INFLUENCE OF ETHANOL ON AROMA COMPOUNDS SORPTION INTO A POLYETHYLENE FILM

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Abstract

The effect of ethyl alcohol concentration on four aroma compounds sorption into a Polyethylene film was studied using partition coefficients (K_{polysol}) determination. In aqueous solution without ethanol, a high sorption of hydrophobic esters (ethyl butanoate and hexanoate) into the apolar PE film was observed while the phenolic compounds, with high solubility in water, were weakly sorbed. Excepted for 4-ethyl phenol, sorption into the PE film was lower in the presence of ethanol than in water. The concentration of ethanol and the interactions between the matrix and each aroma compound appeared to influence the scalping rates. Moreover, higher partition coefficients, i.e. higher affinity for the PE was obtained when the aroma compounds were present in mixture comparatively to the flavour compound alone.

Introduction

Due to their good water and oxygen barrier properties, plastic materials are commonly used for food packaging. However, they can interact with the food itself, and particularly with aroma compounds causing the rejection of the product by consumers. Polyethylene (PE) film, which is one of the most common type food contact packaging, sorbs a wide range of flavour compounds (1-2) leading to an unbalanced aromatic profile (scalping). The interactions of aroma compounds with plastic films are more complex than interactions between packaging and gazes or water molecules. Indeed, the aroma compounds characteristics, the properties of the polymer, the environmental conditions and the composition and structure of food matrices have an effect on the sorption and the transfer of aroma compounds (3).

For alcoholic beverages, the concentration of ethanol could influence the sorption phenomena. Hence, this work focused on the effect of ethanol concentration on the sorption of four aroma compounds into a PE film. The impact of the presence of other aroma compounds on the sorption behaviour was studied by comparing the sorption of each individual compound with that in mixture.

Experimental

Sorption experiment. The PE film was a commercial film with a thickness of 50 µm. Aroma compounds, ethyl butanoate (MW 116.16, logP= 1.9), ethyl hexanoate (MW 144.21, logP= 2.8), 4-ethyl phenol (MW 122.16, logP= 1.6) and 2-phenyl ethyl alcohol (MW 122.16, logP= 2.6) were purchased from Sigma-Aldrich and Fluka. The sorption of aroma compounds has been investigated in acidified water (pH= 3.5) and in acidified hydro-alcoholic solutions (pH= 3.5) with different concentrations of ethyl
alcohol: 10%, 12% and 15% (v/v). The concentration of the aroma compound in the solution was 40 ppm for 2-phenyl ethyl alcohol and 1 ppm for ethyl butanoate, ethyl hexanoate and 4-ethyl phenol respectively. Small pieces of film (9 cm²) were immersed in the different solutions containing the aroma compounds in mixture or alone. The experiments were realised in triplicate at 25°C, during 21 days. For this time, a constant amount of each volatile compound was reached and sorption coefficients (g m⁻³) could be determined.

Aroma extraction and K determination. The aroma compound amounts absorbed into the film were extracted using dichloromethane during 16h at 500 rpm. Internal standard was added to the organic phase and quantification was performed by gas chromatography analysis. The results were expressed by calculating the partition coefficients K_{PE/solution} between material and solution. K is defined as the aroma compound concentration into the PE film in g m⁻³ related to the residual aroma compound concentration in g m⁻³ of the solution. The residual concentration was deducted by subtracting the amount absorbed into the film to the initial amount of aroma compound in solution at the beginning of experiment. The higher K was, the higher sorption in PE was.

Results

Partition coefficients in water. First, the partition coefficients of each aroma compound were determined when the PE was in contact of the mixture of compounds in acidified water (Table 1).

Table 1. Partition coefficients (K_{PE/solution}) of ethyl butanoate, ethyl hexanoate and phenyl-2-ethyl alcohol in water.

<table>
<thead>
<tr>
<th>Aroma compound</th>
<th>Ethyl butanoate</th>
<th>Ethyl hexanoate</th>
<th>2-Phenyl-ethyl alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_{PE/water}</td>
<td>1158 ± 172</td>
<td>3769 ± 360</td>
<td>0.71 ± 0.07</td>
</tr>
</tbody>
</table>

The sorption of 4-ethyl phenol into PE was not detected and the sorption of 2-phenyl ethanol was very weak despite a concentration 40 times higher than 4-ethyl phenol. In contrast, the sorption of esters into PE was strong and particularly for the most apolar ester according to the apolar nature of the film. These results clearly showed the affinity of esters for PE comparatively to phenolic compounds in relation to their high water solubility.

