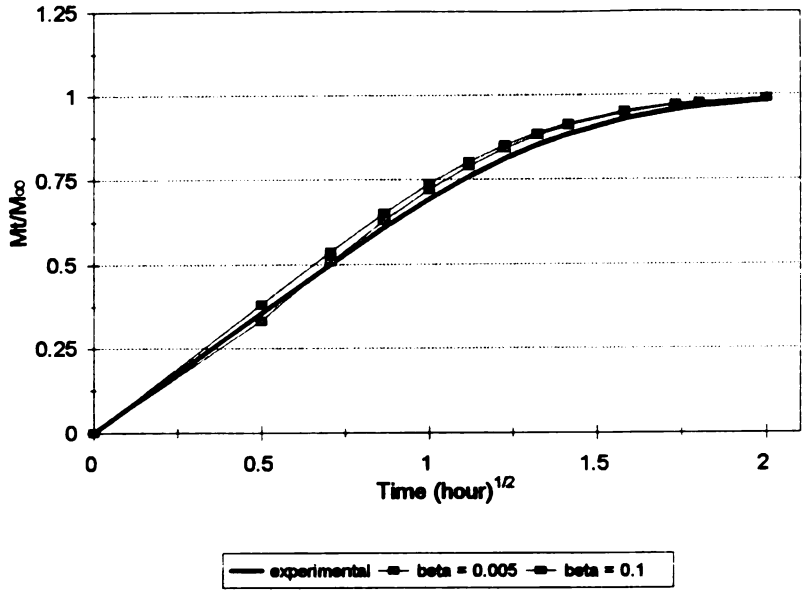

Figure 49. Sorption profile curves obtained using different values of beta

Similarly, the agreement between the theoretical and experimental sorption profile curves as a function of the diffusion coefficient value was examined by substituting a range of D values into Equation 38, while maintaining a constant value of β. As shown in Figure 50, changing the diffusion coefficient value did not appear to produce a marked deviation between the experimental and theoretical sorption profile curves. The results obtained from the described treatment suggest that the time required for the ethyl acetate vapor to displace the electrobalance hangdown tube volume did not significantly impact the $t_{0.5}$ value used in calculating the sorption diffusion coefficient (D_s), and therefore does not appear to be the source of the disagreement between the diffusion coefficient values obtained by the gravimetric and isostatic permeability techniques.

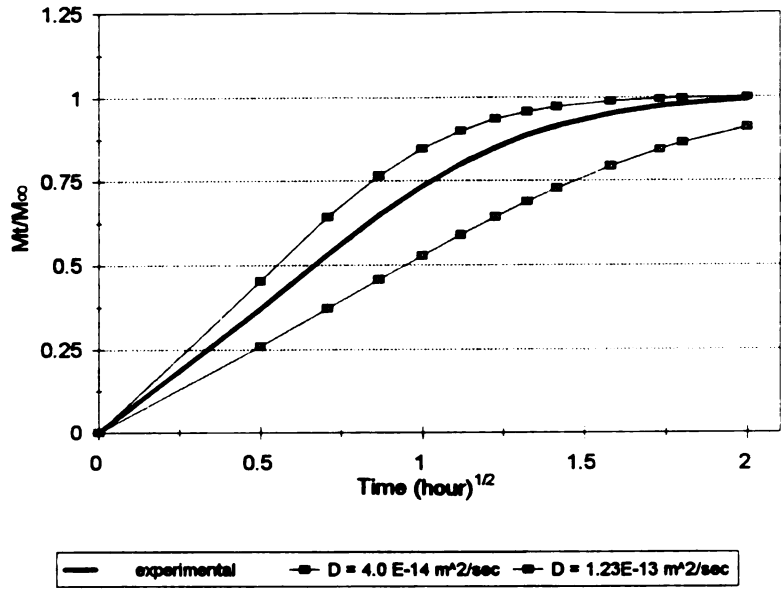

Figure 50. Sorption profile curves obtained using different diffusion coefficient values

Additional experimental variables associated with the gravimetric procedure which may affect the resultant mass transfer parameters are summarized in Table 14. Also contained in Table 14 are qualitative comments on the respective variables and the assumption that the test parameters such as temperature and vapor concentration were well controlled during the test run. As shown, all test parameters listed contribute to the accuracy of the solubility coefficient value obtained by the gravimetric procedure, with the exception of accurate time advancement by the strip chart recorder. The chart speed function, in contrast to the other test parameters listed, is directly related to the accurate determination of the time required to reach half of the steady state rate of transmission ($t_{0.5}$), and ultimately, the sorption diffusion coefficient value.

