

## Effect of Concentration and Relative Humidity on the Transfer of Alkan-2-ones through Paper Coated with Wheat Gluten

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The transport properties of two methyl ketones, 2-heptanone and 2-nonanone, through a paper coated with a wheat gluten (WG) solution were studied as a function of aroma compound concentration differential and relative humidity. Whatever the conditions, coating improved the aroma barrier properties of the paper. Whereas permeability of 2-nonanone through WG coated paper was not affected by the concentration differential, a high concentration of 2-heptanone induced a permeability increase, which can be explained by a slight plasticization effect of this compound. The moisture content of the films markedly affected the barrier properties depending on the aroma compound. For 2-heptanone, the most polar compound, the increase of permeability with relative humidity was related to the increase of diffusivity and solubility coefficient of this compound. With 2-nonanone, permeability and diffusivity coefficients strongly decreased with the increase of moisture content. This decrease could be linked to the hindrance in diffusivity of the less polar compound induced by the presence of water molecules. The different behavior in permeation properties seems to be related to the hydrophobic nature of the aroma compound. At intermediate and high humidity levels, coated papers are found to have better aroma barrier properties than LDPE films.

**KEYWORDS:** Wheat gluten; coated paper; aroma compounds; transfer; relative humidity

### INTRODUCTION

Losses of aroma compounds by sorption on or diffusion through polymeric packaging materials are detrimental to the organoleptic quality of food and the acceptance of a product by the consumer. Losses can be selective—they can affect one or a few components in a complex flavor mixture—and result in changes of the aromatic profile and significant alteration in the perception of the product, causing important economic losses (1–4). The excessive sorption of flavor compounds may also affect the package integrity and facilitate the diffusion of other aroma components or gases by plasticization of the package (5, 6).

Plastic materials have been shown to possess a range of affinities for aroma compounds. Low-density polyethylene (LDPE) film, which is the food contact surface of the most common type of packaging, sorbs a wide variety of flavor compounds such as aldehydes, methyl ketones, methyl esters, and sulfur compounds (7, 8). Factors that affect sorption include molecular size, polarity, solubility, and concentration of the aroma compounds along with the properties of polymers such as morphology, glass transition, crystallinity, and polarity (9–12). Generally, polyolefins such as LDPE absorb larger quantities of aroma compounds than more polar polymers, such as

polyesters [polyethylene terephthalate (PET), polycarbonates (PA), or ethyl vinyl alcohol (EVA)] (6). The barrier properties of these polymers could be also affected by external factors such as temperature and, in the case of polar polymers, relative humidity (13–16).

With increasing demand for biodegradable packaging, there has been a growing interest in the development of paper-based packaging. Paper constitutes one of the most widely used materials; it is biodegradable but has weak barrier properties for water vapor, oil, gas, and aroma. Barrier properties can be improved by coating with synthetic or natural polymers as latex, starch, or proteins (17). Paper coating from corn, wheat, soy, and milk proteins has already been performed; mechanical and grease, water, and oxygen barrier properties have been studied (18–20). It has been shown that protein coating could improve packaging material performances of paper by increasing oil resistance and, to a lesser extent, water vapor resistance without modification of mechanical properties of paper.

The film-forming properties of proteins have been used to develop edible or biodegradable, food protective films having the potential to improve the shelf life of food products (21). Due to its polymeric structure, wheat gluten forms a cohesive and elastic material responsible for its film-forming capability (22). WG films in a dry state are a very effective oxygen barrier and exhibit a very high selectivity value toward oxygen and carbon dioxide permeability at high moisture conditions (23).

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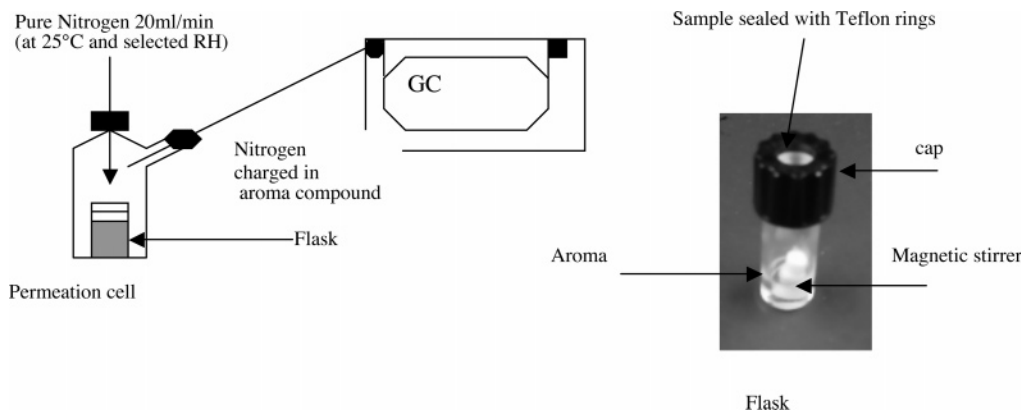


Figure 1. Schematic diagram of the permeability system measurement.

