

## Characterization of the Interaction between Two Food Aroma Components, $\alpha$ -Pinene and Ethyl Butyrate, and Ethylene–Vinyl Alcohol Copolymer (EVOH) Packaging Films as a Function of Environmental Humidity

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The ethylene–vinyl alcohol copolymers (EVOHs) are well-known high oxygen barrier materials that are being used successfully in the design of packaging structures for oxygen-sensitive food or pharmaceutical products. Recently, there has been increasing interest in using EVOH materials to provide a high barrier to organic compounds as a means to reduce food aroma scalping. However, the barrier function of this family of materials diminishes significantly in humid environments, and it is supposed that so does the organic vapor barrier. In this work, a new sorption-based method to characterize the interaction between food aroma and polymer films for packaging as a function of relative humidity is presented and is used to determine the barrier to ethyl butyrate and  $\alpha$ -pinene of EVOH at 23 °C. The results show that although EVOH is an excellent barrier to food aroma when dry, a property that even improves at low relative humidity (RH), the solubility and diffusivity of the compounds tested increase dramatically with humidity at medium to high water activities. However, even in the worst case (100% RH), EVOH outperforms low-density polyethylene (LDPE) as a barrier to organic vapors at least 500 000-fold.

**KEYWORDS:** Food aroma mass transport; sorption process; water plasticization; diffusion; organic compounds

### INTRODUCTION

Plastic materials are increasingly being used in the manufacture of food packages and containers as they are versatile, their properties can easily be adjusted to specific demands, and these qualities come at a reasonable cost. In these applications, one of the most crucial properties of plastics is their capacity (to an extent that depends on the polymeric material) to allow the sorption and diffusion of low molecular weight compounds, which ultimately are responsible for the permeation, migration, and retention of gases and vapors.

Among the plastic materials, polyethylenes and polypropylenes (homo- and copolymers) are the most commonly used materials in package design. They are selected for contact with the product both in monolayer and in laminated or coextruded structures, because these polyolefins present chemical resistance and inertness to most foods, a good barrier to water (humidity), and thermosealability. However, their polyolefinic nature gives them high lipophilicity; therefore, they are able to retain large amounts of nonpolar compounds such as most of the aroma compounds. This food–packaging interaction, known as aroma

scalping, causes a loss of aroma content and/or an aroma imbalance, because scalping of the diverse aroma components of a food product progresses to different extents and at different rates.

Many studies reflect the high capacity of these polymers to absorb organic compounds (1–3). Mannheim et al. (4) observed that the D-limonene content of orange juice packaged in a carton container decreased by 40% during the first 6 h of storage. Lagaron and co-workers (5, 6) proved by gravimetry and FT-IR spectroscopy that low-density polyethylene (LDPE) can sorb up to 17% of limonene.

With the aim of minimizing this effect, which inherently leads to a reduction in product quality, high-barrier plastic materials could present an alternative to commodity polyolefins. Such materials are being used in the design of food packages because they provide very low permeability to oxygen and other permanent gases. Whether these materials also provide a barrier to water or organic compounds should be tested, because the “high-barrier” qualifier exclusively reflects such behavior with respect to oxygen. Indeed, ethylene–vinyl alcohol copolymers (EVOH), which are among the materials with the highest oxygen barrier, are medium to poor water barrier plastics (7). Moreover, the hydrophilic nature of these materials is known to promote

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the sorption of large amounts of water, which results in plasticization of the copolymers and the subsequent loss of mechanical and barrier properties. The oxygen permeability of EVOH copolymers is known to increase by a factor of 100–1000 on changing from dry to humid conditions. For this reason they are currently used sandwiched between layers of LDPE (or similar materials) to protect them from water.

This paper considers the use of EVOH as a food contact material to decrease the interaction with food aroma. The character of EVOH as a barrier to food aroma components has scarcely been studied, and how this interaction is affected by the food's relative humidity was unknown. In this work, sorption of ethyl butyrate and  $\alpha$ -pinene, two substances present in the aroma of fruit juices and selected as representatives of food aroma components, was characterized as a function of the environment's relative humidity. With this aim, a new and simple method to characterize organic vapor transport through polymer films was used. The barrier character of EVOH was then compared to that of LDPE.