Table 14. Experimental variables associated with the gravimetric procedure and qualitative comments pertaining to the present study

Experimental variable	Comment
Cahn 2000 control unit calibration	Performed by manufacturer prior to initiation of the current study and validated regularly
Cahn 2000 weighing unit calibration	Performed before each experimental run
Penetrant vapor concentration	Monitored before and after each experimental run
Carrier gas flow rate	Verified to be between 10 and 15 cc/min before each experimental run
Vapor generator system condition	Condition inspected regularly
Experimental temperature	Protective chamber used to minimize laboratory temperature changes
Sorbate concentration level at time zero	Verified by GC analysis before each experimental run to be less than 500 AU
Steady state transmission attained	Experiment was not terminated before 6 to 8 hours of unchanged sample weight
Chart speed of strip chart recorder	Set at 2 cm/hr and assumed to be accurate

The marked difference between the diffusion coefficient values obtained by the gravimetric and isostatic permeability procedures thus cannot be attributed to the differences in the physical design of the respective test apparatus used in this study. However, the diffusion coefficient values obtained in this investigation by the isostatic technique, and the diffusion coefficients reported by other investigators for similar polymer/penetrant systems appear to agree within acceptable limits (Huang, 1996; Nielsen and Giacin, 1994; Hensley, 1991; Wangwiwatsilp, 1993). This is illustrated by Table 15, which contains diffusion coefficient values for ethyl acetate in high density polyethylene

(HDPE), and oriented polypropylene (OPP) films. Diffusion coefficients determined in the present study for LDPE, LLDPE, and ionomer films are summarized for comparison. This agreement suggests that the diffusion coefficient values obtained by the isostatic permeability technique employed in this study are correct and accurately reflect the mass transport behavior of the polymer/penetrant systems investigated.

Table 15. Diffusion coefficient values for ethyl acetate in HDPE, OPP, LDPE, LLDPE and ionomer films

Film	Vapor activity	Diffusion coefficient [m^2/sec ($\times 10^{-13}$)]
HDPE [a]	0.095	4.0
OPP [a]	0.095	3.0
OPP [b]	0.1	0.13
LDPE	0.1	11.8
LLDPE	0.1	10.7
Ionomer	0.1	2.3

[a] Huang, 1996
[b] Nielsen and Giacin, 1994

As previously stated, since the solubility coefficient value determined by the gravimetric procedure is a steady state value, it can be assumed to be a very accurate measure of the solubility coefficient. If this assumption is correct, the agreement between the S values obtained by these two procedures can still be considered to be within acceptable limits for the polymer/penetrant systems investigated, given the different procedural methods by which the respective solubility coefficient values are determined.

In contrast, the diffusion coefficient value obtained by both the gravimetric and isostatic permeability techniques are based on transient state data and rely on accurate determination of the $t_{0.5}$ value for their calculation. While the diffusion coefficient values obtained by the isostatic procedure seem to agree reasonably well with the values reported in the literature, the diffusion coefficient values obtained by the gravimetric technique differed significantly from the literature values, both in magnitude and in the $t_{0.5}$ values used in their calculation. It is therefore reasonable to suggest that error in the $t_{0.5}$ values obtained from the gravimetric sorption measurements could account for the disagreement between the diffusion coefficient values determined by the respective methods and may have resulted from incorrect time advancement of the strip chart recorder used to record the gravimetric sorption data in this study. While the recorder's chart speed was set at a rate of 2 cm/hr during the gravimetric experiments, this rate was not independently verified, but was instead assumed to be accurate. An inaccurate chart speed may account for the abnormally high $t_{0.5}$ values obtained from the gravimetric experiments, and may consequently explain the disparity observed between the diffusion coefficient values obtained by the gravimetric and isostatic permeability experiments conducted in this investigation.

SUMMARY AND CONCLUSIONS

Solubility coefficient values were determined by gravimetric and isostatic permeation procedures for ethyl acetate vapor in the following heat sealant polymer structures: low density polyethylene, linear low density polyethylene, and ionomer. The solubility coefficient values obtained from sorption studies conducted at vapor activities of 0.05, 0.1, 0.2, and 0.4, showed excellent agreement as a function of vapor concentration, with no statistically significant difference observed over the vapor activity range evaluated at an alpha level of 0.01. Similarly, the S values obtained from isostatic permeability experiments conducted at vapor activities of 0.1, 0.2, and 0.4, agreed well over the vapor activity range considered. For the solubility coefficient values derived from permeability experiments, no statistically significant difference was observed over the permeant concentration range employed at an alpha level of 0.01. The consistency of the solubility coefficient values obtained from the gravimetric and isostatic permeability techniques suggests that the S values obtained were independent of penetrant vapor activity, and the sorption process followed a Henry's law relationship over the vapor concentration range evaluated.

