

Food Aroma Mass Transport in Metallocene Ethylene-Based Copolymers for Packaging Applications

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The permeation of five volatile organic compounds found in Iberian ham aroma (*n*-hexanal, *n*-hexanol, *n*-decane, ethyl caproate, and *d*-limonene) through films of ultra-low-density polyethylene (ULDPE) and two metallocene copolymers was evaluated at 23 °C. Values of the diffusion, permeability, and solubility coefficients were determined. The polymer films were characterized by differential scanning calorimetry, size exclusion chromatography, and oxygen permeability. Compared to ULDPE, the metallocene copolymers were lower in molecular weight, showed narrower molecular weight distributions, presented less crystallinity, and offered greater oxygen permeability. Solubility coefficient values were lower for compounds having higher polarity, and diffusion coefficients were higher for compounds of smaller molecular size. The permeability coefficients, which combine the effects of diffusion and sorption contributions, indicated that the films were more permeable to nonpolar small-size aromas. Overall, metallocene copolymers showed higher permeability values than ULDPE.

Keywords: *Metallocene polyethylene; aroma permeation; polarity; size*

INTRODUCTION

The use of polymeric materials continues to increase in the percentage of materials applied to food packages (Catalá and Gavara, 1996). Among the materials used in food packaging, polyolefins (polyethylenes and polypropylenes) represent the largest share of the global market (Hernandez, 1996). Many properties make their use attractive: low cost, processability, and flexibility, but without doubt the most important ones are their good thermal sealability (hermeticity) and water barrier (moisture control) (Brody and Marsh, 1997). Despite their high permeability values to gases and organic vapors, hermeticity and water barrier are so important that polyolefins are useful even when the product is sensitive to oxygen and/or aromas. In these cases multilayer structures in which a high barrier film is sandwiched between two polyolefin layers are commonly used.

Though aroma compounds do not contribute to the nutritional characteristics of foodstuffs, they are essential for food quality. One of the primary concerns of food packaging is to retain the product's original flavor characteristics since it directly affects the consumer's perception of product quality and shelf life. Flavor components are organic volatile compounds such as esters, terpenes, alcohols, aldehydes, and ketones (Pieper et al., 1992). Food products lose flavor compounds by both chemical reactions and transport through the packaging material. Loss of flavor by permeation and sorption processes has been the subject of many studies (Nielsen and Jaegerstad, 1994). The majority

of these studies have focused on polyolefins since they are the most common materials used in food packaging. Permeabilities to organic aroma compounds through polyolefins have been characterized by Mohny et al. (1988), Tou et al. (1990), Apostopoulos and Winters (1991), Leufven and Stoellman (1992), Kobayashi et al. (1995), and Doyon et al. (1995). Sorption and partition of aromas between polyolefins and foods or food simulants have been determined by Kwapong and Hotchkiss (1987), Imai et al. (1990), Nielsen et al. (1991, 1992), Pieper et al. (1992), Johansson et al. (1993), and Nielsen (1994).

Recently, new polyolefins obtained by a metallocene-catalyzed process have been made available for food packaging (Thayer, 1995). Metallocene catalysts yield polyolefins (polymers and copolymers) which are characterized by a greater regularity of molecular architecture than the conventional Ziegler–Natta (ZN)-catalyzed polyolefins. Metallocene ethylene-based copolymers (mPE) are the first group of such plastics to be used for packaging applications. mPEs were introduced to the market as having better mechanical properties and sealability than the ZN-catalyzed polyethylenes (ZN-PE). However, data on aroma mass transport through these novel materials are scarce (Singleton, 1998).

This work is part of a broader study on the optimization of packaging structures for Iberian ham. As a dry-cured meat product, Iberian ham is highly stable from a microbiological point of view; therefore, packaging and storage conditions must be selected to maintain organoleptic quality (i.e., to avoid flavor loss and lipid oxidation). Depending on product stock turnover and distribution radius, Iberian ham can be stored at room temperature or refrigerated (5–10 °C) and contained in low- or high-barrier packages (Flores and Toldra, 1993).