Aroma barrier properties of edible films or coated paper have not been as thoroughly studied as water and oxygen transfers have been (24). A few studies on aroma have been carried out; however, they highlighted the potential of edible films and coating to provide efficient barrier properties (25–28).

The aim of this study is to investigate the potential ability of wheat gluten as a coating of paper to improve the barrier properties of two volatile compounds (i.e., 2-heptanone and 2-nonanone) through paper. These two compounds, which are characteristic of cheese aroma and more specifically of blue cheese aroma, are of interest in the use of coated papers for cheese wrapping. The effectiveness of the material will be evaluated by measuring diffusion, permeability, and solubility coefficients for two methyl ketones, 2-heptanone and 2-nonanone, belonging to the same chemical family but with different physical–chemical properties. The effect of differential concentration and relative humidity on these parameters will be studied in relation to the characteristic of the aroma compounds.

## MATERIALS AND METHODS

**Materials. Aroma Compounds.** Methyl ketones (2-heptanone and 2-nonanone) were obtained from Sigma Chemical Co. Their purities were superior to 99%. 2-Heptanone is characterized by a molecular mass of 114.18 g mol<sup>-1</sup>, a saturated vapor pressure at 25 °C of 470 Pa, and an estimated hydrophobicity (log *P*) of 1.8. 2-Nonanone has a molecular mass of 142.24 g mol<sup>-1</sup>, a saturated vapor pressure at 25 °C of 75 Pa, and an estimated hydrophobicity (log *P*) of 2.9.

**Plastic Film.** The LDPE 50 μm thick films were supplied by BBA Emballage-Manu pack, St Jean de Védas, France.

**Base Paper.** The paper used as a base for coating was a Condat 4 NVSF08E017 paper sheet supplied by Smurfit WR (France) with an average thickness of 130 μm (±1.6) and a weight density of 105 g m<sup>-2</sup> (±1.6) at 25 °C and 50% relative humidity (RH).

**Methods. Wheat Gluten Solutions.** Vital wheat gluten (80% of protein) was supplied by Amylum Aquitaine (France). Coating solutions were prepared according to a modified procedure used for film preparation (22). One hundred milliliters of coating solution was prepared by dispersing 20% (w/v) of wheat gluten in distilled water containing 0.6% (v/v) acetic acid and 0.2% (w/v) anhydrous sulfite sodium under stirring at ambient temperature. No plasticizers (such as glycerol) were added, and the solution was supplemented with sulfite sodium to cut the disulfide bonds of the gluten protein.

**Coating Application and Film Formation.** The coating was performed using a micrometric applicator (Braive Instruments, France), previously adjusted to the selected thickness (500 μm). After coating, the papers were dried at ambient temperature for at least 24 h until a constant weight was obtained. The wheat gluten coated paper had an average thickness of 190 μm (±3.2) and a coat weight of 160 g m<sup>-2</sup> (±1.6) at 25 °C and 50% RH. The average thickness was determined using a hand-held caliper digital micrometer (Braive Instruments) from 10 measurements taken at random over the surface. The average coating

weight was the result of 10 determinations of the coated mass paper to a defined area. Consequently, the coating of gluten had an estimated average 60 μm thickness and a 55 g m<sup>-2</sup> coat weight.

**Aroma Permeation Measurements.** The permeation of aroma compounds was measured by two methods: a dynamic method previously described by several authors (10, 25, 28, 29) and a semidynamic method developed in our laboratory.

