Effect of Ethanol on the Sorption of Four Targeted Wine Volatile Compounds in a Polyethylene Film

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ABSTRACT: The objectives of this study were to demonstrate that the presence of ethanol in a solution containing two esters and two aromatic alcohols has several consequences on the sorption of these compounds into polyethylene (PE) film. First, sorption of ethanol into the PE film occurred at the same time as water and reached 8 kg m^{-3} using 12% v/v of ethanol. This sorption was associated with an increase in PE crystallinity, which may have prevented the sorption of volatile compounds despite their strong affinity with PE film, as evaluated by Hansen solubility parameters. Moreover, increasing the ethanol concentration increased the solubility of the four volatile compounds. In the case of aromatic alcohols, the sorption was decreased in the presence of ethanol as expected. In the case of esters, as their hydrolysis was substantial in the presence of water, the consequence was a higher sorption into the PE film in the presence of ethanol than in its absence. Nevertheless, the sorption also depended on the concentration of ethanol and the heterogeneity of the ethanol–water mixture as well as the presence of other volatile compounds, as in the case of 4-ethylphenol. In conditions simulating wine packaging, losses of volatile compound by sorption and by permeation estimated after only 5 days of contact varied between 0.08 and 25% for 2-phenylethanol and ethyl hexanoate, respectively.

KEYWORDS: ethanol, volatile compounds, polyethylene, sorption, wine

■ INTRODUCTION

The extensive use of plastics for food packaging is related not only to their low cost, flexibility, variability in size and shape but also to their thermal stability and their mechanical and barrier properties. Plastic materials can be used either alone or in combination with other barrier plastics or materials such as paperboard to optimize their properties for the specific needs of food products. Their convenience explains their boost in growth in wine packaging through bag-in-box (or BIB). These packages consist of a flexible bag made up of multilayer oxygen barrier plastic films with a spout welded on, inside a cardboard box. The wine is poured due to gravity, and as its volume decreases, the bag collapses and the liquid inside remains without any contact with the air outside; oxidation is prevented, and most of the organoleptic qualities (aroma and color) of the product are retained. However, losses of ethanol and aroma components by sorption into the plastic film or by permeation through the film can occur during storage and could have an impact on product quality. In the most common BIB-type package, different types of polyethylene films (LLDPE, LDPE, MDPE, HDPE) are used as the wine contact material. PE films are known to sorb a wide range of flavor components and more specifically most hydrophobic components, involving a potential unbalanced aromatic profile of the packaged food. Due to their extensive use in plastic-lined aseptic containers for fruit juices, sorption phenomena in PE films have been widely studied,[1−7] and it has been reported that the sorption of volatile compounds depends on the packaging material used as well as on the flavor molecules present, the composition of the food

matrix, and the environmental conditions. The modification of the aromatic profile could be detectable by the human senses.[2,3]

The aroma of a wine consists of several hundred different compounds, the total content reaching approximately 0.8−1.2 g/L, with the fusel alcohols formed during fermentation being responsible for 50% of the content.[8] The concentration of the other volatile compounds ranges between 10^{-4} and 10^{-10} g/L, but their potential losses by interactions with the package can strongly modify the aromatic profile of the packaged wine because their threshold values as perceived by human sensory organs differ dramatically and can vary from 10^{-13} to 10^{-4} g/L.[9] Among the factors affecting the sorption of volatile compounds into the PE, the concentration and chemical characteristics (polarity, volatility, molar mass, and volume) of molecules are substantial. Moreover, the presence of numerous compounds can induce cooperative or competitive effects regarding the transport through the packaging material of each volatile compound.[2,6,9] As far as we know, only one study focused on the sorption of two volatile compounds from a model wine into plastic films such as PE and demonstrated that the loss of ethyl octanoate by sorption determined the imbalance of the original aroma composition.[10] However, no data could be found on the sorption of ethanol into PE films, which is surprising, as it can indirectly affect the volatile compound barrier properties and the aromatic profile of a wine.

As the composition of a food matrix plays an important role in the volatility and retention of volatile compounds, it consequently influences flavor and packaging material interactions.[11−13] Only a few studies have dealt with the potential interaction of volatile compounds with the food matrix components such as proteins, lipids, or polysaccharides.[14−17] Water is often used as the liquid food model even in the case of fruit juices; a study carried out with orange juice has shown that the presence of pulp decreased the absorption of volatile compounds into the polymeric material.[18] The effect of an oily phase has been extensively investigated and resulted either in a lack of the sorption of volatile compounds into the polymer due to their affinity with the oily phase[6] or a plasticization of the polymeric matrix and an increase of aroma sorption.[16] As far as we know, only one study has reported the effect of ethanol concentration on the sorption of volatile compounds in low-density polyethylene (LDPE) films.[19] Maximal sorption of esters, alcohols, and aldehydes was measured for relatively low ethanol concentrations, between 5 and 10% (v/v) depending on volatile compounds. For the highest ethanol concentrations, a decrease of sorption was observed, which was explained by a structural change of water molecule association induced by the addition of ethanol. Moreover, independent of packaging presence, it has been recently described[20−23] that even at relatively low concentrations, ethanol can affect the volatility of volatile compounds by modifying their solubility. This effect has to be taken into account to explain the aroma distribution between packaging material and the ethanolic solution.

The overall aim of this study was to evaluate the losses by sorption and permeation of two esters and two aromatic alcohols from an ethanolic solution into a PE film, usually used as packaging material for wine, with a particular focus on the impact of ethanol on the modification of PE structure and on the hydrolysis and volatility of the four compounds.