Comparison of the solubility coefficient values determined by the gravimetric and isostatic permeability procedures showed acceptable agreement for the polymer/penetrant systems evaluated. The sorption of ethyl acetate by the test films seemed to follow typical

Fickian behavior over the vapor concentration range investigated in this study. Solubility coefficient values derived from isostatic permeability experiments were found to be approximately 25 to 30% higher than solubility coefficient values obtained from sorption studies conducted at the same penetrant vapor concentrations. Because the methods of calculating the solubility coefficient value by the two procedures are inherently different, this agreement is considered to be within acceptable limits.

In terms of practical importance, these results indicate that, for the polymer/permeant systems studied, the solubility coefficient values obtained from the isostatic permeability experiments provided a good estimation of the equilibrium solubility coefficient values obtained from gravimetric sorption studies. In addition, this agreement also suggests that the solubility coefficient values obtained from isostatic permeability experiments could provide an accurate indication of the amount of "flavor scalping" that could be expected from the polymer/penetrant systems investigated.

The gravimetric and isostatic procedures used in this investigation also provided a measure of the diffusion coefficient value for ethyl acetate in the test films considered. While the diffusion coefficient values obtained from the isostatic permeability experiments were found to agree (within reasonable limits) with D values reported by other investigators for similar polymer/penetrant systems, the diffusion coefficient values obtained by the gravimetric technique were found to differ significantly from the D values obtained by the isostatic permeation procedure. It was suggested that this marked lack of agreement may be due to the differences in the physical design of the gravimetric electrobalance and the isostatic permeability cell. However, the results of a treatment

designed to test the validity of this argument indicated that the time required to displace the electrobalance hangdown tube volume did not significantly impact the $t_{0.5}$ value used in calculating the sorption diffusion coefficient (D_s). Thus, the disparity between the diffusion coefficient values obtained by the gravimetric and isostatic permeability procedures cannot be attributed to the differences in the physical design of the respective test apparatus used in this study.

The agreement between the diffusion coefficient values from the isostatic permeability experiments and the D values reported by other investigators suggests that the diffusion coefficients obtained from the permeability experiments are correct and accurately reflect the mass transport behavior of the polymer/penetrant systems considered. While not fully understood, the results of the present studies suggest that the diffusion coefficient values obtained from the gravimetric sorption measurements may have been the result of inaccurate time advancement by the strip chart recorder used in this study. Of the experimental variables associated with the gravimetric technique, the accuracy of the strip chart recorder's time advancement function is the only factor that could have potentially impacted the $t_{0.5}$ value, and ultimately, the sorption diffusion coefficient value. The remaining variables identified with the gravimetric procedure are not associated with the calculation of the sorption diffusion coefficient, but instead contribute to the accuracy of the solubility coefficient value. While the recorder's chart speed was set at a rate of 2 cm/hr throughout the gravimetric experiments, this rate was not independently verified, but was instead assumed to be accurate. An inaccurate chart speed may account for the abnormally high $t_{0.5}$ values obtained from the gravimetric experiments, and may

consequently explain the disparity between the diffusion coefficient values obtained by the gravimetric and isostatic permeability experiments conducted in this investigation.

If the above argument is correct, the solubility coefficient values obtained by the gravimetric procedure remain valid, as these values are independent of $t_{0.5}$. The solubility coefficient determined by the gravimetric technique is a steady state value, and can be assumed to be a very accurate measure of the solubility coefficient. Based on this assumption, the agreement between the S values obtained by these two procedures can still be considered to be within acceptable limits for the polymer/penetrant systems investigated, given the different procedural methods by which the respective solubility coefficient values are determined.

After completion of the gravimetric sorption studies conducted in this investigation, several improvements were made to enhance the capability of the Cahn 2000 electrobalance system. These improvements are described in Appendix F, and include the direct interface of the electrobalance control unit with a computer for data interpretation and storage. Because computers are equipped to process data only in digital form, an analog-to-digital (A/D) converter had to be used to digitize the analog signal output produced by the Cahn 2000. Improving the Cahn 2000 as described will allow for more accurate collection of raw data from the electrobalance system, and will ultimately lead to more accurate determination of polymer/permeant mass transport parameters.

RECOMMENDATIONS

Based on the results of this investigation, a number of recommendations for future research can be made. The following proposed studies may lead to an increased understanding of organic molecular mass transport through polymeric materials.

1. The polymeric films selected for this study were chosen because of their range of barrier property values, as well as their cost, processibility, and use in food packaging. It is proposed that a similar investigation be conducted using polar polymeric films, glassy polymers above the glass transition temperature, or films fabricated from copolymers or polymer blends.