The objective of this work was to study and compare the mass transport characteristics of metallocene eth-

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ylene-based copolymers and ZN ultra-low-density polyethylene (ULDPE) films to selected organic aroma compounds found in Iberian ham. The mass transport of the systems was fully characterized by the permeability, diffusion, and solubility coefficients obtained by permeation experiments at 23 °C. It is known that these coefficients are temperature-dependent (Arrhenius's and Van't Hoff's laws), and therefore values are only valid for the particular temperature under study. However, due to the similar chemical composition of the polymers and that none of the substances under study experience a thermal transition between 0 and 25 °C, one can expect the results to be useful for comparisons of packaging structures even for foodstuffs under refrigeration.

MATERIALS AND METHODS

Materials. Three polymer films were used in this work: two metallocene ethylene-based copolymers identified as Affinity PL1880 (mPE1) and Affinity PF1140 (mPE2), and an ultra-low-density polyethylene (ULDPE) commercially known as Attane 4002. All films, intended for packaging applications, were obtained from Dow Chemical (Midland, MI). Thicknesses measured in a micrometer (Metrotec, Spain) were 57(±1) for mPE1, and 54(±1) for mPE2, and 78(±1) μm for ULDPE. No further information about the properties and structure of ULDPE and metallocene films was available.

Five organic compounds were selected from those present in Iberian ham aroma (Garcia et al., 1991; Lopez et al., 1992; Barbieri et al., 1992) as representatives of the different aroma families: 1-hexanol (HxOH), hexanal (HxO), ethyl caproate (EtCp), *d*-limonene (LIM), and *n*-decane (DEC). All liquids were reagent quality (Sigma, Teknokroma, Barcelona, Spain).

Polymer Characterization. Polymeric materials were characterized by differential scanning calorimetry (DSC), gel permeation chromatography (GPC), and oxygen permeability.

Thermal analysis was carried out in a Mettler TA Instruments 4000 thermal analyzer equipped with a DSC30 cell. Samples of film were put into open 40-μm aluminum sample pans. Indium of 99.999% purity, with a melting temperature of 156.6 °C and $\Delta H_m = 38.4$ J/g, was used as calibration standard. The heating chamber was purged with a dry nitrogen stream (15 mL/min) to avoid moisture condensation and programmed to run from -40 to 240 °C at 20 °C/min. Values of T_m and ΔH_m were obtained from the thermograms using the thermal analyzer application software.

Gel permeation chromatography was used to determine the molecular weight distribution of the three polymeric samples. The GPC instrument used was a Waters 150-C ALC-GPC (Waters Associates Inc., Milford, MA) equipped with a series of four μstyragel columns (pore size 10³, 10⁴, 10⁵, and 10⁶ Å). Experimental conditions were solvent, 1,2,4 trichlorobenzene; flow rate, 0.5 mL/min; injection volume, 0.1 mL; temperature, 135 °C. All solutions were filtered using PTFE filters (13-mm diameter, 0.2-mm porous diameter) from Millipore Corp. (Bedford, MA). A molecular weight calibration curve was constructed using standardized polystyrene from Analabs Inc. (New Haven, CO) having the following values of weight-average molecular weight (M_w): 1.80 × 10⁶, 6.00 × 10⁵, 3.90 × 10⁵, 2.33 × 10⁵, 1.00 × 10⁶, 5.00 × 10⁴, and 1.75 × 10⁴ Da. The calibration curve was based on the hydrodynamic volume of the macromolecules [universal linear relationship between the logarithm of the intrinsic viscosity multiplied by the molecular weight and retention time (Tejero et al., 1987)]. The intrinsic viscosity [η] of polystyrene and polyethylene (PE) samples was calculated by the Mark-Houwink-Sakurada relation [η] = KM_w^a . The following values of K and a were used: $K = 1.75 \times 10^{-3}$, $a = 0.67$; $K = 9.54 \times 10^{-2}$, $a = 0.64$ (Brandrup and Immergut, 1989). By plotting $\log([\eta]M_w)$ versus time a straight line was obtained for polyethylene in the range of 4700 = $M_w = 5.00 \times 10^5$. From the molecular weight distribution of PE, both the weight-average molecular weight

M_w and number-average molecular weight M_n were obtained. From these values the dispersity index of the molecular weight distribution was calculated as the ratio of the two molecular weight averages: $I_D = M_w/M_n$.