■ MATERIALS AND METHODS

Plastic Films. A film commonly used for wine packaging in BIB was selected. According to the supplier, the PE film is made up of 75% linear low-density polyethylene (LLDPE) and 25% LDPE; the thickness is equal to 50 μm and the density to 920 kg m^{-3}. The film exhibits a water vapor permeability of 2.8×10^{-12} g m^{-1} s^{-1} Pa^{-1} and a crystallinity rate of 25%.[24]

Volatile Compounds and Solvents. Dichloromethane with a purity of >99.5% (Carlo Erba, France) was used as an extraction solvent and 2-heptanol with a purity of >99 (Fluka, France) as the internal standard. Esters (ethyl hexanoate and ethyl butyrate) and aromatic alcohol compounds (2-phenylethanol and 4-ethylphenol) with purity in excess of 99% were obtained from Sigma-Aldrich (France). The four aroma compounds are characterized by the following physicochemical properties: for ethyl butanoate, molecular weight = 116.16 g/mol, saturated vapor pressure at 25 °C = 1885 Pa, solubility in water = 4.6 g/L,[20] and estimated hydrophobicity log P = 1.9, partition coefficient between *n*-octanol and water; for ethyl hexanoate, molecular weight = 144 g/mol, saturated vapor pressure at 25 °C = 215 Pa, water solubility = 0.51 ± 0.1 g/L,[20] and estimated hydrophobicity log P = 2.83; for 2-phenylethanol, molecular weight = 122.16 g/mol, saturated vapor pressure at 25 °C = 9.62 Pa, solubility in water 16 ± 3.5 g/L,[25] and estimated hydrophobicity log P = 1.6; for 4-ethylphenol, molecular weight = 122.16 g/mol, saturated vapor pressure at 25 °C = 8.96 Pa, solubility in water 5.65 ± 0.39 g/L,[25] and estimated hydrophobicity log P = 2.6. For aromatic alcohols, vapor pressure was calculated from vapor pressure/temperature couples of *Handbook of Chemistry and Physics* (85th ed., CRC Press), whereas experimental values were used for esters.[26] Log P was calculated with SRC's estimation software (www.syrres.com/esc/).

Model Solution To Simulate Wine. Hydroalcoholic solutions (12 and 15% ethanol v/v) acidified with 3.5 g/L of tartaric acid were used to simulate a simplified wine. The pH was adjusted to 3.5 with 1 N KOH, and 1 mg/L ethyl butyrate, 1 mg/L ethyl hexanoate, 1 mg/L 4-ethylphenol, and 40 mg/L 2-phenylethanol were added. Concentrations of volatile compounds were selected from values found in the literature.[25,27,28]

Ethanol Sorption Measurement. Sorption of ethanol in the liquid phase was determined by immersing small pieces of the film (9 cm^2) in pure ethanol or in an alcoholic solution at 12% v/v (250 mL). The ratio of film surface to volume of solution was 0.036 m^{-1} to favor the sorption phenomena. The total amount of ethanol absorbed by the film at a given time (20 days) was determined after extraction of the PE film with a solvent and GC analysis. Before extraction, the film was wiped to eliminate the solution remaining on its surface. Dichloromethane (10 mL) was used as the extractive solvent, and an internal standard (2-heptanol) was added for quantification by GC analysis. Moreover, the extraction yield was determined by depositing known amounts of ethanol on films and by completing the extraction and GC analysis. By comparing the amount deposited and recovered, a yield of 100% recovery was found.

In parallel, the mass uptake of the film immersed in pure ethanol or ethanol solution at 12% v/v was evaluated at different times by a gravimetric method and expressed in kg m^{-3}. The samples of PE film in contact with ethanol were weighed with a balance having an accuracy of 0.1 mg.

FTIR Measurement. PE film samples were analyzed by FTIR using a triple-reflection diamond crystal. Spectra were acquired using a Nexus 6700 spectrometer (ThermoElectron Corp.) equipped with a HeNe beam splitter and a cooled MCT detector. Spectral data were taken from 64 scans with a resolution of 2 cm^{-1} in the range of 750−4000 cm^{-1}. Three samples of each PE were employed for the measurements, and three spectra were recorded for each sample. All spectra pretreatments were performed using Omnic v7.3 and TQ Analyst v7.3 software (ThermoElectron). Processing included (i) a multipoint linear baseline correction and (ii) a normalization according to the CH$_2$ binding band (1463 cm^{-1}). Spectral analysis was performed on median spectra issued from the nine acquisitions.

Determination of Gas−Liquid Partition Coefficient K_{gl} in Static Conditions. The K_{gl} is defined as the ratio between the gas and liquid concentrations of the volatile compound at thermodynamic equilibrium

$$K_{gl} = \frac{C_{gas}}{C_{liq}} \tag{1}$$

with C_{gas} the concentration of volatile compound in the gas phase and C_{liq} the concentration in the liquid phase. The partition coefficients were determined by the phase volume ratio method (PRV) as described by Ettre et al.[29]

Each volatile compound was first diluted in the model wine solution at the chosen concentration C_{liq}. Aliquots of the solution (0.05−10 mL) were introduced in headspace vials (20.5 mL), which were closed with Teflon/silicone septa in metallic caps, to obtain different volume ratios between the gas (V_g) and liquid phases (V_l). The vials were maintained at 25 °C during 12 h until thermodynamic equilibrium was reached. The area of peak (A) obtained by the headspace measurement by GC is proportional to the concentration of the volatile compound concentration in the headspace. It can be demonstrated that the GC peak area is given by eq 2 and its linear form by eq 3:

$$A = \frac{F \times C_{liq}}{K_{lg} + \beta} \quad \text{with} \quad K_{lg} = \frac{C_{liq}}{C_{gas}} = \frac{1}{K_{gl}} \tag{2}$$

$$\frac{1}{A} = \frac{1}{F \times C_{liq}} \times \frac{1}{K_{gl}} + \frac{1}{F \times C_{liq}} \times \beta \tag{3}$$

with β the volume ratio in the vial $\beta = V_g/V_l$ and F the response factor of the detector.