2. Ethyl acetate was chosen as the sorbate in this study because of its presence in many food flavor profiles. A similar study comparing the solubility and diffusion coefficient values obtained by the gravimetric and isostatic permeability techniques could be made using a series of sorbates of varying polarity and chemical composition.

3. In the present study, all gravimetric and isostatic permeability measurements were conducted at ambient temperature. It is proposed that additional experiments be conducted over a range of temperatures, to investigate:

(i) whether the temperature dependence of the permeability, solubility, and diffusion coefficient values can be described by the Arrhenius equation,

(ii) whether the permeability, solubility, and diffusion coefficient values obtained by the gravimetric and isostatic permeability techniques agree as a function of temperature.

APPENDICES

APPENDIX A

Procedure for Calibration Curve Construction

Materials

- 100 mL volumetric flask with stopper
- 25 mL volumetric flasks with stoppers (4)
- 500 μL high performance gas tight syringe
- 1 and 5 mL sterile pipettes with automatic pipette fixtures
- Research grade ethyl acetate and acetonitrile

Procedure

To determine the relationship between area response and the ethyl acetate quantity injected, a calibration curve was constructed using the following procedure:

1. Prepare a 1000 ppm (v/v) stock solution of ethyl acetate/acetonitrile.
   - 1a. Using a high performance gas tight syringe, add 0.1 mL of research grade ethyl acetate to a 100 mL volumetric flask.
   - 1b. Fill to 100 mL with acetonitrile.
   - 1c. Stopper the flask and swirl to ensure proper mixing.
2. From the 1000 ppm stock solution, prepare 25 mL standard solutions of the following concentrations: 10, 20, 40, and 80 ppm (v/v).
   - 2a. To the four 25 mL volumetric flasks, add 0.25, 0.5, 1.0, and 2.0 mL of the 1000 ppm stock solution, respectively.
   - 2b. Fill to 25 mL with acetonitrile.

2c. Stopper the flasks and swirl to ensure proper mixing.

3. Using the GC settings presented in Table 16, analyze each standard solution by injecting a 1 μL aliquot directly into the gas chromatograph for quantification. Repeat until consistent area response values are obtained for each concentration.

4. Plot the average area response value obtained for each concentration as a function of the ethyl acetate quantity injected. The injected quantity of ethyl acetate can be calculated from the following expression:

$$q_i = v_i \times c \times 0.902 \frac{g}{mL} \qquad (39)$$

where q_i represents the quantity injected, v_i is the injection volume, c is the concentration of the standard solution, and 0.902 g/mL is the density of ethyl acetate. The ethyl acetate calibration curve is presented in Figure 51.

5. Using linear regression, determine the slope of the standard curve. Take the inverse of this value to obtain the ethyl acetate calibration factor.

Table 16. Gas chromatographic conditions used for ethyl acetate quantification

Column	Supelcowax 10 60 m, 0.25 mm ID, 0.25 µm film thickness
Injection temperature	220 °C
Detector temperature	250 °C
Initial temperature	100 °C
Initial time	9 min
Rate	7.5 °C/min
Final temperature	220 °C
Final time	15 min
He carrier gas	7.0 mL/min
H_2	40 mL/min
Air	400 mL/min
Nitrogen (make-up gas)	30 mL/min