In the dynamic method, the permeation cell was composed of two chambers separated by the films to be studied. Complete separation and closure of each chamber were accomplished with Teflon O-rings placed between the films and the contact surfaces of the chamber. The film area exposed to transfer was 2.29 × 10<sup>-3</sup> m<sup>2</sup>. The two chambers were continuously flushed by a 30 mL min<sup>-1</sup> helium flow. The flow containing aroma vapors was obtained from bubbling dry helium through pure compound and flowed in the upper chamber. The highest aroma concentration in the vapor phase (saturation) was obtained at 25 °C and atmospheric pressure by bubbling the gas through pure aroma, whereas the lowest concentrations were obtained by mixing the flow containing the volatile compound with a dry helium flow. The outgoing flow from the lower chamber, charged in aroma compounds, was injected (1 mL) at regular time intervals with an automatic valve in a gas chromatograph.

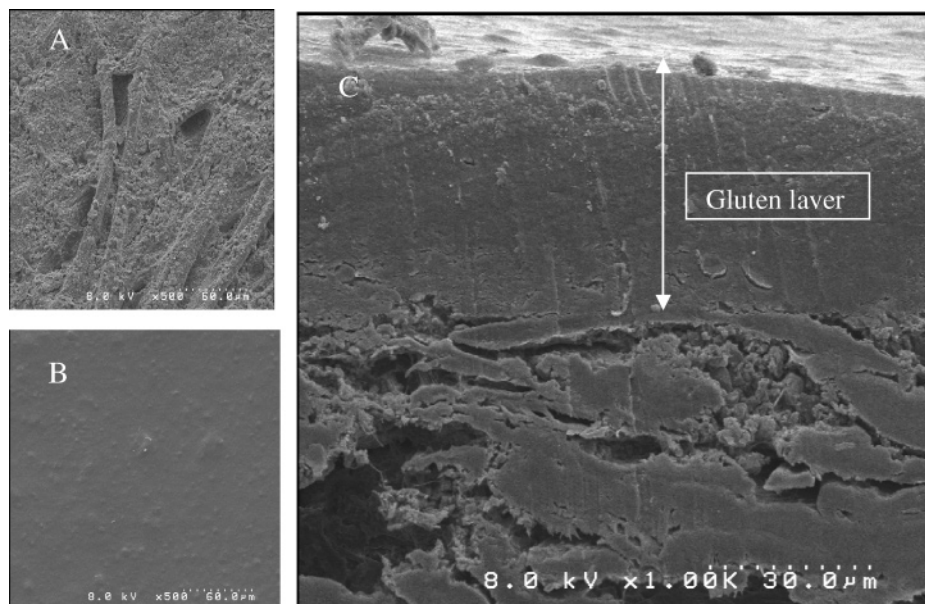
In the semidynamic method, the test film was sealed (with a Teflon ring) directly on the top of a flask containing pure aroma compound. The flask was placed in a permeation diffusion cell, which was flushed by a 20 mL min<sup>-1</sup> nitrogen flow (Figure 1). At regular time intervals, 1 mL of the outgoing flow charged in aroma compound was injected with an automatic valve into the gas chromatograph. The film area exposed was 0.785 × 10<sup>-3</sup> m<sup>2</sup>.

For the two methods, permeation measurements were carried out at 25 °C, placing the permeation cells in an oven adjusted to the selected temperature. Films were equilibrated at 25 °C and at the selected humidity before permeability tests. To maintain the humidity conditions, the gas (helium or nitrogen) was humidified by bubbling in a wash bottle containing water and placed in a cryostat at controlled temperature. The differential of temperature imposed between the cryostat and the oven permitted the selected humidity to be reached. After each experiment, film humidity was controlled using an *a<sub>w</sub>*-meter (Fa-st/1, GBX, France).

The 3800 Varian (Les Ulis, France) gas chromatograph was equipped with a flame ionizing detector (FID; hydrogen, 30 mL min<sup>-1</sup>; air, 300 mL min<sup>-1</sup>) and a column (Poraq Q, 3 m i.d., 3 mm). The gas vector was helium at 20 mL min<sup>-1</sup>. Isothermal condition (100 °C) was used, and injector and detector temperatures were adjusted to 250 °C.

The aroma compound flow rate (g m<sup>-2</sup> s<sup>-1</sup>) was determined by comparing the aroma compound peak surface obtained when using the film with that obtained without the film and by applying the perfect gas law. Depending on the vapor pressure of the volatile, vapor concentration differentials varied between 0 and 4.3 mg L<sup>-1</sup> for 2-nonanone and between 0 and 21.6 mg L<sup>-1</sup> for 2-heptanone.