## MATERIALS AND METHODS

**Materials.** Films of Soarnol EVOH copolymer (10  $\mu\text{m}$  thick) with a 32% ethylene molar content (EVOH-32) and 80- $\mu\text{m}$  thick films of LDPE were supplied by the Nippon Synthetic Chemical Industry Co. Ltd. (Nippon Gohsei, Osaka, Japan). Actual thickness was measured for each sample with a manual Mitutoyo Alfa-Mirage micrometer (Metrotec, San Sebastian, Spain).

$\alpha$ -Pinene and ethyl butyrate of the highest purity were purchased from Aldrich (Steinheim, Germany). They were used as selected components of food aromas.

Saturated salt solutions were used to obtain constant relative humidity (RH) environments: 23% ( $\text{CH}_3\text{-COOK}$ ), 54% [ $\text{Mg}(\text{NO}_3)_2$ ], and 75% ( $\text{NaCl}$ ). Salts of "for synthesis" grade were supplied by Panreac (Barcelona, Spain) (8). Distilled water was used to prepare the solutions and to obtain a water-saturated environment (100% RH).

**Sample Preparation.** Polymer film samples ( $\sim 50\text{ cm}^2$ ), previously vacuum-dried for at least 24 h at 70  $^\circ\text{C}$ , were placed in 250-mL glass jars together with a 20-mL vial containing the saturated salt solution (or pure water). The jars were hermetically sealed with a twist-off closure and stored in an environmental chamber at  $23 \pm 1\text{ }^\circ\text{C}$ . Samples were allowed to equilibrate for at least 1 month (period required to guarantee that the EVOH samples were equilibrated at a given RH, as stated in independent gravimetric experiments) (9). The humidity obtained with each salt was previously measured in independent containers with high-precision hydrodynamic hygrosensors (Jessup, MD) and checked in each container with a humidity indicator (Panreac).

Once the samples had been equilibrated in the humidity conditions employed, a vial containing  $\sim 2\text{ mL}$  of the pure liquid organic compound was placed in the jar and the film samples were exposed to its vapor. This moment is considered time zero for the sorption process. The jars were then stored at 23  $^\circ\text{C}$ . Additionally, dry film samples were placed in empty jars and immersed in the pure organic compound, stored at 23  $^\circ\text{C}$ , and analyzed in a similar manner (these films are named throughout this work as the 0% RH samples).

**GC Analysis.** Analysis of the organic compound uptake was conducted using a Dynatherm Thermal Desorber (Supelco, Teknokroma, Barcelona, Spain) connected in series to the column of an HP5890 gas chromatograph via a heated transfer line. At different time intervals, a cut piece of the film was cleaned with a paper tissue to remove any organic compound or water that might have condensed on the film surface and then inserted into an empty desorption tube. The tube was placed in the desorber chamber, which was immediately sealed. Conditions for desorption were as follows: desorption temperature, 170  $^\circ\text{C}$  (150  $^\circ\text{C}$  for LDPE); transfer line, 180  $^\circ\text{C}$ ; desorption time, 300 s. The GC was equipped with an Ultra 2 (25 m, 0.2 mm, 0.33  $\mu\text{m}$ ) column and a flame ionization detector (Agilent Technologies, Barcelona, Spain). After the analysis, the film sample was recovered from the desorption tube and weighed (free of volatile sorbates) on an

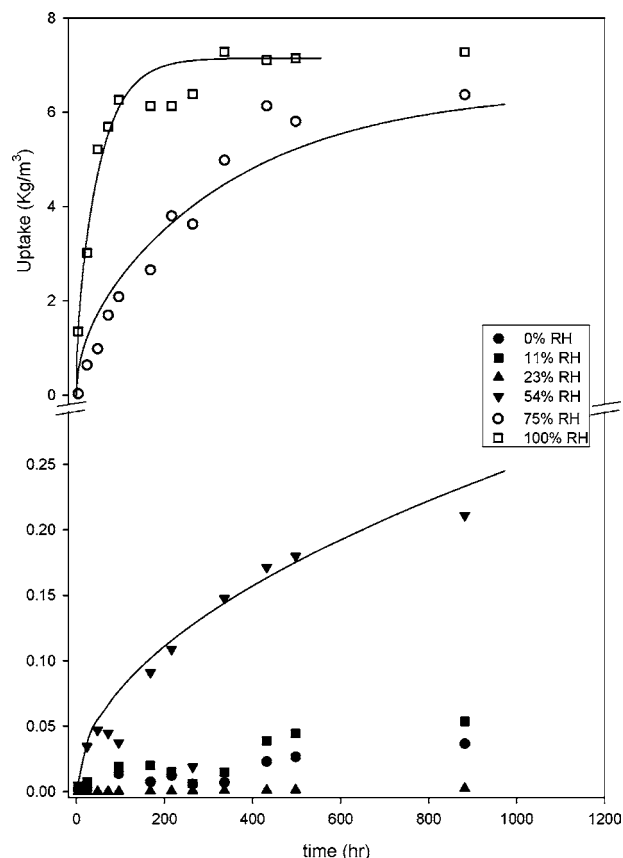
analytical balance. The desorber-GC was calibrated by measuring other polymeric film samples with known amounts of each aroma (measured independently by gravimetry).