Oxygen permeability was determined using a Mocon Oxtran MS-200 (Minneapolis, MN). All measurements were carried out at 25 °C and 0% relative humidity.

Aroma Permeability. Permeability measurements were carried out in an isostatic permeation apparatus at 23 ± 2 °C. A test film was placed in the two-chamber permeation cell, where a gas stream of the aroma vapor and nitrogen gas was flown through the upper chamber. The lower chamber was flushed with dry nitrogen at a flow rate of about 1 mL/min. This stream carried the permeated aroma to a gas chromatograph which was used as detector. Permeant concentration at a vapor activity of around 0.1 was obtained by 10-fold dilution of an aroma-saturated gas with nitrogen at 23 ± 2 °C (concentrations of about 300 ppb for HxOH and LIM and 600 ppb for HxO, EtCp and DEC). In these concentration ranges, mass transport can be considered to be concentration-independent (Hernandez-Muñoz et al., 1998). An HP 5890 series II plus gas chromatograph (Hewlett-Packard, Barcelona, Spain) was used to measure the concentration of aroma in both cell chambers. Additional details of the permeation cells, aroma vapor control and generation, and data treatment are described elsewhere (Debeaufort and Voilley, 1994; Gavara et al., 1996a).

Calculations. The fraction of crystallinity (α_c) of a polyethylene sample was calculated according to eq 1,

$$\alpha_c = \frac{\Delta H_m}{\Delta H_m^c} \quad (1)$$

where ΔH_m is the sample melting enthalpy and ΔH_m^c is the melting enthalpy of 100% crystalline polyethylene.

The values of the permeability, diffusion, and solubility coefficients were determined considering that Henry's and Fick's laws were applicable (Crank, 1975). From the steady-state mass transport rate in the continuous flow permeation method, F_{ss} , the permeability coefficient values, P , were calculated as

$$P = \frac{q}{t} \frac{l}{A \Delta p} = F_{ss} \frac{l}{A \Delta p} \quad (2)$$

where q is the mass of permeant, l is film thickness, A is film area, t is time, and Δp is the driving force expressed as the pressure gradient across the film during the permeation process. Since the permeant concentration was experimentally controlled through gas chromatography, the values were converted into partial pressures based on the ideal gas law. When the units for all magnitudes in eq 2 are consistent with any system of units, the final values are given in units of time, i.e., seconds. However, the values of P expressed in seconds are very low, and the use of attoseconds (as = 10⁻¹⁸ s) is more convenient. In SI, 1 s is equivalent to (kg·m)/(m³·s·Pa).

From the transient state data, the kinetics of the process can be determined. The diffusion coefficient of the permeant through the film was obtained from the time at which permeant flow was one-half of that at the end of the experiment, $t_{1/2}$ (Crank, 1975):

$$D = \frac{l^2}{7.205 t_{1/2}} \quad (3)$$

However, the use of this equation to determine D may result in significant errors if the experiment does not follow 'ideal' conditions. In a previous paper (Gavara and Hernandez, 1993) a consistency test was presented to check the applicability of expression 3. From this test it was deduced that it was more accurate to use an average value for D from the three data obtained through

$$D = \frac{l^2}{10.784 t_{1/4}}; D = \frac{l^2}{7.205 t_{1/2}}; D = \frac{l^2}{4.751 t_{3/4}} \quad (4)$$

where $t_{1/4}$, $t_{1/2}$, and $t_{3/4}$ are the times at which the permeant flows are $1/4$, $1/2$, and $3/4$ of the flow at the end of the experiment, respectively. The values of D presented in this paper were obtained through this procedure.