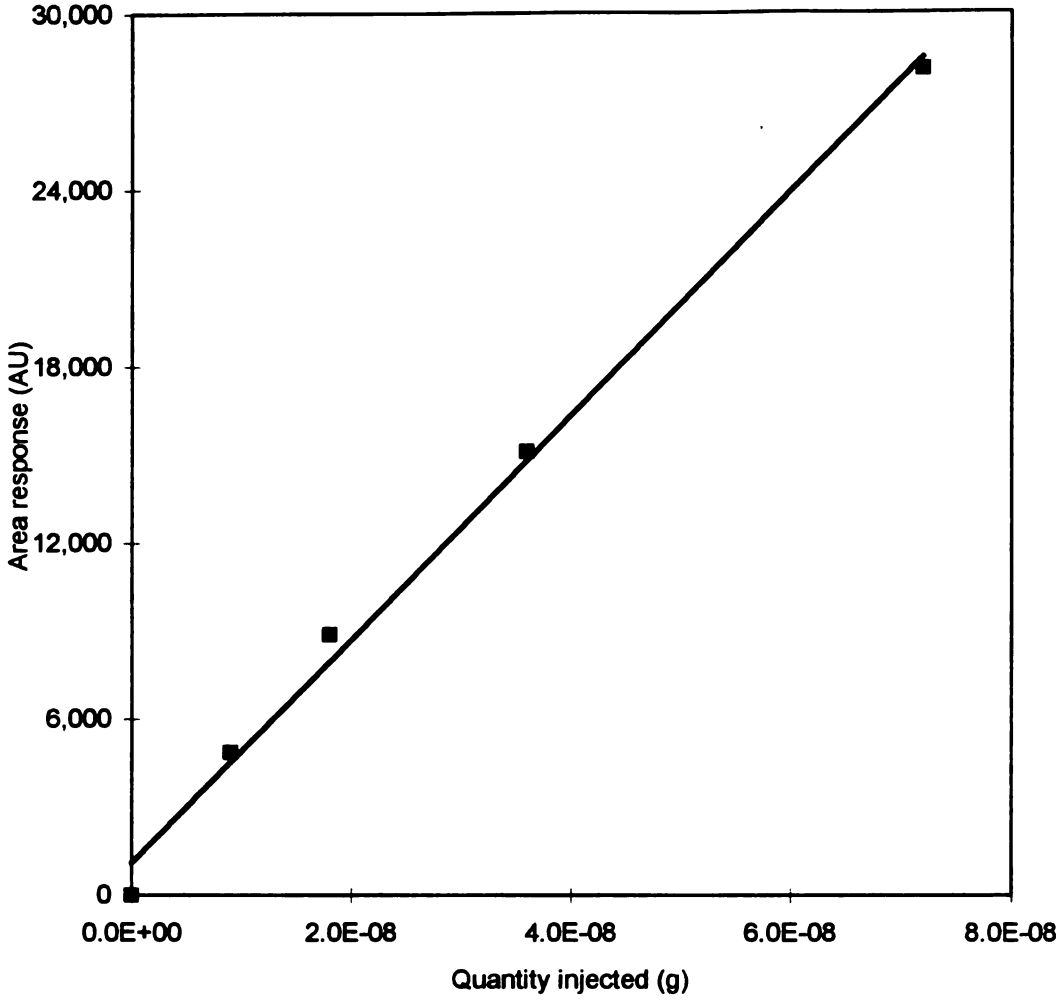

Figure 51. Ethyl acetate calibration curve

APPENDIX B

Calculation of the Saturation Vapor Pressure and Vapor Activity of Ethyl Acetate

Materials

- 500 μL high performance gas tight syringe
- 50 mL crimp seal vials (5)
- Aluminum crimp cap (5)
- Teflon coated septa seals (5)
- 5 mL sterile pipettes with automatic pipette fixtures
- Research grade ethyl acetate

Procedure

The saturation vapor pressure and the vapor activity of ethyl acetate were experimentally determined using the following procedure:

1. Add 10 mL of ethyl acetate to each vial and seal using a Teflon coated septa seal and an aluminum crimp cap.
2. Store the samples at 22 ℃ for one week to allow the vial headspace to equilibrate.
3. Using the GC conditions summarized in Table 16, analyze the ethyl acetate vapor pressure within the headspace by withdrawing a 50 μL aliquot and injecting the sample directly into the gas chromatograph for quantification.
4. Determine the ethyl acetate saturation vapor pressure from the ideal gas law:

$$pV = nRT \tag{40}$$

5. Determine the vapor activity of the ethyl acetate test vapor.

5a. Using GC conditions identical to those presented in Table 16, analyze the diluted ethyl acetate vapor by withdrawing a 50 μL aliquot from the vapor stream sampling port and injecting the sample directly into the gas chromatograph for quantification.

5b. Determine the vapor pressure of the sample using the ideal gas law.

5c. Determine the vapor activity from the following expression:

$$A_v = \frac{p_i}{p_s} \tag{41}$$

where A_v represents the vapor activity, p_i is the vapor pressure of diluted ethyl acetate, and p_s is the saturation vapor pressure of ethyl acetate.

APPENDIX C

Least Significant Difference Test Results for Solubility Coefficient Values Determined by the Gravimetric Technique

Table 17. Least Significant Difference test results for solubility coefficient values determined by the gravimetric technique for the system ethyl acetate/LDPE at 22 °C

K value	Source	D_f	SS	Mean Square	F value	Prob
1	Replication	1	0.016	0.016	1.1825	0.3564
2	Factor A	3	0.083	0.028	2.0207	0.2891
-3	Error	3	0.041	0.014		
Total		7	0.14			

Coefficient of variation:	5.17%		
$S_{\bar{y}}$ for means group 1:	0.0585	Number of observations:	4
$S_{\bar{y}}$ for means group 2:	0.0828	Number of observations:	2

Least significant difference value:	0.3766	Alpha level:	0.05

Original order			Ranked order		
Mean 1	2.170	A	Mean 3	2.420	A
Mean 2	2.175	A	Mean 4	2.285	A
Mean 3	2.420	A	Mean 2	2.175	A
Mean 4	2.285	A	Mean 1	2.170	A