**FTIR Analysis.** In previous works (5, 6), a method based on the analysis of film samples by transmission FT-IR spectroscopy was optimized to determine the mass transport of vapors in thin polymeric films. In this study, this technique was employed to corroborate that the amount of water sorbed by the EVOH films remained constant throughout the sorption experiment. At different intervals during the organic vapor sorption process, film samples of  $\sim 15\text{ cm}^2$  surface area were thoroughly wiped to remove the volatile condensate over the surface and immediately placed in the measuring chamber, where the transmission spectra were recorded. Specimens were analyzed by means of FT-IR transmission experiments with a Bruker FT-IR Tensor 37 equipment with 4  $\text{cm}^{-1}$  resolution and 5 s as the typical acquisition time. The spectra were first normalized by using the 1333  $\text{cm}^{-1}$  band as reference (10) to remove any film thickness effect and then compared to check for differences in water content.

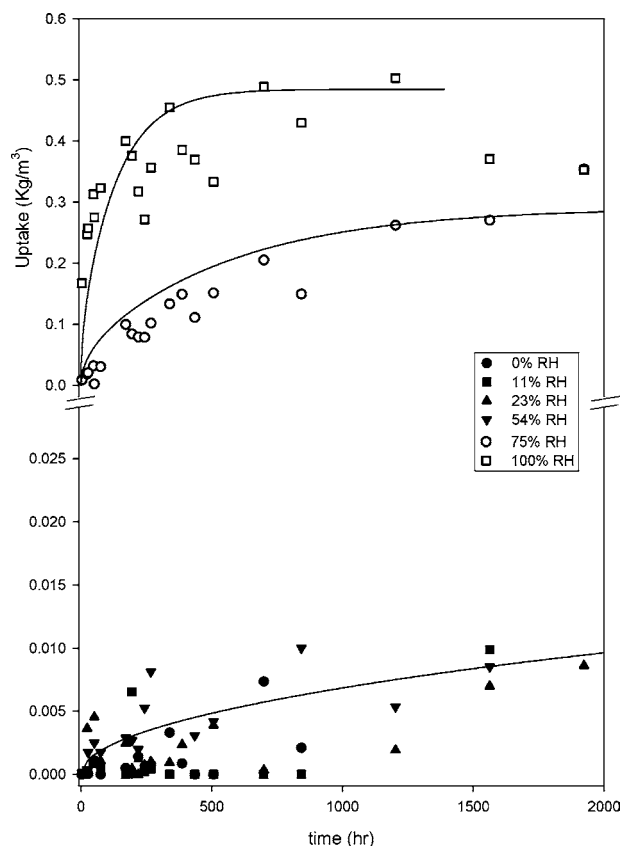
LDPE films of  $\sim 150\text{ mg}$  were dried at 70  $^\circ\text{C}$  under vacuum ( $P < 50\text{ mmHg}$ ) for 48 h and immediately immersed in pure liquid organic compound and stored. The samples' weight was monitored until they reached constant weight. Once equilibrated, the sample was thoroughly wiped to remove the volatile condensate over the surface and immediately placed in the FT-IR measuring chamber, which was constantly purged with dry nitrogen to keep the environment free of the organic compound. Transmission spectra were recorded until no changes were detected. The area of the bands assigned to the sorbed organic compound was monitored as a function of time. A detailed description of the technique has been already published (5, 6).

## RESULTS AND DISCUSSION

The interaction of two food aroma components in EVOH-32 in humidity conditions ranging from 0 to 100% was investigated



**Figure 1.** Sorption of ethyl butyrate in EVOH-32 as a function of time. Symbols correspond to experimental data at the relative humidity specified in the legend, and lines are the theoretical curves obtained with the mass transport constants listed in Table 1.