Influence of ethanol concentration. In ethyl alcohol solutions, the sorption of 2-phenyl ethyl alcohol into PE film was not detected in spite of its high concentration. It may be due to its relative polar nature and its greater affinity for hydro alcoholic solution than for the PE film. In contrast, 4-ethyl phenol which was more apolar (logP= 2.6) than 2-phenyl ethanol (logP= 1.6), was highly sorbed by the PE film. Excepted for 4-ethyl phenol, sorption into the PE film was lower in the hydro-alcoholic solutions than in water (Figure 1). The presence of ethyl alcohol is known to favour the solubility of aroma compounds but the gain in solubility is function of the aroma compound. It was shown that for 4-ethyl phenol, the solubility was unchanged (4). It could be suggested that ethyl alcohol acted as a carrier in the sorption phenomena of 4-ethyl phenol. This hypothesis was confirmed by its increased sorption with the ethyl alcohol concentration and by the high sorption of ethanol (30Kg m⁻³) into the film.
For ethyl butanoate as for 4-ethyl phenol, maximal sorption was observed at 15% (v/v) of ethyl alcohol in solution. For ethyl hexanoate the maximal sorption was reached for 10% (v/v) ethanol solution. Subsequently, the sorption strikingly decreased. Fukamachi et al. (5) found partition coefficient values for ethyl butanoate and ethyl hexanoate in LDPE film equal to 2.1 and 30 respectively, i.e. inferior to the values obtained in this study, due certainly to different experimental procedure (20°C against 25°C) and PE physical characteristic. However, similar sorption behaviour was observed with a maximal sorption detected at 5%-10% (v/v) for ethyl hexanoate and followed by a decrease and the highest sorption for the most apolar ester. It is known that for a chemical family, the sorption in apolar films is the highest for the most hydrophobic compound. However, the impact of hydrophobicity was not relevant when ethyl hexanoate (log P= 2.8) sorption was compared to that of 4-ethyl phenol (log P= 2.6), leading to suppose the influence of chemical aroma nature in the sorption phenomena.

![Graph showing partition coefficients (K PE/solution) of ethyl butanoate, ethyl hexanoate and 4-ethyl phenol as a function of ethanol concentration.](image)

**Figure 1.** Partition coefficients (K_{PE/solution}) of ethyl butanoate, ethyl hexanoate and 4-ethyl phenol as a function of ethanol concentration.

**Influence of the presence of other aroma compounds on PE sorption.** Partition coefficients of aroma compounds obtained when they were in mixture, were compared to partition coefficients obtained when each aroma compound was alone, both in 12% (v/v) ethanol solution (Figure 2). As previously observed, 2-phenyl ethyl alcohol was not detected into the PE film. The sorption of ethyl butanoate was weakly modified. In contrast, for the most apolar compounds - ethyl hexanoate and 4-ethyl phenol - partition coefficients were found ~2 and 21 times respectively lower than when the aroma compounds were in mixture. This surprising behaviour could be explained by a stimulant effect of the other aroma compound favouring the sorption into the PE films.

Aroma compounds sorption was strongly affected by the presence of ethanol in solution but also by the presence of other aroma compounds. The sorption of aroma compound in PE film was not easily predictable since parameters other that polarity...
and chemical nature must be taken account such as interactions with matrix and competition between aroma compounds.

![Graph showing partition coefficients K (PE/12% (v/v) ethanol solution) of ethyl butanoate, ethyl hexanoate and 4-ethyl phenol present in mixture (empty bar) or alone (full bar) in the hydro-alcoholic solution.]

**Figure 2.** Partition coefficients $K$ (PE/12% (v/v) ethanol solution) of ethyl butanoate, ethyl hexanoate and 4-ethyl phenol present in mixture (empty bar) or alone (full bar) in the hydro-alcoholic solution.

**References**