Table 18. Least Significant Difference test results for solubility coefficient values determined by the gravimetric technique for the system ethyl acetate/LLDPE at 22 °C

K value	Source	D_f	SS	Mean Square	F value	Prob
1	Replication	1	0.034	0.034	6.1084	0.0899
2	Factor A	3	0.189	0.063	11.3825	0.0380
-3	Error	3	0.017	0.006		
Total		7	0.239			

Coefficient of variation:	3.27%		
$S_{\bar{y}}$ for means group 1:	0.0327	Number of observations:	4
$S_{\bar{y}}$ for means group 2:	0.0526	Number of observations:	2

Least significant difference value:	0.2465	Alpha level*:	0.05

Original order			Ranked order		
Mean 1	2.240	B	Mean 3	2.530	A
Mean 2	2.130	B	Mean 1	2.240	B
Mean 3	2.530	A	Mean 4	2.190	B
Mean 4	2.190	B	Mean 2	2.130	B

(*) If an alpha level of 0.01 is used, all means are designated "A"

Table 19. Least Significant Difference test results for solubility coefficient values determined by the gravimetric technique for the system ethyl acetate/ionomer at 22 °C

K value	Source	D_f	SS	Mean Square	F value	Prob
1	Replication	1	0.482	0.482	8.4036	0.1012
2	Factor A	2	0.263	0.132	2.2946	0.3035
-3	Error	2	0.115	0.057		
Total		5	0.859			

Coefficient of variation:	5.90%		
$S_{\bar{y}}$ for means group 1:	0.1382	Number of observations:	3
$S_{\bar{y}}$ for means group 2:	0.1693	Number of observations:	2

Least significant difference value:	1.459	Alpha level:	0.05

Original order			Ranked order		
Mean 1	3.954	A	Mean 2	4.350	A
Mean 2	4.350	A	Mean 1	3.945	A
Mean 3	3.875	A	Mean 3	3.875	A

APPENDIX D

Least Significant Difference Test Results for Diffusion Coefficient Values Determined by the Gravimetric Technique

Table 20. Least Significant Difference test results for diffusion coefficient values determined by the gravimetric technique for the system ethyl acetate/LDPE at 22 °C

K value	Source	D_f	SS	Mean Square	F value	Prob
1	Replication	1	0.383	0.383	1.000	
2	Factor A	3	9.646	3.215	8.3993	0.0570
-3	Error	3	1.148	0.383		
Total		7	11.177			

Coefficient of variation:	7.34%		
$S_{\bar{y}}$ for means group 1:	0.3094	Number of observations:	4
$S_{\bar{y}}$ for means group 2:	0.4375	Number of observations:	2

Least significant difference value:	1.970	Alpha level*:	0.05

Original order			Ranked order		
Mean 1	7.030	B	Mean 4	10.00	A
Mean 2	7.905	B	Mean 3	8.780	AB
Mean 3	8.780	AB	Mean 2	7.905	B
Mean 4	10.00	A	Mean 1	7.030	B

(*) If an alpha level of 0.01 is used, all means are designated "A"

Table 21. Least Significant Difference test results for diffusion coefficient values determined by the gravimetric technique for the system ethyl acetate/LLDPE at 22 °C

K value	Source	D_f	SS	Mean Square	F value	Prob
1	Replication	1	0.123	0.123	0.4178	
2	Factor A	3	5.069	1.690	5.7620	0.0921
-3	Error	3	0.880	0.293		
Total		7	6.071			

Coefficient of variation:	7.36%		
$S_{\bar{y}}$ for means group 1:	0.2708	Number of observations:	4
$S_{\bar{y}}$ for means group 2:	0.3829	Number of observations:	2

Least significant difference value:	2.985	Alpha level:	0.05

Original order			Ranked order		
Mean 1	6.440	A	Mean 2	8.260	A
Mean 2	8.260	A	Mean 3	8.035	A
Mean 3	8.035	A	Mean 4	6.710	A
Mean 4	6.710	A	Mean 1	6.440	A

Table 22. Least Significant Difference test results for diffusion coefficient values determined by the gravimetric technique for the system ethyl acetate/ionomer at 22 °C

K value	Source	D_f	SS	Mean Square	F value	Prob
1	Replication	1	0.031	0.031	0.0316	
2	Factor A	2	3.408	1.704	1.7471	0.3640
-3	Error	2	1.950	0.975		
Total		5	5.389			

Coefficient of variation:	13.81%		
$S_{\bar{y}}$ for means group 1:	0.5702	Number of observations:	3
$S_{\bar{y}}$ for means group 2:	0.6983	Number of observations:	2

Least significant difference value:	4.249	Alpha level:	0.05

Original order			Ranked order		
Mean 1	7.905	A	Mean 1	7.905	A
Mean 2	6.120	A	Mean 3	7.420	A
Mean 3	7.420	A	Mean 2	6.120	A