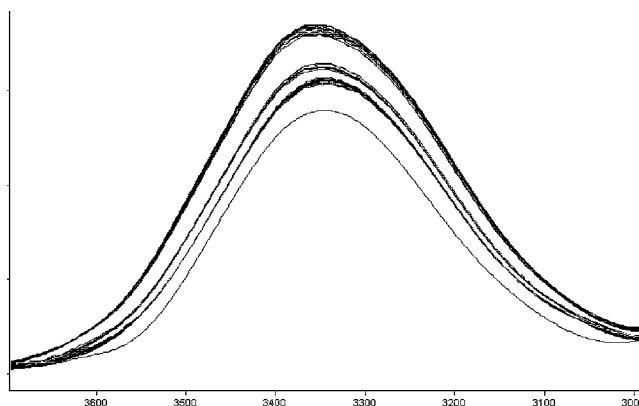


**Figure 2.** Sorption of  $\alpha$ -pinene in EVOH-32 as a function of time. Symbols correspond to experimental data at the relative humidity specified in the legend, and lines are the theoretical curves obtained with the mass transport constants listed in **Table 1**.

**Table 1.** Values of the Equilibrium Concentration ( $C$ ), Solubility ( $S$ ), Diffusion ( $D$ ), and Permeability ( $P = DS$ ) Coefficients Obtained from Ethyl Butyrate and  $\alpha$ -Pinene Sorption Experiments in EVOH-32 at 23 °C under Different Relative Humidity (RH) Conditions

RH (%)	$C$ (kg/m <sup>3</sup> )	$S$ (kg/[m <sup>3</sup> ·Pa])	$D$ (m <sup>2</sup> /s)	$P$ (kg·m/[m <sup>2</sup> ·s·Pa])
Ethyl Butyrate				
0	<0.028	<1.3e-5	<1e-18	<1.3e-23
11	<0.025	<1.2e-5	<1e-18	<1.2e-23
23	<0.01	<4.8e-6	<1e-18	<4.8e-24
54	0.58	2.7e-4	1e-18	2.7e-22
75	6.5	3.1e-3	8e-18	2.5e-20
100	7.15	3.4e-3	5e-17	1.7e-19
$\alpha$ -Pinene				
0	<0.005	<8.4e-6	<1e-18	<2.4e-24
11	<0.002	<3.4e-6	<1e-18	<1e-25
23	<0.003	<5.0e-6	<1e-18	<1.4e-24
54	1.42e-2	2.4e-5	1e-18	2.4e-23
75	0.291	3.8e-4	5e-18	1.9e-21
100	0.485	5.3e-4	2e-17	1.1e-20

by monitoring the sorption process through the method described under Materials and Methods. **Figures 1** and **2** present the amount of ethyl butyrate and pinene sorbed by the EVOH-32, respectively, as a function of time and relative humidity. As expected, the aroma uptake by this hydrophilic copolymer was greatly influenced by the water present in the polymeric matrix: the concentration of the two compounds increased dramatically with the relative humidity. **Table 1** summarizes the results obtained, expressed as equilibrium concentration values and solubility, diffusion, and permeability coefficients. In dry or low relative humidity conditions, EVOH-32 behaves like a quasi-infinite barrier to the transport of organic com-

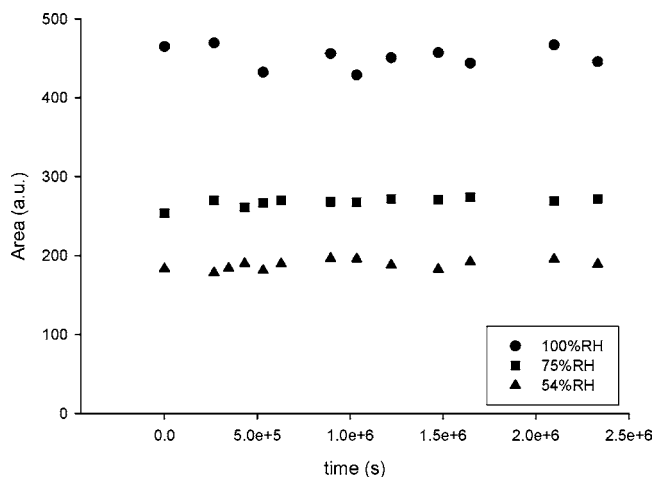


**Figure 3.** Detail of the OH stretching band of EVOH-32 films equilibrated at 0, 54, 75, and 100% RH (bottom to top) obtained by FT-IR spectroscopy during the ethyl butyrate sorption experiments (1-month exposure time).