Diffusion, *D* (m<sup>2</sup> s<sup>-1</sup>), and permeability, *P* (kg m m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>), coefficients were determined from the curve of flow rate plotted against time. The diffusion step was considered to follow Fick's laws (30).



**Figure 2.** SEM images of base paper surface (A) and WG coated paper (B) ( $\times 500$ ) and cross section of WG coated paper (C) ( $\times 1000$ ).

$P$  was calculated at the steady state using the equation

$$P = (Fe/\Delta P) \quad (1)$$

where  $F$  is the flow rate of the volatile ( $\text{kg m}^{-2} \text{s}^{-1}$ ),  $\Delta P$  is the aroma vapor pressure gradient, and  $e$  is the film thickness (m).

$D$  was determined from data at the transition state from the half-time  $t_{0.5}$  at which the flux is equal to half of the maximal flux using the following equation:

$$D = e^2/7.2t_{0.5} \quad (2)$$

This approach is generally applied when using the differential permeation method and was used in this study for the two methods (28, 30, 31).

**Aroma Vapor Sorption Measurements.** The quantity of volatiles adsorbed in the film was obtained using a modified microatmosphere method (28): small pieces of film ( $10 \text{ cm}^2$ ) were exposed to an atmosphere saturated with pure volatile in a closed chamber. The atmosphere inside the chamber was kept at a constant concentration of volatiles by filling a flask with pure volatile. The headspace concentration of the chamber was controlled by a sample removal of air with a gastight syringe and injection of the sample into a gas chromatograph. The chamber was held at  $25 \text{ }^\circ\text{C}$ , and the headspace was kept at the selected relative humidity using silica gel, salt solutions, or water. The total amount of volatile compound absorbed at a given time until a constant amount in the sample was extracted with a mixture (50:50 v/v) of water and *n*-pentane for 16 h under magnetic agitation (300 rpm). A known quantity of internal standard (2-heptanol) was added; the resulting organic phase was dried using sulfate sodium and analyzed by gas chromatography. A Varian 3800 GC-FID equipped with a CP-Sil 5 column (Varian) ( $15 \text{ m}$ ,  $0.32 \text{ mm}$ ,  $0.25 \text{ }\mu\text{m}$ ) and a flame ionization detector (FID) was used. Hydrogen was used as vector gas with a flow rate of  $2 \text{ mL min}^{-1}$ . The oven temperature initially at  $60 \text{ }^\circ\text{C}$  was raised by  $4 \text{ }^\circ\text{C min}^{-1}$  to  $150 \text{ }^\circ\text{C}$ , then by  $15 \text{ }^\circ\text{C min}^{-1}$  to  $250 \text{ }^\circ\text{C}$ , and was kept at  $250 \text{ }^\circ\text{C}$  for 10 min. Injector and detector temperatures were  $250 \text{ }^\circ\text{C}$ . Injection was done in split mode with a ratio of 1:20. The extraction yield was determined by depositing known amounts of volatile on films and was equal to  $98 (\pm 2.5)\%$ . The solubility coefficient was expressed in  $\text{g m}^{-3} \text{ Pa}^{-1}$ . Three replicates were made for each experiment.

**Water Sorption Isotherm Measurement.** The water sorption isotherm for the papers was determined at  $25 \text{ }^\circ\text{C}$  by using a controlled atmosphere microbalance (dynamic vapor sorption, DVS, apparatus, Surface Measurement System Ltd., London, U.K.). The device was equipped with a micro-electrobalance (model D-200 Cahn) housed in a controlled-

temperature incubator. The required humidity was generated by mixing dry and saturated vapor gas flows in the correct proportions using a flow controller and was measured by a hygrometer (model I-C/CI Rotronics). Samples ( $30\text{--}50 \text{ mg}$ ) were loaded and pre-equilibrated at 0% relative humidity by a continuous flow of dry air. Samples (three replicates) were then equilibrated at the successive levels of relative humidity, and the experimental isotherm curve was obtained for  $a_w$  from 0 to 0.97. Because the DVS apparatus is not adapted for measurement at high water activity such as 0.97, the result obtained for  $a_w = 0.97$  was confirmed by using a conventional method based on equilibrium over a standard saturated solution (a solution of  $\text{K}_2\text{SO}_4$  with  $a_w = 0.976$  was used).