Considering that the transport process accomplishes Henry's law at the concentration range of the tests, the solubility coefficient can be estimated as:

$$S = \frac{P}{D} \quad (5)$$

This approach is commonly used in permeation experiments (Apostopoulos and Winters, 1991; Leufven and Stoellman, 1992; Kobayashi et al., 1995).

RESULTS AND DISCUSSION

Molecular Weight Distribution. The molecular weight distributions of the three polymeric samples are presented in Figure 1, and Table 1 summarizes the values of M_w and dispersion index (I_D). ULDPE had both a higher value of weight-average molecular weight and a broader molecular weight distribution than the metallocene copolymers. The values of M_w for ULDPE was 7.92×10^4 , while those for metallocene copolymers were 6.55×10^4 and 6.02×10^4 Da. All three distributions can be considered to be narrow molecular distributions according to the accepted criteria that a narrow molecular distribution has a dispersion index < 6 . The dispersion index for ULDPE was 4.4 and for metallocenes 2.7 and 2.4. These results confirm one of the most significant claims made by manufacturers about metallocenes being narrower in molecular weight distribution than any other polyethylene. Such narrow distributions result from the stereoregularity of the polymerization process obtained with metallocene catalysts (Thayer, 1995).

Melting Temperatures. Differences in molecular weight and molecular distribution affected melting temperature and melting enthalpy. The melting temperature of ULDPE was 120.7°C , while those of the two metallocenes were 99.4 and 92.7°C (Table 1). The lower melting temperatures for metallocene copolymers were consistent with the lower M_w values. Figure 2 presents the thermograms corresponding to the three samples around the melting temperature region. From Figure 2 we can see that the metallocene samples had lower values of melting temperature, and their melting temperature ranges were narrower than that of ULDPE, as expected. For packaging applications where polyethylene is used as heat-seal layer or heat-sealable film, a polyethylene of low melting temperature will have a low heat-seal temperature. Similarly, a polyethylene with narrow melting range will have better hot-tack characteristics than a polyethylene of broader distribution since the temperature seal will cool below the melting range in a shorter time. These results confirm the good hot-tack sealability of metallocene ethylene-based copolymers.

Crystallinity. Crystallinity was calculated from eq 1. The melting enthalpies ΔH_m of the samples were obtained by numerical integration of the curves of Figure 1 around the peaks and are presented in Table 1. For polyethylene $\Delta H_m^c = 260 \text{ J/g}$ (Brandrup and Immergut, 1989). Therefore the calculated crystallini-

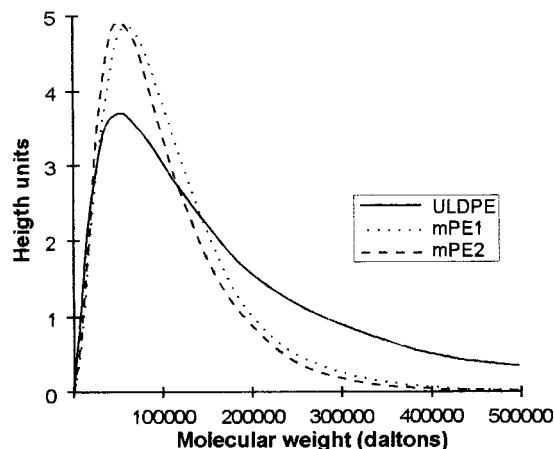


Figure 1. Molecular weight distribution of the three polymeric samples: ULDPE, mPE1, and mPE2.

Table 1. Characterization of LLDPE and Metallocene Ethylene-Based Copolymers (mPE1 and mPE2)^a

sample	thickness (μm)	M_w (g/mol)	I_D	T_m ($^\circ\text{C}$)	ΔH_m (J/g)	α_c	P [($\text{m}^3 \cdot \text{m}$)/($\text{m}^2 \cdot \text{s} \cdot \text{Pa}$)]
ULDPE	78	79 200	4.4	120.7	107.0	0.46	8.2×10^{-17}
mPE1	57	65 500	2.7	99.4	87.7	0.34	12.9×10^{-17}
mPE2	54	60 200	2.4	92.7	78.2	0.30	13.6×10^{-17}

^a Molecular weight average and distribution ratio (M_w and I_D), melting temperature, enthalpy of melting and crystallinity (T_m , ΔH_m , and α_c), and oxygen permeability (P).