Table 1. Hansen's Solubility Parameter Values of Plastic Film (PE), Volatile Compounds (ac), Solvents (s), and Solutions (eth12% and eth15%) and the Δδ Difference between Them[a]

substance	δ_D	δ_P	δ_H	δ_T	Δδ PE/s or PE/ac	Δδ water/ac	Δδ eth12%/ac	Δδ eth15%ac	Δδ eth100%ac
LDPE[b]	17.9	0	0	17.9					
ethyl butyrate[c]	15.5	3.7	7.3	17.5	8.5	37.0	36.1	35.5	31.1
ethyl butyrate[d]	13.8	7.6	6.4	17.0	10.7	35.7	35.8	34.7	32.3
ethyl hexanoate[e]	15.1	3.1	8.2	17.5	8.7	36.4	35.4	34.8	31.4
2-phenylethanol[e]	19.1	3.7	12.7	23.3	13.3	32.2	31.3	30.7	27.1
4-ethylphenol[e]	17.7	3.8	11.9	21.6	12.5	32.8	31.8	31.2	28.6
water[d]	15.6	16	42.3	47.8	46.1				
ethanol[d]	15.8	8.8	19.4	26.5	22.9	24.0			
ethanol 12% (v/v)[f]	15.6	16.0	41.2	46.9	45.1	9.6			
ethanol 15% (v/v)[f]	15.6	15.6	40.8	46.4	44.5	11.7			

[a]δ_D, dispersive parameter; δ_P, permanent dipole−dipole interaction parameter; δ_H, hydrogen bonding parameter; δ_T, solubility parameter. [b]Reference 30. [c]Reference 44. [d]Reference 32. [e]Calculated by Molecular Modelling Pro software. [f]Calculated from the reference of ethyl alcohol and water considering their respective molar fractions.

By plotting $1/A$ against β and carrying out regression analysis, K_{gl} can be determined as the ratio between the slope and the interception.

Hansen's Solubility Parameters. The affinity between chemical compounds and a polymer or a solvent is often predicted using solubility parameters and more specifically by Hansen's solubility parameters (δ_T), which take into account the overall solubility parameter including the dispersive, polar, and hydrogen-bonding contributions.[30−32] The calculated Hansen solubility parameter values for the polymer, the different solutions, and the volatile compounds are reported in Table 1. For the hydroalcoholic solutions, the parameters were calculated from the value of pure ethanol and pure water taking into account the ratio between the molar fraction of ethanol and water. As the ethanol molar fraction is negligible compared to the water molar fraction, the values of solubility parameters are almost unchanged for 0−15% v/v of ethanol solutions (Table 1). The interactions between the polymer and each volatile compound or between solutions and each volatile compound can be deduced by calculating the Δδ using the following equation (here given for polymer (P) and volatile compound as solute (S)):

$$\Delta\delta = [(\delta_{DP} - \delta_{DS})^2 - (\delta_{PP} - \delta_{PS})^2 - (\delta_{HP} - \delta_{HS})^2]^{1/2} \quad (4)$$

Hydrolysis of Esters. One hundred milliliters of solutions of ethyl hexanoate or ethyl butyrate at 1 mg L^{-1} were prepared in acidified water (containing sodium azide at 2% w/v) or in acidified ethanol solution at 12% v/v. The pH was adjusted to 3.5 with 1 N KOH. After 21 days, the solutions were extracted with 2 × 25 mL of dichloromethane in the presence of the internal standard (100 μL of 2-heptanol solution at 25 g L^{-1} in ethanol). The organic extract was evaporated under nitrogen flux and analyzed by GC. The percentage of hydrolysis was calculated as the ratio between the concentration of hydrolyzed ester (initial concentration minus residual concentration) and the initial concentration. The initial concentration was evaluated according to the same method as residual concentration.

Aroma Sorption Measurements. The amount of volatile compounds adsorbed in the film was studied by immersing small pieces of the film (9 cm^2) in the model wine solutions containing the volatile compounds alone or in mixture (250 mL). The ratio of film surface to volume of solution was 0.036 m^{-1} as for ethanol sorption measurement. The experiments were carried out in triplicate at 25 °C.

The total amount of volatile compound sorbed by the film at a given time was determined by extraction with 10 mL of dichloromethane. Before extraction, the film was wiped to eliminate the solution remaining on its surface. A known amount of internal standard (100 μL of 2-heptanol solution at 25 g L^{-1} in ethanol) was added to the mixture, which was submitted to magnetic agitation (300 rpm) for 16 h. The resulting organic phase was dried using ammonium sulfate and analyzed by gas chromatography. For each compound, the extraction yield was determined by depositing known amounts of the compound on films and by completing the extraction and GC analysis. By comparing the amount deposited and recovered, the following yields

were found: 87% for ethyl butyrate, 88% for ethyl hexanoate, 86% for 2-phenylethanol, and 96% for 4-ethylphenol. The sorption into the PE were determined at different times and expressed in g m^{-3}. The value at 21 days was used to evaluate the material/solution partition coefficient $K_{m/s}$ defined as the ratio of the concentration into the PE film (expressed in g m^{-3}) and the residual aroma concentration in the solution (expressed in g m^{-3}). This concentration was measured by extraction of the solution after 21 days as described previously for the hydrolysis of esters.

Volatile Compound Losses by Sorption and Permeation. To determine the volatile compound losses in conditions close to wine packed in BIB, a specific experimental system was used. The film was placed between two Teflon rings screwed directly to a vial containing 5 mL of the solution modeling wine. The area of exposed film was 7.85 × 10^{-5} m^2, and the ratio of film surface to solution volume was 15.7 m^{-1} and was close to that encountered for wine packaged in 3 L BIB (26.1 m^{-1}). The vial was reversed to mimic the contact of liquid with the film and was put on a clerestory support in a flask with a volume of 100 mL, which was sealed with hole-caps and PTFE/silicone septa allowing the entry of an SPME fiber. The flask was maintained in a ventilated oven regulated at 25 °C. After 5 days, the volatile compounds, having permeated through the film, were concentrated for an hour on an SPME fiber. The fiber employed was a 50/30 μm, 2 mm DVB−CAR−PDMS fiber previously conditioned by heating (270 °C for 2 h) in the injection port of the GC according to the manufacturer's instructions (Supelco, Bellefonte, PA, USA). After extraction, the fiber was retracted and then inserted into the GC injector for thermal desorption at 250 °C for 5 min.

The quantity of each volatile compound, which had permeated, was estimated from the amount in the headspace using the gas/liquid partition coefficient K_{gl} and from calibration curves using SPME analysis of the model solution in the absence of the film. The calibration curve for each compound was obtained using four different dilutions of the model wine solution. The ratio between the peak area of the aroma compound obtained by GC for diluted solutions and for the model wine solution was plotted against the volatile compound amount in the headspace determined from K_{gl}. The analyses were performed in triplicate, and the linear regression was determined using the least-squares method for the four components with the linear regression coefficient varying between 0.97 and 0.99.