**Scanning Electron Microscopy.** For scanning electron microscopic observations, two different procedures of sample preparation were used depending on the cross section or the material surface examination. Cross-sectional views of coated paper were obtained from thin sections ( $6 \text{ }\mu\text{m}$  thick) realized after resin embedding as described above. To visualize the coated surface of the materials, small pieces of sample ( $10 \text{ mm} \times 10 \text{ mm}$ ) were cut up and directly mounted on the stub with double-sided carbon tape. After degassing and platinum coating ( $5 \text{ nm}$  thick), samples were examined with a JEOL JSM-6400F field emission scanning electron microscope (Croissy sur Seine, France). All micrographs were obtained using an accelerating voltage of  $15 \text{ kV}$ .

**Contact Angle.** Surface hydrophobicity of films was evaluated by contact angle measurements using a contact angle meter (Digidrop, GBX, France), equipped with a diffuse light source, a CCD camera (25 frames per second), and a closed chamber with controlled temperature ( $25 \pm 1 \text{ }^\circ\text{C}$ ) and relative humidity (at 58%, in the presence of NaBr saturated solution). A droplet ( $\approx 3 \text{ }\mu\text{L}$ ) of distilled water, corn oil, or volatile was deposited on the film surface and, thanks to video acquisition, a magnified image of the drop profile was conveyed to a computer via the CDD camera. Changes in the droplet shape over a period of time were recorded as a sequence of images that was then analyzed frame by frame with the GBX software (Windrop, GBX, France). Data experimentally acquired as a function of time were the contact angle,  $\theta$ , which is an averaged value of contact angles measured on both sides of the drop, the droplet volume, and the width of the droplet basis. For each film, hydrophobicity was deduced from angle value at equilibrium contact obtained for water and oil. Five measurements per film were carried out.

## RESULTS AND DISCUSSION

**Characterization of Wheat Gluten Coated Papers.** Wheat gluten coated papers were observed by scanning electron microscopy and compared to the base paper (Figure 2). A

surface view of the base paper showed a porous fibrous structure partially covered with a coating with a granular nature, which suggested the impregnation of paper by a starch solution as indicated by the supplier (Smurfit WR, France). Comparison of the surface images of the base paper and coated paper showed that the WG coating produced a homogeneous smooth surface. The cross-section view confirmed the presence of a continuous homogeneous layer corresponding to the WG coating. Comparison between thickness and density weight of base and coated paper allowed determination that the coating layer has a  $60 \mu\text{m}$  thickness and a  $55 \text{ g m}^{-2}$  coat weight. However, a partial penetration of gluten solution in the base paper during the coating process was observed by Gastaldi et al. (32). This penetration induced a swelling of the base paper and a change in its initial thickness. Consequently, the real thickness of the coating layer was not measurable and could only be estimated by calculation. The SEM observation verified that coating by proteins decreased the roughness of paper as previously described (33) and that coated paper could be considered as multilayer packaging.

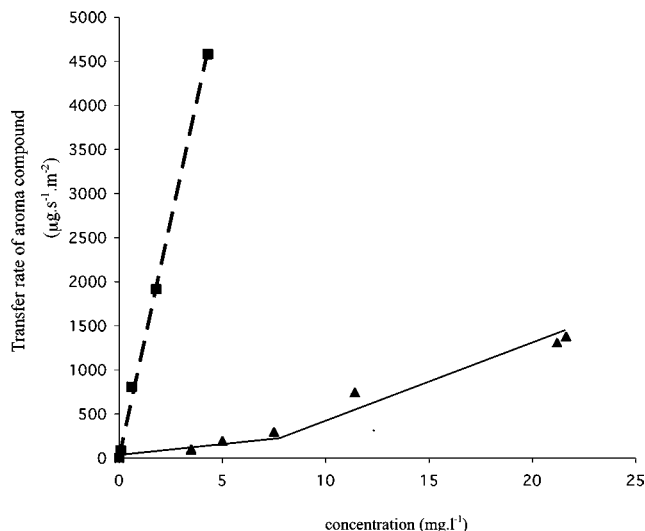
**Aroma Permeation Method.** Two aroma permeation methods were used in this study: a commonly used dynamic method (10, 12, 25, 28) and a method developed in our laboratory combining the outgoing flow charged in aroma (dynamic method) and the static source of volatile (static method). This method (called semidynamic) was adapted to allow permeability measurements of uncoated paper. Indeed, with the dynamic method in the conditions used in the study (size of the cell, flow), permeability measurements of the uncoated paper were not possible. The base paper presents a heterogeneous and partially porous structure inducing high aroma transfers and an unwanted mixture of the fluxes through each side of the cell.