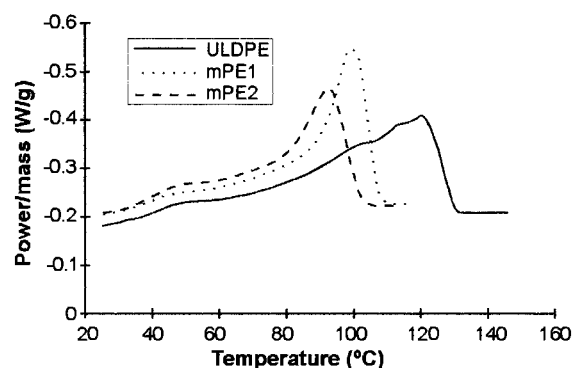


Figure 2. Melting profiles of the three polymeric samples obtained by DSC.

ties of the samples were 0.46 for ULDPE, 0.34 for mPE1, and 0.30 for mPE2 (see Table 1).

Oxygen Permeability. Oxygen permeabilities of the films were measured at 23°C and 0% relative humidity and are presented in Table 1. As seen, polymer morphology, α_c , affects the mass transport characteristics of polymers since penetrant molecules diffuse exclusively through the amorphous regions of the polymer matrix (Hernandez, 1996). Since the fraction of amorphous region is $1 - \alpha_c$, the experimental oxygen permeability values can be normalized dividing experimental values by $1 - \alpha_c$ to give P for a 100% amorphous PE. Normalized P values were $15.2 \times 10^{-17} (\text{m}^3 \cdot \text{m})/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$ for ULDPE and $19.4 \times 10^{-17} (\text{m}^3 \cdot \text{m})/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$ for the two metallocenes indicating that the difference between ZN-PE and mPE is not only due to differences in crystallinity (Table 1).

Aroma Permeability. From the experimental data of permeated flow expressed as a function of time, values of P , S , and D for the organic aroma vapors through the three films were calculated from eqs 2, 4, and 5. Values hereafter presented are those directly

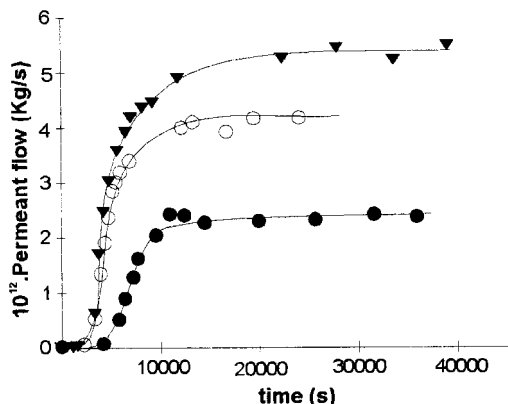


Figure 3. Permeation data of *n*-hexanol through the three films obtained by isostatic experiments and their theoretical curves: (●) ULDPE, (○) mPE1, and (▼) mPE2.

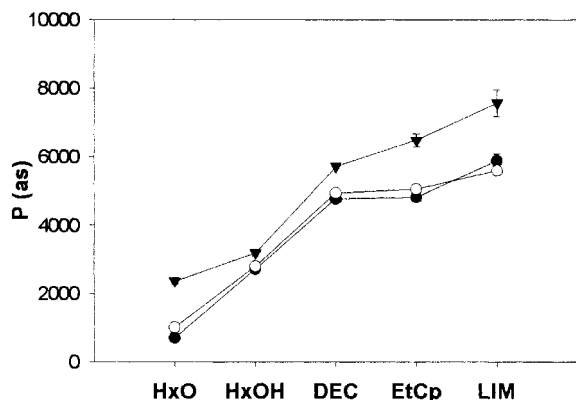


Figure 4. Values of the permeability coefficient for the five aromas and three polymers: (●) ULDPE, (○) mPE1, and (▼) mPE2.