APPENDIX E

Least Significant Difference Test Results for Permeability, Diffusion, and Solubility Coefficient Values Determined by the Isostatic Permeability Technique

Table 23. Least Significant Difference test results for permeability coefficient values determined by the isostatic permeability technique for the system ethyl acetate/LDPE at 22 °C

K value	Source	D_f	SS	Mean Square	F value	Prob
1	Replication	1	0.002	0.002	0.0083	
2	Factor A	2	0.059	0.029	0.1217	
-3	Error	2	0.484	0.242		
Total		5	0.545			

Coefficient of variation:	14.04%		
$S_{\bar{y}}$ for means group 1:	0.2840	Number of observations:	3
$S_{\bar{y}}$ for means group 2:	0.3479	Number of observations:	2

Least significant difference value:	2.117	Alpha level:	0.05

Original order			Ranked order		
Mean 1	3.430	A	Mean 3	3.645	A
Mean 2	3.440	A	Mean 2	3.440	A
Mean 3	3.645	A	Mean 1	3.430	A

Table 24. Least Significant Difference test results for permeability coefficient values determined by the isostatic permeability technique for the system ethyl acetate/LLDPE at 22 °C

K value	Source	D_f	SS	Mean Square	F value	Prob
1	Replication	1	0.006	0.006	0.0359	
2	Factor A	2	0.183	0.091	0.5458	
-3	Error	2	0.335	0.167		
Total		5	0.524			

Coefficient of variation:	12.50%		
$S_{\bar{y}}$ for means group 1:	0.2363	Number of observations:	3
$S_{\bar{y}}$ for means group 2:	0.2894	Number of observations:	2

Least significant difference value:	1.758	Alpha level:	0.05

Original order			Ranked order		
Mean 1	3.515	A	Mean 3	3.515	A
Mean 2	3.205	A	Mean 2	3.205	A
Mean 3	3.105	A	Mean 3	3.105	A

Table 25. Least Significant Difference test results for permeability coefficient values determined by the isostatic permeability technique for the system ethyl acetate/ionomer at 22 °C

K value	Source	D_f	SS	Mean Square	F value	Prob
1	Replication	1	0.004	0.004	1.6954	0.3227
2	Factor A	2	0.028	0.014	5.6093	0.1513
-3	Error	2	0.005	0.003		
Total		5	0.037			

Coefficient of variation:	4.34%		
$S_{\bar{y}}$ for means group 1:	0.0290	Number of observations:	3
$S_{\bar{y}}$ for means group 2:	0.0355	Number of observations:	2

Least significant difference value:	0.2357	Alpha level:	0.05

Original order			Ranked order		
Mean 1	1.065	A	Mean 2	1.230	A
Mean 2	1.230	A	Mean 3	1.175	A
Mean 3	1.175	A	Mean 1	1.065	A

Table 26. Least Significant Difference test results for diffusion coefficient values determined by the isostatic permeability technique for the system ethyl acetate/LDPE at 22 °C

K value	Source	D_f	SS	Mean Square	F value	Prob
1	Replication	1	0.011	0.011	0.5849	
2	Factor A	2	0.005	0.002	0.1269	
-3	Error	2	0.038	0.019		
Total		5	0.054			

Coefficient of variation:	11.72%		
$S_{\bar{y}}$ for means group 1:	0.0798	Number of observations:	3
$S_{\bar{x}}$ for means group 2:	0.0978	Number of observations:	2

Least significant difference value:	0.5931	Alpha level:	0.05

Original order			Ranked order		
Mean 1	1.220	A	Mean 1	1.220	A
Mean 2	1.155	A	Mean 3	1.165	A
Mean 3	1.165	A	Mean 2	1.155	A

Table 27. Least Significant Difference test results for diffusion coefficient values determined by the isostatic permeability technique for the system ethyl acetate/LLDPE at 22 °C

K value	Source	D_f	SS	Mean Square	F value	Prob
1	Replication	1	0.004	0.004	0.5115	
2	Factor A	2	0.013	0.006	0.7375	
-3	Error	2	0.017	0.009		
Total		5	0.034			

Coefficient of variation:	8.64%		
$S_{\bar{y}}$ for means group 1:	0.0534	Number of observations:	3
$S_{\bar{y}}$ for means group 2:	0.0654	Number of observations:	2

Least significant difference value:	0.4082	Alpha level:	0.05

Original order			Ranked order		
Mean 1	1.046	A	Mean 3	1.135	A
Mean 2	1.031	A	Mean 1	1.046	A
Mean 3	1.135	A	Mean 2	1.031	A