In parallel, the quantity sorbed by the film was quantified as previously described. The quantity of aroma remaining in the solution was extracted with 2 × 30 mL of dichloromethane in the presence of the internal standard. The extract was evaporated under nitrogen flux and analyzed by GC.

GC Analysis. A Varian 3800 GC-FID equipped with a DB-5 column (30 m × 0.25 mm, film thickness of 0.25 μm, J&W Scientific) and a flame ionization detector (FID; hydrogen, 30 mL min^{-1}; nitrogen, 30 mL min^{-1}; air, 300 mL min^{-1}) was used. Hydrogen was the carrier gas at a flow rate of 2 mL min^{-1}. The temperature was 250

°C for the injector and 300 °C for the detector. For the determination of gas−liquid partition coefficients, isothermal conditions were used (100 or 200 °C for 5 min) depending on the volatile compound. Injections were done in splitless mode.

For the other analysis, programmed thermal conditions were used. Oven temperature initially at 40 °C was raised by 4 °C min^{-1} to 150 °C, then by 15 °C min^{-1} to 250 °C, and was kept at 250 °C for 10 min. Injections were done in split mode, employing a ratio of 1:20, except for SPME for which splitless mode was used.

Statistical Analysis. Statistical analysis was carried out using XLSTAT2008.1.01. A one-way analysis of variance, followed by Tukey's test at 95%, was applied to determine significant differences ($p < 0.05$) between the sorption coefficients and K_{mg} for each condition. For K_{gl}, a 95% confidence interval of mean was determined.

■ RESULTS AND DISCUSSION

Effect of Ethanol Sorption on the PE Film. *Sorption of Ethanol.* The sorption of ethanol was determined after 21 days of contact of the PE film with pure ethanol or ethanol solution at 12% v/v. The film was extracted, and the ethanol amount was estimated by GC analysis. The mass uptake of ethanol by the PE film reached 32.7 ± 0.7 kg m^{-3} using pure ethanol and decreased by a factor of 8.4 using the solution at 12% v/v ethanol (3.89 ± 0.25 kg m^{-3}). Therefore, the sorption appeared to be related to ethanol concentration with a maximal ethanol value representing 3.8% w/weight of film. Thus, the presence of water as a cosolvent did not prevent the ethanol sorption into PE film. In parallel, the total amount sorbed into PE film of pure ethanol or ethanol solution at 12% v/v (Figure 1) was
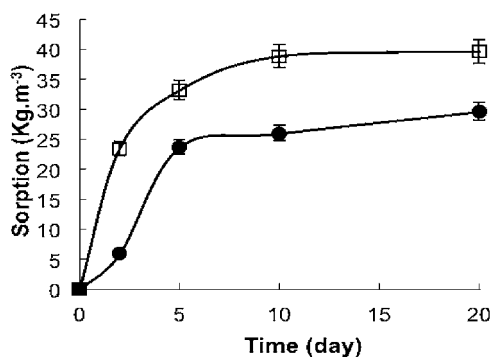

Figure 1. Kinetic sorption of pure ethanol (□) and of a solution at 12% v/v of ethanol (●) into a PE film.

determined using a gravimetric method. For pure ethanol, the mass uptake was found to be similar to that determined by the extraction method, whereas for the ethanol solution at 12% v/v the mass uptake was higher than when using the extraction method. This was due to the water sorption, the ethanol representing only 13% of total amount sorbed. These experiments suggested that ethanol has a stronger affinity for PE than water. It was predicted by the values of the affinities between water or ethanol and the polymer using Hansen's solubility parameters (Table 1). Furthermore, it was also assumed that the sorption of ethanol is limited because the affinities between ethanol and PE or between ethanol and water were close and the affinities of hydroalcoholic solutions for the polymer increased with the ethanol content. The sorption of ethanol and water in PE was substantial, and changes in the material can occur with ethanol and water acting as a plasticizer of PE film and favoring the sorption of ethanol itself or other compounds such as volatile compound.

FTIR Analysis of PE Film. FTIR analysis was applied to specifically investigate sorption of both water and ethanol by the polymer. Indeed, the formation of water clusters due to the vapor sorption in the apolar material has been already observed by FTIR for an LDPE film.[33,34] Three O−H bending bands at 1676, 1645, and 1592 cm^{-1} [32] typically evidence the state of water in polyolefin. Vibration bands at 1645 and 1676 cm^{-1} were assigned to discrete hydrogen-bonded assembly and revealed the occurrence of clusters of water molecules. The band at 1592 cm^{-1} is assigned to free water. Because of the usual higher band intensity of the fundamental stretching mode, water sorption is mainly investigated within a 3900−2800 cm^{-1} range. Spectral fingerprints of the sample after immersion into water or ethanol solutions (Figure 2) exhibited a more intense bending band at 1645 cm^{-1}, and the absence of signal at 1592 cm^{-1} revealed an exclusive water organization under cluster structure within the polymer network. Focused investigation of band intensity at 1645 cm^{-1} revealed a significant decrease in water uptake due to the presence of ethanol in the solution (at both 12 and 15% content). However, no sorption of ethanol into PE film by FTIR was monitored for either alcoholic solutions or for pure ethanol, allowing us to suppose that sorption of ethanol was weaker than water sorption or that ethanol was not detectable due to its dispersed state in the PE film. As previous results (Figure 1) suggested that ethanol sorption was higher than water sorption, the second hypothesis was the most likely.

Additionally, water sorption appeared concomitantly associated with a decrease in PE crystallinity. Change in the degree of crystallization is usually investigated in the frequency region 1440−1480 cm^{-1} (CH$_2$ bending region), which includes the two orthorhombic bands at 1463 and 1472 cm^{-1}. It is well established that a decrease in band intensity at 1472 cm^{-1} is specifically related to an increase of degree of disorder of the polymer resulting from the relaxation of the intermolecular force in the crystal lattice.[35,36] By comparison with the spectra of the initial PE sample, a slight decrease in band intensity at 1472 cm^{-1} was observed on PE samples immersed in water and, to a lesser extent, in pure ethanol and ethanolic solutions. The diffusion of low molecular weight molecules in semicrystalline polymers is known to occur exclusively through amorphous areas. A possible decrease in the crystalline level of PE induced by water sorption would affect the transport of ethanol and volatile compounds through the packaging material.