measured and not normalized for crystallinity. Figure 3 shows permeation results of hexanol vapor through the three films. As can be seen, the theoretical curves are in agreement with the experimental data (Gavara and Hernandez, 1993). All curves were in agreement with the consistency test (eq 4) confirming the applicability of the expressions presented. Similar curves were obtained for hexanal, ethyl caproate, *d*-limonene, and *n*-decane. Figure 4 presents the values of the permeability coefficients for all five compounds and polymers under study. Despite differences in the experimental procedure, permeant concentrations, and films, values are within the same range as those published for similar systems: $P(\text{LLDPE}/\text{LIM}) = 30000$ as at 25 °C (Kobayashi et al., 1995), $P(\text{LLDPE}/\text{HxO}) = 4000$ as at 23 °C (Mohny et al., 1988). From Figure 4 it is apparent that the permeability coefficient increases in the following order for the three polymers: hexanal < hexanol < ethyl caproate \approx decane < limonene.

As Figure 4 shows, ULDPE presents the lowest permeability values. Comparing the two metallocene copolymers, the permeabilities of mPE2 were the highest in all cases. These results are in agreement with the values of crystallinity as stated above in the section on oxygen transport.

Calculated values of D and S are presented in Figures 5 and 6, respectively. Values of solubility for ULDPE were lower than those for metallocene materials, but there were no significant differences between mPEs. With respect to diffusion, all permeants diffused faster in mPE2 than in mPE1. This may be a consequence of

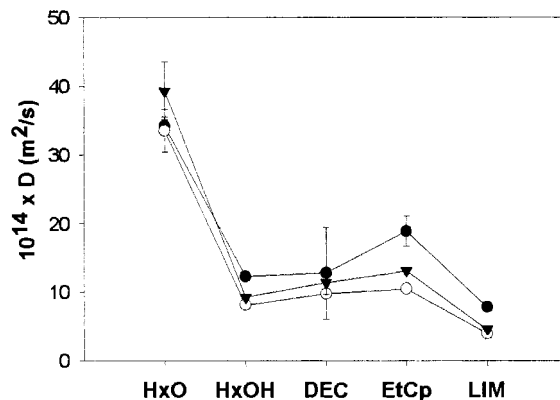


Figure 5. Values of the diffusion coefficient for the five aromas and three polymers: (●) ULDPE, (○) mPE1, and (▼) mPE2.

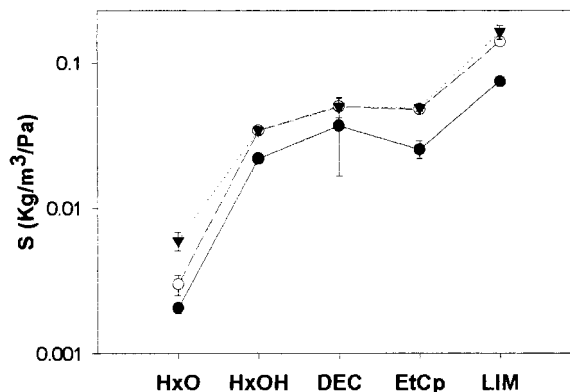


Figure 6. Values of the solubility coefficient for the five aromas and three polymers: (●) ULDPE, (○) mPE1, and (▼) mPE2.

both lower crystallinity and lower weight-average molecular weight of the metallocene polymers. However, the lowest diffusion was found for ULDPE.

Hexanal, which has the smallest molecular weight and is the most volatile aroma (boiling temperature $T_b = 128$ °C), presented the lowest P and S values but the highest D value, while limonene, which has the largest molecular weight and is the least volatile ($T_b = 177$ °C), presented the highest S and the lowest D values. From Figure 6 it can be seen that aroma compounds of greater molecular weight are sorbed nearly 100 times more than those of smaller molecular weight. This difference in sorption may result in significant changes in the flavor profiles of foods in contact with PE.