Table 28. Least Significant Difference test results for diffusion coefficient values determined by the isostatic permeability technique for the system ethyl acetate/ionomer at 22 °C

K value	Source	D_f	SS	Mean Square	F value	Prob
1	Replication	1	0.010	0.010	0.6713	
2	Factor A	2	0.212	0.106	6.8324	0.1277
-3	Error	2	0.031	0.016		
Total		5	0.253			

Coefficient of variation:	5.57%		
$S_{\bar{y}}$ for means group 1:	0.0719	Number of observations:	3
$S_{\bar{y}}$ for means group 2:	0.0881	Number of observations:	2

Least significant difference value:	0.5442	Alpha level:	0.05

Original order			Ranked order		
Mean 1	2.495	A	Mean 1	2.495	A
Mean 2	2.050	A	Mean 3	2.170	A
Mean 3	2.170	A	Mean 2	2.050	A

Table 29. Least Significant Difference test results for solubility coefficient values determined by the isostatic permeability technique for the system ethyl acetate/LDPE at 22 °C

K value	Source	D_f	SS	Mean Square	F value	Prob
1	Replication	1	0.049	0.049	0.2924	
2	Factor A	2	0.103	0.051	0.3085	
-3	Error	2	0.332	0.166		
Total		5	0.484			

Coefficient of variation:	12.56%		
$S_{\bar{y}}$ for means group 1:	0.2354	Number of observations:	3
$S_{\bar{y}}$ for means group 2:	0.2883	Number of observations:	2

Least significant difference value:	1.753	Alpha level:	0.05

Original order			Ranked order		
Mean 1	3.090	A	Mean 3	3.410	A
Mean 2	3.240	A	Mean 2	3.240	A
Mean 3	3.410	A	Mean 1	3.090	A

Table 30. Least Significant Difference test results for solubility coefficient values determined by the isostatic permeability technique for the system ethyl acetate/LLDPE at 22 °C

K value	Source	D_f	SS	Mean Square	F value	Prob
1	Replication	1	0.084	0.084	5.3799	0.1462
2	Factor A	2	0.474	0.237	15.1644	0.0619
-3	Error	2	0.031	0.016		
Total		5	0.589			

Coefficient of variation:	3.75%		
$S_{\bar{y}}$ for means group 1:	0.0721	Number of observations:	3
$S_{\bar{y}}$ for means group 2:	0.0884	Number of observations:	2

Least significant difference value:	0.5442	Alpha level*:	0.05

Original order			Ranked order		
Mean 1	3.655	A	Mean 1	3.655	A
Mean 2	3.370	AB	Mean 2	3.370	AB
Mean 3	2.970	B	Mean 3	2.970	B

(*) If an alpha level of 0.01 is used, all means are designated "A"

Table 31. Least Significant Difference test results for solubility coefficient values determined by the isostatic permeability technique for the system ethyl acetate/ionomer at 22 °C

K value	Source	D_f	SS	Mean Square	F value	Prob
1	Replication	1	0.001	0.001	0.0051	
2	Factor A	2	3.473	1.736	6.5183	0.1330
-3	Error	2	0.533	0.266		
Total		5	4.007			

Coefficient of variation:	9.28%		
$S_{\bar{y}}$ for means group 1:	0.2980	Number of observations:	3
$S_{\bar{y}}$ for means group 2:	0.3650	Number of observations:	2

Least significant difference value:	2.219	Alpha level:	0.05

Original order			Ranked order		
Mean 1	4.545	A	Mean 2	6.375	A
Mean 2	6.375	A	Mean 3	5.765	A
Mean 3	5.765	A	Mean 1	4.545	A

APPENDIX F

Improvements Made to the Cahn 2000 Electrobalance System

In the course of this investigation, the following steps were taken to upgrade the Cahn 2000 electrobalance system:

1. A protective chamber was constructed to enclose the entire electrobalance apparatus. In doing so, the effects of temperature changes and physical disturbances in the laboratory will be minimized.

2. To enhance the capability of the system, the electrobalance control unit was interfaced with a computer for data interpretation and storage. Because computers are only capable of processing data in digital form, an analog-to-digital (A/D) converter was also integrated into the system to digitize the analog signal output produced by the Cahn 2000. By improving the system as described, raw data obtained from the electrobalance by future researchers will be even more accurate than data obtained through the use of a strip chart recorder.

3. A temperature controlled bath was interfaced with the Cahn 2000 electrobalance system. Because the relationship between temperature and vapor pressure is well documented in the literature, future investigators using the Cahn 2000 electrobalance will be able to achieve a wide range of vapor activities by monitoring the temperature of the bath, rather than using a vapor generator system based on a dilution/blending procedure to develop the desired vapor pressure of the permeant.

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