To conclude, the sorption of ethanol or water was in a similar order of magnitude, but the crystalline structure of the material was affected to a lesser extent by the presence of ethanol solutions than of water. Therefore, by using ethanolic solutions, the sorption of volatile compounds might be limited.

Effect of Ethanol on Volatility and Solubility of Compounds. The volatile compounds selected were two esters, ethyl butyrate and ethyl hexanoate, currently found in wine and two aromatic alcohols, 2-phenylethanol, a major fermentative alcohol, and 4-ethylphenol, an off-flavor of wine. The affinity of volatile compounds for ethanol is known and evidenced by a decrease in volatility due to an increase of their solubility in the ethanol solutions.[20−23] For instance, the solubility of ethyl hexanoate in a 12% v/v ethanol solution was found to increase by 50% relative to its water solubility.[23] Because the sorption can be affected by the affinity between the volatile compound and the solutions, the partition coefficients between the headspace and the liquid phase K_{gl} were
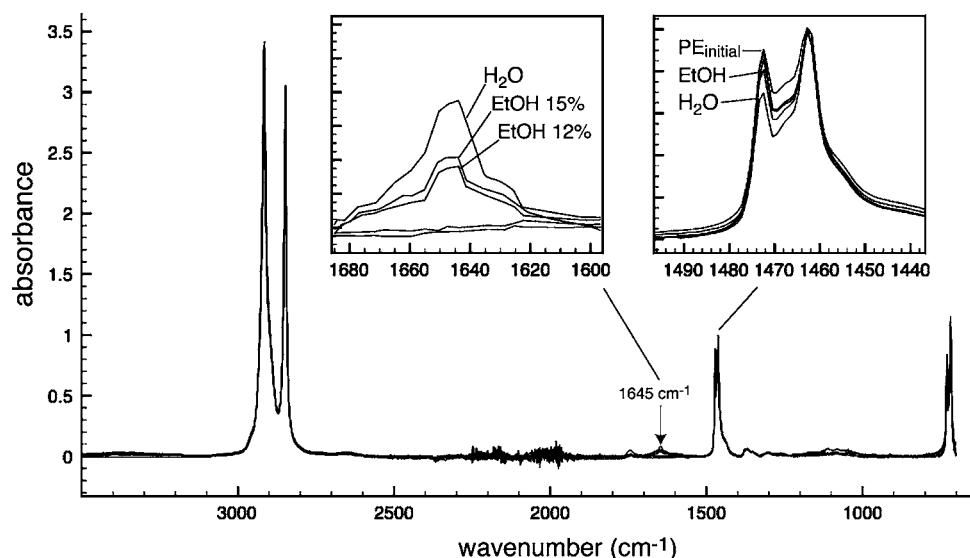
Figure 2. FTIR spectra of PE film after immersion in water (H_2O), in 12% v/v ethanol solution (ETOH 12%), in 15% v/v ethanol solution (ETOH) solution, and in pure ethanol ETOH.

Table 2. Partition Coefficients of Volatile Compounds between the Gas Phase and the Water ($K_{g/water}$) or the Model Wine Solution at 12 or 15% v/v of Ethanol ($K_{g/12\%ethanol}$ and $K_{g/15\% ethanol}$) Measured at 25 °C[a]

	$K_{g/water}$ ($\times 10^2$)		$K_{g/12\%ethanol}$ ($\times 10^2$)		
volatile compd	exptl	lit.	exptl	lit.	$K_{g/15\%ethanol}$ ($\times 10^2$)
ethyl butyrate	2.27 [2.08−2.41]	0.9[b] 1.35[c] 1.79−2.31[d]	1.71 [1.47−1.94]	0.7[b]	1.59 [1.48−1.71]
ethyl hexanoate	3.33 [2.93−3.78]	3.4[c] 3.23−3.35[d] 3.05[e]	2.29 [2.19−2.39]		2.51 [2.26−2.76]
2-phenylethanol	0.134 [0.128−0.139]		0.0086 [0.0077−0.0095]		nm[f]
4-ethylphenol	1.24 [1.16−1.32]		0.135 [0.124−0.146]		nm

[a]95% confidence intervals are shown in brackets. [b]Reference 41. [c]Reference 21. [d]Reference 38. [e]Reference 39. [f]nm, not measurable.

determined (Table 2). Experimental values of K_{gl} were in agreement with the literature[23,37−39] and confirmed the effect of ethanol on the volatility of the esters because a reduction between 25 and 29% was observed in the presence of ethanol at 12% v/v for ethyl butyrate and ethyl hexanoate, respectively. Reductions in volatility of 38 and 58% were reported for ethyl hexanaoate in ethanol solutions of 10 and 20% v/v, respectively,[21] whereas for ethyl butyrate, its headspace concentration decreased by 19% for a 12% v/v ethanol solution compared to water.[23] No significant difference of K_{gl} was found between 12 and 15% (v/v) of ethanol, whereas Whiton and Zoecklein[40] observed for ethyl hexanaote and other compounds a decrease of 20−30% in the headspace concentration between 11 and 14% of ethanol. A reduction in volatility of 90% was observed for 4-ethylphenol in the presence of ethanol. At 15% v/v of ethanol, the volatility of 4-ethylphenol was so weak that K_{gl} could not be measured. These results were in contradiction with previous research, which did not indicate any changes in solubility.[25] Furthermore, a higher K_{gl} value of 4-ethylphenol at 12% v/v of ethanol was found in the presence of other volatile compounds (data not shown) than alone. The presence of ethanol at 12% v/v had the same impact on the volatility of 2-

phenylethanol because a reduction of 93% was observed. Although some authors have shown that the solubility of 2-phenylethanol was not affected by the presence of ethanol,[20] a recent study about interactions between wine volatile compounds and the wine components showed that ethanol at 14% v/v involved a decrease of the headspace concentration of 2-phenylethanol.[41]

In short, the presence of ethanol decreased the volatility of all volatile compounds tested, and their solubilities in ethanol solutions were higher than in water. The impact on sorption will depend on the relative affinity of the volatile compound toward PE and ethanol.