Many parameters affect the mass transport process of organic vapors through polymers such as permeant size, shape, condensability (or volatility) of the vapor, and polarity (Leufven and Stollman, 1992). Molecular dimensions can be measured by molecular weight (M), molecular volume (V), or number of carbon atoms and condensability through the boiling temperature (T_b) or vapor partial pressure (p°_v) at saturation (Gavara et al., 1996b; Aucejo et al., 1998). Promising attempts to describe equilibria using group contribution theories have been published (Strandburg et al., 1991; Baner, 1992; Paik and Tigani, 1993). In this work we have evaluated the dependency of P , D , and S on M , V , T_b , and p°_v . None of these variables by themselves show any statistically significant effect on the transport coefficients.

The polarities of both permeant and polymer have been used to show their compatibility, although often

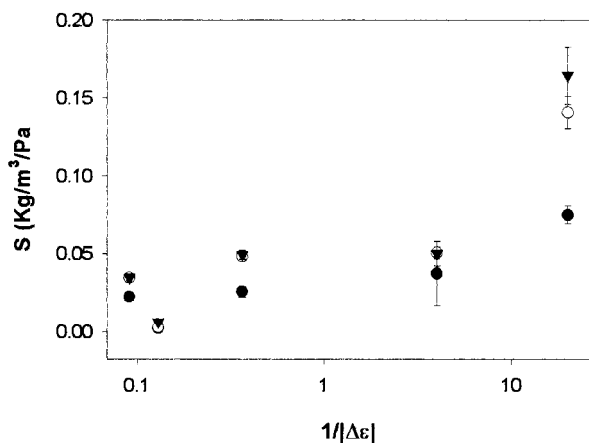


Figure 7. Values of S as a function of the inverse of the difference in dielectric constants between polymer and permeant: (●) ULDPE, (○) mPE1, and (▼) mPE2.

Table 2. Values of Molecular Weight, Boiling Temperature, and Dielectric Constant of the Compounds Studied

compound	M_w (g/mol)	T_b °C	dielectric constant
<i>n</i> -hexanal	100.2	128	10 ^a
<i>n</i> -hexanol	102.2	158	13.3
ethyl caproate	144.2	168	4.2 ^a
<i>n</i> -decane	142.3	174	1.99
<i>d</i> -limonene	136.0	177	2.3
PE			2.26

^a Approximated value.

in qualitative comparisons. The dielectric constant (ϵ) gives a direct measurement of the polarity of an organic compound (Yu et al., 1998) and is commonly used in liquid chromatography to correlate the mobile phase with the stationary phase. The difference in the dielectric constant between polymer and permeant ($\Delta\epsilon$) may therefore quantify their degree of compatibility. Figure 7 presents a plot of the solubility coefficients as a function of the inverse of the absolute difference in dielectric constant between the permeant and the polymer ($1/|\Delta\epsilon|$). Values for dielectric constants of the permeant compounds and PE are listed in Table 2 (Weast et al., 1987). Using Sigma Plot version 4.0, the values of the solubility were fit to a straight line ($S = y_0 + a/|\Delta\epsilon|$) with a regression coefficient of 0.99. The correlation parameters were $y_0(\text{ULDPE}) = 0.018 \pm 0.006$, $y_0(\text{mPE1}) = 0.027 \pm 0.010$, $y_0(\text{mPE2}) = 0.027 \pm 0.009$, $a(\text{ULDPE}) = 0.0029 \pm 0.0007$, $a(\text{mPE1}) = 0.0057 \pm 0.0010$, and $a(\text{mPE2}) = 0.0068 \pm 0.0010$. This indicates that S depends significantly on polarity with a confidence higher than 95%. Applying the same procedure to the diffusion and permeability coefficient values, no statistical correlations were found. D appeared to increase as both the differences in dielectric constant and the boiling temperature decreased.

A significantly larger pool of data (P , D , S) is necessary to correlate the above parameters combined. It would be necessary to characterize the mass transport of permeants with wider ranges in size, shape, condensability, and polarity. Currently efforts are being carried out to optimize a fast method to determine P , D , and S in vapor/polymer systems which would facilitate the obtention of a larger database.

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