To assess the validity of the developed method, 2-heptanone permeability measurements were done with the two methods for the wheat gluten coated paper under similar conditions (at  $25 \text{ }^\circ\text{C}$  and 10% RH). Permeability coefficients were found to be close and equal to  $(546 \pm 4) \times 10^{-15} \text{ kg m m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  with the dynamic method versus  $(530 \pm 44) \times 10^{-15} \text{ kg m m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  using the semidynamic method.

Consequently, the two methods could be used indifferently for gluten coated paper, whereas the semidynamic method will be used for uncoated papers. However, the dynamic method was preferentially used for the concentration effect study, because dilution of pure aroma can be easily achieved by mixture with dry helium, avoiding the use of a solvent and possible interactions between solvent and aroma or films.

**Effect of Physicochemical Properties and Volatile Concentration on Transfer.** The aim of this part of the experiment was to study the effect of volatile concentration differential on transfer through coated paper. The two methyl ketones selected belong to the same chemical class but possess different physicochemical characteristics: 2-nonanone has a higher molecular weight and size than 2-heptanone. The maximal vapor concentration of 2-nonanone ( $4.6 \text{ mg L}^{-1}$ ) is largely inferior to that of 2-heptanone ( $21.6 \text{ mg L}^{-1}$ ) and the C9 methyl ketone ( $\log P = 2.9$ ) is more hydrophobic than the C7 ( $\log P = 1.8$ ).

Figure 3 presents the evolution of 2-heptanone and 2-nonanone flux through WG coated paper versus aroma vapor concentration differential at  $25 \text{ }^\circ\text{C}$  and 10% RH. The flux of 2-nonanone through the gluten coated paper increased linearly with the concentration differential increase, and a constant permeability coefficient of  $(8980 \pm 960) \times 10^{-15} \text{ kg m m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  was thus obtained whatever the differential. In contrast, the flux of 2-heptanone exhibited an increase in the slope of the transfer



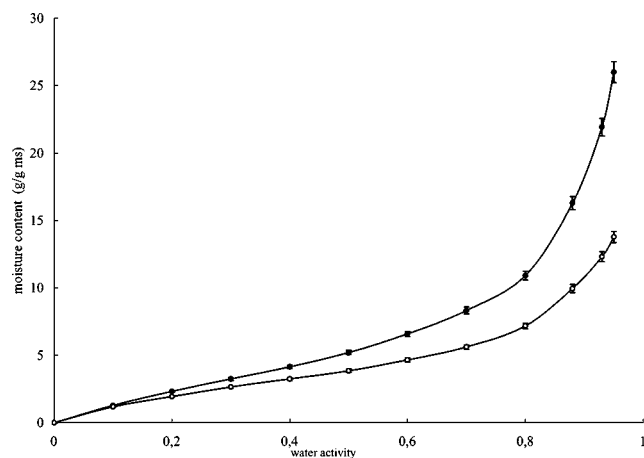
**Figure 3.** Transfer rate of 2-heptanone (▲) and 2-nonanone (■) through WG coated paper as a function of concentration differential at  $25 \text{ }^\circ\text{C}$  and 10% RH.

rate when the concentration differential became higher than  $7 \text{ mg L}^{-1}$ . For the low range such as  $3.5 \text{ mg L}^{-1}$ , the permeability was equal to  $(340 \pm 12) \times 10^{-15} \text{ kg m m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ , whereas for a higher differential of  $23 \text{ mg L}^{-1}$ , the permeability was 1.5 times higher [ $(546 \pm 14) \times 10^{-15} \text{ kg m m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ ].

Thus, whatever the concentration differential, the permeability of 2-heptanone was substantially lower than that of 2-nonanone.