Affinity of Volatile Compounds for Ethanol and PE Calculated by Hansen Solubility. The difference of values of Hansen solubility parameters between a polymer and a penetrant or between a solvent and a solute can be used to assess their potential affinity. The lower the $\Delta\delta$, the more in affinity are the polymer or the solution and the volatile compounds. By comparison of both $\Delta\delta$ values, all of the volatile compounds were supposed to have a higher affinity for PE films than for the ethyl alcoholic solutions (Table 1). The prediction also suggested a decrease of sorption into PE film
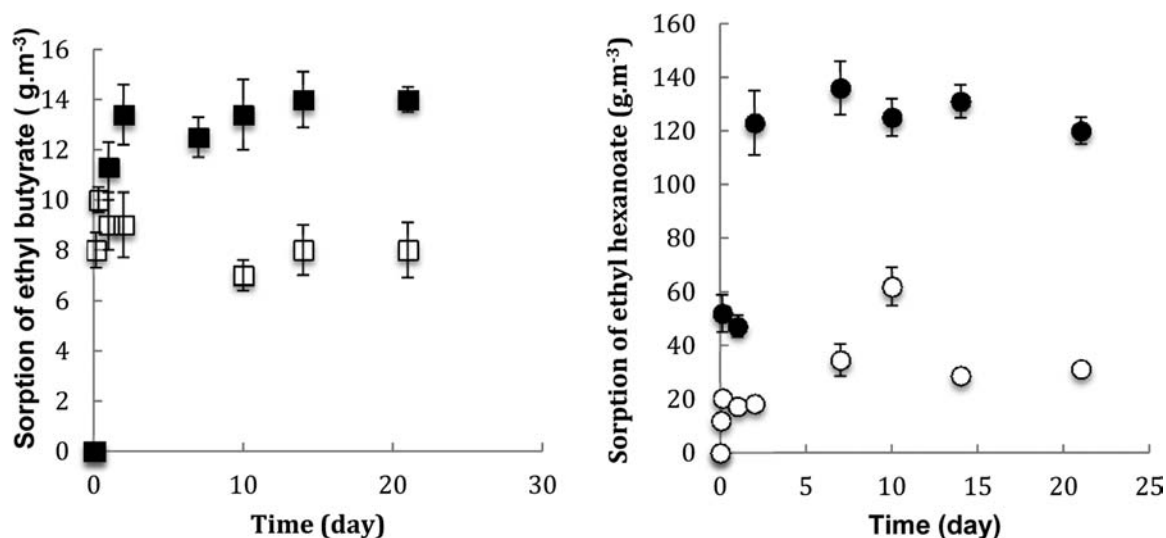
Figure 3. Kinetic of sorption of ethyl butyrate (left) or ethyl hexanoate (right) into a PE film in the presence of acidified water (□, ○) or solution at 12% v/v of ethanol (■, ●).

Table 3. Ethyl Butyrate, Ethyl Hexanoate, 2-Phenylethanol, and 4-Ethylphenol Sorption Coefficients into PE Film and Partition Coefficients $K_{m/s}$ between the PE Film and the Different Ethanol Solutions[a]

	sorption[b] (g m^{-3})			$K_{m/s}$[b]			$K_{m/s}$[c]	
	0% v/v ethanol	12% v/v ethanol	15% v/v ethanol	0% v/v ethanol	12% v/v ethanol	15% v/v ethanol	12% v/v ethanol	15% v/v ethanol
ethyl butyrate	8 ± 0.1a	14.1 ± 0.5b	30 ± 3c	1158 ± 172a	16 ± 1b	34 ± 3c	22 ± 4e	68 ± 9f
ethyl hexanoate	31 ± 2.5a	120 ± 5b	69 ± 4c	3769 ± 368a	125 ± 11b	80 ± 7c	58 ± 5d	69 ± 6cd
2-phenylethanol	14 ± 2	nd[d]	nd	0.71 ± 0.07				
4-ethylphenol	nd	256 ± 10a	526 ± 95b		269 ± 11a	585 ± 89b	13 ± 1c	5.7 ± 0.75d

[a]For each volatile compound, the different letters indicate significant differences ($p > 0.05$) among sorption and the $K_{m/s}$ value [b]The value was determined for volatile compound in mixture. [c]The value was determined for volatile compound alone. [d]nd ; non detectable.

with increasing concentration of ethanol in the solution. However, in regard to $\Delta\delta$ values between solutions and each volatile compound and whatever the ethanol concentration was, phenolic compounds exhibited higher affinity for the solutions than esters and consequently should be less sorbed than the esters. Moreover, the esters should possess more affinity for the PE films than the phenolic compounds. Depending on parameter values found in the literature,[31,42] the affinities of ethyl butyrate and ethyl hexanoate for PE film were found very close or slightly superior for the most apolar ester. The estimation of the Hansen solubility parameter can lead to large uncertainties as previously stated[31] and in relation to some shortcomings applied in its use or determination. For instance, the heat of mixing is estimated from properties of pure substances. Furthermore, this method is able to predict the general trends but not to take into account the occurrence of specific interactions between volatile compounds themselves and those with ethanol.

To conclude, it can be predicted that the presence of ethanol will slightly decrease the sorption of volatile compounds into the PE film.

Hydrolysis of Esters. As the model solution to simulate wine was acidified, the hydrolysis of ethyl esters can occur. However, it can be supposed that ethanol, as a product of the reaction, might limit the hydrolysis. This hypothesis was confirmed by experiments. After 21 days, changes in volatile compound concentrations were evidenced in the presence of water but not in the presence of ethanol solution 12%v/v. As

expected, hydrolysis was negligible in ethanol solution but substantial in water. The percentage of hydrolysis depended on the ester and was equal to 29 ± 6% for ethyl butyrate and to 68 ± 8% for ethyl hexanoate. In consequence, the presence of ethanol prevented the hydrolysis of esters, which were more available for sorption phenomena.

Effect of Ethanol on Volatile Compound Sorption. As demonstrated, numerous phenomena can affect the sorption of volatile compounds into PE film in contact with ethanol solutions. Overall, the presence of ethanol should induce a decrease of the sorption of aromatic alcohols, but not for esters due to hydrolysis.