pounds. In fact, some concentration values at equilibrium were below the experimental error of the technique (0.01 kg/m<sup>3</sup> for ethyl butyrate and 0.001 for pinene) and were 1000 times lower than those measured in LDPE. Another interesting feature is that the mass of the two compounds sorbed by EVOH-32 at 11 and 23% RH was below the values obtained under dry conditions. This improvement in barrier function at low humidity compared to that under dry conditions was also observed in the characterization of oxygen permeation processes through EVOH copolymers (7) and can be explained as a phenomenon of competition between the water molecules and the organic substance for the available free volume sites. However, at intermediate to high relative humidity the uptake increased and the diffusion process quickened. This can be interpreted as a consequence of the well-known plasticizing effect of water on these copolymers (9). The reduction of the glass transition temperature to values below room temperature increases polymeric chain mobility and, concomitantly, more free volume becomes available for the sorption process.

To fully characterize the mass transport process, the experimental values obtained during the transient state must be adjusted to a suitable solution of Fick's laws. Therefore, the boundary conditions must be clearly defined. Initially, it must be assumed that the initial concentration of the organic compound in the film is zero and that at  $t = 0$  the film is exposed to a constant concentration of the organic compound, which is maintained invariant throughout the experiment. In this study, the film was exposed to the environment generated by the pure liquid organic compounds. Throughout the experiments, gas samples were withdrawn from the container and analyzed by gas chromatography. Values obtained were  $0.09 \pm 0.01$  kg/m<sup>3</sup> for ethyl butyrate and  $0.025 \pm 0.002$  kg/m<sup>3</sup> for pinene, practically invariant throughout the tests irrespective of the relative humidity of the test jar. Due to the significant effect of water on the properties of EVOH copolymers, it was fundamental for the analysis of the results to confirm that the water sorbed in the samples did not vary during the assay. Initially, the storage of the jars in a temperature-controlled chamber and the presence of salt precipitate in the vials placed in the jars are factors that point to a constant relative humidity. Nonetheless, the amount of water sorbed by the films was checked regularly throughout the experiment, using Fourier transform infrared spectroscopy according to the procedure already described.

An example of the results obtained is given in **Figure 3**. Specifically, the image shows the OH stretching band of the



**Figure 4.** Area of the OH stretching band of samples equilibrated under different relative humidity conditions throughout the ethyl butyrate sorption experiments in EVOH-32.

spectra recorded during ethyl butyrate sorption experiments lasting 1 month, carried out at different humidities. It will be observed that as the relative humidity increased the polymer sorbed more water molecules and the absorbance of the band increased. However, for a given humidity condition the area of the band does not change significantly with time. **Figure 4** shows the evolution over time of the band area at three relative humidities. The above comments clearly reflect that (a) the area of the band increases with relative humidity as a consequence of the increment in the water taken up by the sample and (b) the water present in the polymer film can be considered constant during the sorption experiment.

With these results and taking into account that the organic compound was placed in the sorption cell when the polymer had already been equilibrated at the relative humidity of the experiment, it is appropriate to assume that any plasticizing effect of water occurs prior to the beginning of the experiment. Subsequently, the diffusion coefficient of the organic compound was considered to be constant during each experiment. With this assumption and the previous boundary conditions, the values of the diffusion coefficient were obtained by fitting the experimental values to the expression

$$\frac{M_t}{M_0} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{-\frac{D(2n+1)^2\pi^2 t}{L^2}\right\} \quad (1)$$

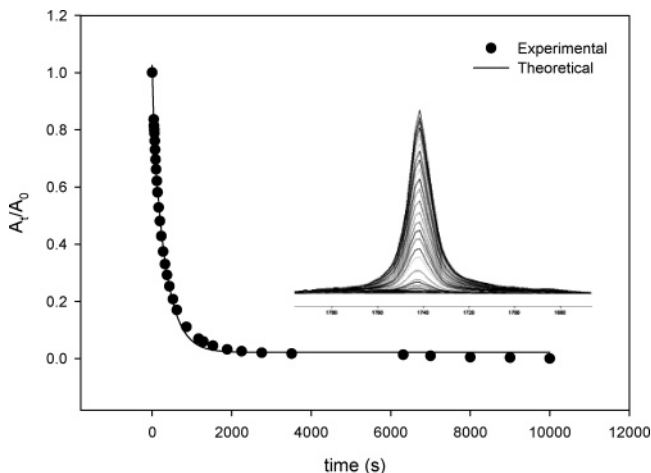
where the ratio between the penetrant mass retained in the sample at time  $t$  and the initial penetrant mass is a function of time ( $t$ ), thickness ( $L$ ), and the diffusion coefficient ( $D$ ).