Similar results and contrasting behavior of 2-heptanone and 2-nonanone have been observed for methylcellulose films (28). Whereas the permeability of 2-nonanone was not affected by the increase of concentration differential, the permeability of 2-heptanone strongly increased. This increase was explained by the plasticizing effect of volatile on the film. A plasticizing agent acts by reducing the intermolecular forces and by increasing the mobility of the polymeric chain (34). The plasticizing effect of volatiles has been already reported for both synthetic and natural films: it leads to a relaxation of polymer chain, a swelling of the film, and a reduction of barrier properties of the film (35–37). This effect is often linked with high aroma concentration. The plasticizing effect of 2-heptanone on WG coated paper compared to the absence of effect of 2-nonanone could be partially explained by the largely superior vapor concentration of the C7 compared to the C9. It could be also related to its more hydrophilic nature compared with 2-nonanone. Indeed, hydrophilic compounds such as water or glycerol are known to notably plasticize gluten film, whereas most hydrophobic substances such as fatty acids have no substantial plasticizing effect (34). In a recent study, the presence of a sufficient hydrophilic part in the plasticizer agent to make it compatible with gluten was described as one of the major criteria to obtain a good film by thermoplastic process (38).

The low permeability coefficient observed for 2-heptanone when compared to that of 2-nonanone could be ascribed to its affinity to gluten being lower than that of 2-nonanone. This affinity was confirmed by the determination of solubility coefficients in WG coated paper. For 2-heptanone, the coefficient was equal to  $1.16 \times 10^{-3} \text{ kg m}^3 \text{ Pa}^{-1}$  at  $25 \text{ }^\circ\text{C}$ , 10% RH, and saturated vapor pressure (470 Pa), whereas for 2-nonanone, it reached  $7.2 \times 10^{-3} \text{ kg m}^3 \text{ Pa}^{-1}$  in the same conditions of temperature and relative humidity but for a lower differential vapor pressure (75 Pa). The difference of sorption between the two methyl ketones may be related to the length



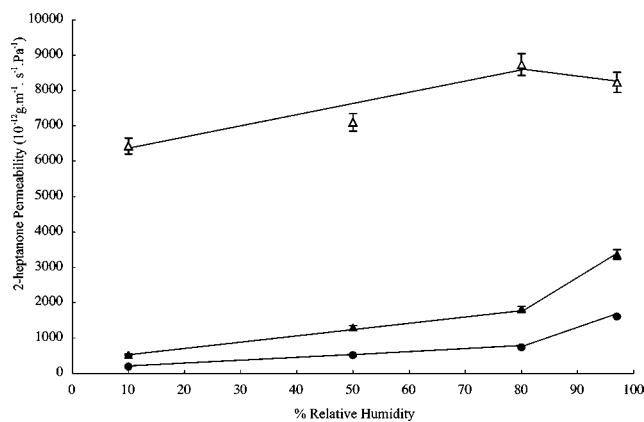
**Figure 4.** Experimental water vapor sorption isotherms at 25 °C for base paper (○) and coated gluten paper (●).

of carbon chain and associated polarity: 2-nonanone possesses a longer chain than 2-heptanone and is less polar. It has been stated that the nonpolar packaging more easily absorbed less polar compounds than polar compounds (9). Wheat gluten proteins and particularly gliadins have a high content (39%) of nonpolar amino acids (39), suggesting the presence of hydrophobic sites with strong affinity to the most hydrophobic compounds.

**Effect of Relative Humidity on Aroma Transfer.** The effect of relative humidity on aroma barrier properties was investigated as a function of gluten coating presence. As has been previously demonstrated for polar films such as EVOH, starch and milk or gluten protein films, relative humidity could strongly affect the transfer properties of gas or volatiles (14, 16, 23, 27, 40).

Water sorption isotherms of base paper and WG coated paper were determined at 25 °C and are presented in **Figure 4**. From 10 to 60% RH, the water content of the WG coated paper increased slightly by 6% (w/w). For higher relative humidity, the water sorption curve of wheat gluten coated paper sharply increased as usually observed for hydrophilic materials (41). The water uptake of base paper was weaker than that of the coated paper. The maximum moisture content of base paper near saturation (97% RH) reached 13.8% (w/w dry weight) against 26% (w/w dry weight) for the WG coated paper. The water uptake of the WG coated paper was clearly inferior to the values obtained in literature for wheat gluten films: for instance, at 80% RH, a moisture content equal to 10.9% (w/w dry weight) was found for the coated paper against 29% (w/w dry weight) for a film made with ethanol and glycerol (42) or 20% for a film made with glycerol (43). For this humidity, the water uptake of base paper was 7.3%. From this value and knowing that base paper represented 66% of dry matter of the coated paper, the moisture content of the gluten layer can be easily calculated and is equal to 17.6%. This value was coherent with the moisture content of gluten film without glycerol (23) and vital wheat gluten power [12.5% (43)]. Indeed, the uptake of water depends on the presence of plasticizing agent and is lower in the absence of glycerol. Because the water uptake of the WG coated paper depended at the same time on the presence of both the base paper and the gluten layer, transfer properties were studied for both papers and calculated for the gluten layer.