Sorption of Esters. This statement was evidenced by the study of the sorption kinetic of esters into the PE film using acidified water at 0 or 12% v/v ethanol (Figure 3; Table 3). Whatever the time, the sorption of ethyl esters into the PE film was higher when the ethanolic solution was used. The effect of ethanol was stronger for ethyl hexanoate than for ethyl butyrate as expected by hydrolysis results. In the presence of the ethanolic solution, the sorption of ethyl hexanoate was characterized by a transient state and a steady state reached after 2 days (Figure 3). However, in the presence of water, the sorption curve did not reveal any equilibrium state but exhibited an increase to 10 days and then a decrease reaching a pseudoequilibrium after 14 days. These variations in the sorption curve were observed for ethyl butyrate but to a lesser extent. This typical trend was also reported for the sorption of these two unstable esters into PET or PVC films when

degradation concomitantly occurred with sorption.[43] The desorption might compensate the decrease of concentration in the solution due to the hydrolysis. The residual concentration of the esters in each solution after 21 days of sorption was calculated. This represented <1% of the initial concentration in the presence of water, whereas it reached 80% of the initial concentration in the presence of ethanol. It was clear that in the presence of acidified water, hydrolysis was the preponderant phenomenon which modified the aromatic profile as previously stated.[43] However, the two esters had strong affinity for the PE film (Table 3), in agreement with the weak crystallinity of PE and with the literature.[1,4] Moreover, ethyl hexanoate, the most apolar ester, was the most sorbed according to its stronger affinity for apolar materials such as PE.

The sorption was also studied at 15% v/v of ethanol concentration and found to decrease with ethanol concentration for ethyl hexanoate as predicted by Hansen solubility parameters. In contrast, the sorption of ethyl butyrate increased. The presence of copermeates such as ethanol or the other volatile compounds can enhance the sorption rate of volatile compounds[44] or induce a competition phenomenon. It was observed that the decrease of ethyl hexanoate sorption was partially compensated by the sorption increase of ethyl butyrate. To highlight the impact of other compounds, the sorption of the esters in the aroma mixture was compared to the sorption of each volatile compound alone in the ethanol solutions at 12 or 15% v/v, using the same concentration in both cases. When it was alone (Table 3), the sorption of ethyl butyrate was up to twice as high, which supported a competition phenomena between the volatile compounds. Moreover, the sorption increased with ethanol concentration. It meant that ethyl butyrate sorption was enhanced by ethanol as a copermeate. When ethyl hexanoate was alone, increasing the concentration of ethanol had no effect on the sorption. In contrast, the presence of other compounds significantly affected the sorption using the ethanol solution at 12% v/v. As the sorption was higher for the compound in the mixture than alone, it could be supposed that the presence of the other compounds interfered by favoring the sorption of ethyl hexanoate.

To conclude, the amount of esters sorbed into PE film was weaker when the film was in contact with water rather than with ethanol. It was explained by the losses of esters due to hydrolysis. At 21 days, it corresponded to from 0.3 to 1.7% of the initial concentration depending on the esters and the ethanol concentration.

Sorption of Aromatic Alcohol Compounds. When sorption occurred, classic curves of sorption were obtained for the two alcohols (data not shown) with a steady state reached after 2 days. The values of sorption after 21 days of contact are reported in Table 3. Despite the fact that the initial concentration of 2-phenylethanol was 40 times higher than the other compounds, its sorption into PE films was dramatically weak or even undetectable in the ethanolic solution. The polar character of 2-phenylethanol (log P = 1.6) explained its weak sorption due to higher affinity for the solutions than for the apolar film. The sorption also seemed to be prevented by the higher crystallinity of the PE film in the presence of ethanol than in the presence of water. Moreover, an absence of sorption was also observed for 2-phenylethanol alone, which eliminated the hypothesis of a competition phenomenon with the other volatile compounds. Losses by sorption were estimated to be inferior to 0.02% of initial

concentration in water and negligible in the presence of ethanol.

The results obtained with 4-ethylphenol were quite surprising because no detectible sorption into the PE film immersed in 0% v/v ethanol solution was observed, whereas a relatively strong sorption was measured when the PE film was immersed in hydroalcoholic solutions (Table 3). This compound is more apolar than 2-phenylethanol and ethyl butyrate and slightly less apolar than ethyl hexanoate; it should justify its affinity for the PE. To explain the absence of sorption using acidified water, it was hypothesized that 4-ethylphenol was not sorbed due to a competition phenomena for the sorption sites with the other volatile compounds. This was confirmed by measuring the sorption of 4-ethylphenol when it was alone because a high value (34 ± 1 g m^{-3}) was found. Moreover, when it was alone, the sorption of 4-ethylphenol decreased in the presence of ethanol as predicted by Hansen solubility parameters (Table 1). These results suggested that the sorption of 4-ethylphenol was dependent not only on the ethanol but also on the presence of other volatile compounds. Sorption can induce up to 10% loss of initial concentration of 4-ethylphenol.

To our knowledge, only one study has reported the effect of ethanol concentration on sorption of volatile compounds in PE.[19] The sorption of ethyl butyrate and ethyl hexanoate into a LDPE film (50 μm thickness) immersed in ethanol 15% v/v solution was found to be equal to 1.4 and 24.4 μg cm^{-3} ppm^{-1}, respectively. These values were in the same order of magnitude as the values determined in our study (taking into account the initial concentration). The differences were probably due to the characteristics of each PE film, to the experimental procedures (the solution was not acidified, the volatile compound was alone, the ester concentration was 15 ppm against 1 ppm in our study, and the temperature measurement of 20 °C compared to 25 °C). These authors observed a contrasting impact of ethanol on the sorption of different volatile compounds (esters, aldehydes, and alcohols) with an increase between 0 and 15% v/v of ethanol followed by a remarkable decrease of the sorption for the highest ethanol concentrations. This behavior was related to the physicochemical properties of ethanol solutions and particularly the dielectric constants. The dielectric constants of hydroalcoholic solutions were roughly unchanged in the range of 5−15% v/v ethanol, but decreased with increasing ethanol content. The anomalous nonlinearity of this parameter with alcohol−water mixing ratio was in agreement with the changes in the ethanol−water molecules association described in the range of 8−22% (v/v) ethanol.[45−47] At low ethanol concentration, that is, <8%, alcohol molecules are monodispersed in water clusters. For border concentrations between 10 and 20% v/v, there is a progressive aggregation of ethanol molecules with water and as a consequence a heterogonous structure; beyond ethanol self-association clusters are observed in detriment to the water pure clusters.[47] As the alcohol self-aggregation cluster is considered to form a microscopic hydrophobic environment,[45] the solvation of hydrophobic molecules might be favored and could consequently explain a decrease of sorption into the PE film, such as for ethyl hexanoate in mixture and for 4-ethylphenol alone.