**Table 1** includes the values of the mass transport coefficient obtained for the two organic compounds at the different relative humidities tested. Due to the experimental error, it was not possible to adjust the experimental data (with an acceptable error) to eq 2 for the sorption processes carried out at the lower relative humidities. Consequently, the  $D$  values at 0, 11, and 23% RH listed in **Table 1** are exclusively an estimated range. At medium and high relative humidity conditions, the sorption processes appear to follow Fick's law. **Figures 1** and **2** include the theoretical curves obtained with the  $S$  and  $D$  values listed in **Table 1**. As can be seen, there is a good agreement between experimental and theoretical values.

Similar tests were carried out on LDPE films; however, the sorption values obtained were invariable with time and relative humidity. This constancy indicates that (a) the sorption of these

**Table 2.** Values of the Equilibrium Concentration ( $C$ ), Solubility ( $S$ ), Diffusion ( $D$ ), and Permeability ( $P = DS$ ) Coefficients Obtained from Ethyl Butyrate and  $\alpha$ -Pinene Sorption Experiments in LDPE at 23 °C

compound	$C$ (kg/m <sup>3</sup> )	$S$ (kg/[m <sup>3</sup> ·Pa])	$D$ (m <sup>2</sup> /s)	$P$ (kg·m/[m <sup>2</sup> ·s·Pa])
ethyl butyrate	59	0.028	2.7e-12	7.6e-14
$\alpha$ -pinene	120	0.203	1.0e-12	2.0e-13



**Figure 5.** Experimental desorption curve of ethyl butyrate from LDPE measured by transmission FT-IR spectroscopy and the predicted curve using eq 1; detail of the evolution of FT-IR spectra (insert).

compounds progresses too quickly for this technique and (b) the barrier properties of LDPE are not dependent on water activity. From the results obtained, average uptake and solubility values were obtained for the two organic compounds and are presented in **Table 2**.

Because the technique used for EVOH was not suitable for LDPE, the diffusion coefficient was obtained by monitoring the desorption of the organic compounds by FT-IR transmission spectroscopy, following the procedure of Lagaron and co-workers (5, 6). Accordingly, LDPE films previously equilibrated by immersion in the pure liquid compound were placed in the FT-IR cell, and spectra were recorded throughout the desorption process. As an example, **Figure 5** shows the evolution of desorption for ethyl butyrate and a detail of the FT-IR spectra (insert). These values were fitted to the suitable solution to Fick's laws:

$$\frac{A_t}{A_0} = \frac{M_t}{M_0} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{-\frac{D(2n+1)^2\pi^2 t}{L^2}\right\} \quad (2)$$

Assuming the constancy of the extinction coefficient, the mass and absorbance ( $A_t/A_0$ ) ratios should be identical. As can be seen in **Figure 5**, this equation provides a good reproduction of the experimental curve using a constant  $D$  value.

A comparison between the two materials assayed reveals that the EVOH-32 is a material with superior barrier properties to organic vapors such as food aroma components, even under the worst-case condition, that is, 100% RH. The solubility values of the two tested compounds in EVOH-32 were at least 10 times lower than  $S$  values in LDPE. With respect to diffusion data,  $D$  values for LDPE are at least 50 000 times higher than those for EVOH-32.

Because permeation values are the most common parameter for defining barrier properties in the food-packaging area, the values of the permeability coefficient ( $P$ ) obtained through the

known relationship  $P = DS$  have been included in **Tables 1** and **2**. As can be seen, the improved barrier to organic compounds exerted by the application of EVOH-32 instead of LDPE varies between 6 and 10 orders of magnitude. Therefore, the application of EVOH copolymers as the food-contact layer in packaging structures will imply (a) a reduction in food aroma scalping through both a slower sorption process and a reduction in the equilibrium concentration and (b) a very significant improvement in the barrier to permeation processes, which could make these materials an alternative to nonpolymeric barrier layers (metallized films or aluminum foil).

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