The classic method of sorption used in this part has been used to compare the sorption of four volatile compounds, to show the complex effect of ethanol on a mixture of volatile compound, and to estimate the losses of volatile compounds. However, when a liquid is packaged, losses of volatile

compounds can also occur by permeation in liquid or vapor phase.

Aroma Losses by Sorption and Permeation. With the device used in this study, only the sorption and permeation of volatile compounds due to the liquid phase were taken into account. Indeed, there is a direct contact between the liquid phase and the PE film because no headspace between the film and the solution existed. The volatile compounds sorbed and diffused in the PE film in liquid form and desorbed in vapor state on the other side of the film. As the amount of permeate can be very weak, a concentration method of the headspace, that is, SPME was set up to assess the losses of volatile compounds by permeation. To establish a mass balance, the sorption into the PE film, the initial amount in the solution, and the residual amount remaining in the solution after sorption and permeation were measured after 5 days.

Ethyl butyrate, ethyl hexanoate, and 4-ethylphenol losses by sorption and permeation are presented in Figure 4. Depending
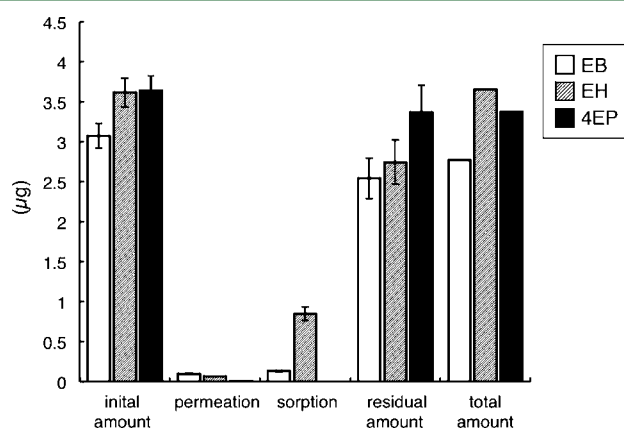

Figure 4. Volatile compound losses by permeation and sorption through a PE film during 5 days of storage at 25 °C, the residual amount in the 12% (v/v) ethanol solution, and the total amount (amount lost by permeation and sorption + residual amount in solution): ethyl butanoate (white bars), ethyl hexanoate (gray bars), and 4-ethylphenol (black bars).

on the volatile compound, the recovery of each volatile compound (ratio of final mass balance/initial measured amount) varied between 90% (ethyl butyrate) and 100% (4-ethylphenol), suggesting a relatively good determination of the different phenomena by the methods used. However, it can be noted that although both esters were present at the same concentration, ethyl butyrate was recovered with less efficiency due to some losses caused by volatility. As no other volatile compounds were detected in the solutions, hydrolysis of esters was excluded.

Losses by permeation were lower for both aromatic alcohols than for esters. The permeation of 4-ethylphenol represented 0.19% of the final mass balance and only 0.08% for 2-phenylethanol (data not shown), the most concentrated compound. Although permeation occurred, their sorption was not quantifiable, suggesting that mass uptake was not detectable according to the experimental design applied for permeation measurement. In the same way, the permeation of 2-phenylethanol was quite surprising because, as previously described, the sorption was not detectible for the film immersed in the 12% (v/v) ethanol solution. In agreement with previous

results of sorption, losses of 4-ethylphenol were higher than losses of 2-phenylethanol, but they were almost negligible.

Losses by permeation and sorption reached for ethyl butyrate and ethyl hexanoate 3.6 and 4.7% and 1.7 and 23% of losses, respectively. As previously stated, the highest sorption was detected for ethyl hexanoate. However, the sorption extent was higher than values estimated by classic sorption method. The sorption was the dominant phenomenon for the most apolar ester in relation with this high affinity for PE film. The dominant phenomenon was permeation for the most volatile and smallest compound, that is, ethyl butyrate, in relation to its small size and easiest diffusivity into PE film.[2]

The present results indicated that the losses of volatile compounds by sorption and by permeation through packaging can be substantial and that the presence of ethanol can involve high sorption of some volatile compounds such as esters. The main purpose of this work was to measure the impact of these phenomena on a wine packed in a BIB. In a 3 L BIB, the surface in contact with the wine was slightly higher than in this experiment, and it can be assumed that the losses will be in the same order of magnitude. Before and after contact with the PE film, odor active values were determined using the threshold of compounds found in ethanolic solution (i.e., 20 μg/L for ethyl butyrate, 14 μg/L for ethyl hexanoate, 14000 μg/L for 2-phenylethanol, and 440 μg/L for 4-ethylphenol).[48,49] The four components were active odorants (i.e., OAV > 1; 46.6 for ethyl butyrate, 70.6 for ethyl hexanoate, 3.0 for 2-phenylethanol, and 2.1 for 4-ethylphenol). After contact with the PE films, no changes in OAV were observed for the two aromatic alcohols, whereas the OAV of esters clearly decreased (42.8 and 53.1 for ethyl butyrate and ethyl hexanoate, respectively). These compounds are characterized by a fruity odor and can strongly contribute to the aroma profile of wine. Transfer through the PE film can affect their sensory perception into wine.

However, these results obtained with a model solution are difficult to extrapolate to a wine. Indeed, wine is a multicomponent medium and volatile compounds can interact with numerous components such as polyphenols, mannoproteins, and tannins. These interactions can also modify the sorption of volatile compounds into the PE film. These aspects have to be taken into account in further studies.

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Notes
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