**Transfer of 2-Heptanone.** The permeability of 2-heptanone through the base and WG coated papers as a function of relative humidity is reported in **Figure 5**. When the permeation data obtained for the base paper and the WG coated paper were compared, it was found that the presence of the coating



**Figure 5.** 2-Heptanone permeability through base paper (Δ), WG coated paper (▲), and gluten layer (●) as a function of relative humidity.

drastically decreased the aroma permeability. The 2-heptanone permeability through the base paper was 2.5–12 times higher than that through the coated paper. Moreover, whereas a slight increase of permeability through the base paper was observed (1.5 times) with the increase of relative humidity, the permeability of 2-heptanone through the WG coated paper was 6 times higher at high humidity than that measured at a lower relative humidity.

Mass transfer in a multilayer packaging may be seen as a series of resistances. According to this approach, the permeability of WG coated paper can be assumed to be the resulting permeability through two layers (the base paper and the gluten layer) as expressed by the equation

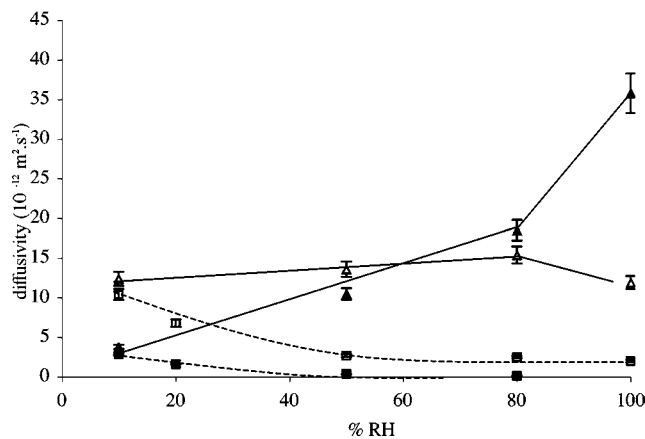
$$e/P = e_1/P_1 + e_2/P_2$$

with  $e$ ,  $e_1$ ,  $P$ , and  $P_1$  the thickness and permeability of WG coated paper and base paper, respectively.  $e_2$  corresponds to the thickness increase of paper due to the coating, and  $P_2$  is the permeability due to the gluten layer.

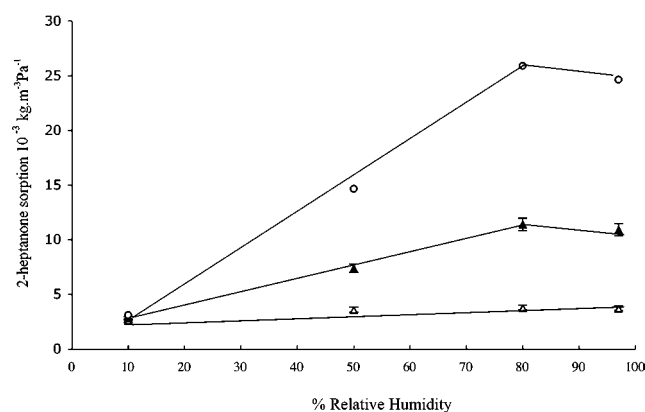
The 2-heptanone permeability through the gluten layer was 5–32 times lower than that through base paper at high and low humidity, respectively. In other terms, the calculated permeability of the wheat gluten layer was particularly weak. This high barrier property toward 2-heptanone of the WG layer was verified for one relative humidity (50%) by permeability measurements of self-supported film made from the same coating solution supplemented with glycerol. A value of  $453 \times 10^{-15} \text{ kg m m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  was obtained versus  $514 \times 10^{-15} \text{ kg m m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  by calculation. This slightly higher value was not surprising and can be explained by the homogeneity deficiency of the gluten coating on the rough support and the possibility of overestimation of the thickness of the layer.

As for permeability, the diffusivity coefficient of 2-heptanone through the WG coated paper increased with relative humidity, whereas it was practically unchanged in the base paper (**Figure 6**). A boosting effect of increasing coated paper water content was observed on 2-heptanone diffusivity between 80 and 100% RH, indicating structural modifications of the wheat gluten network under water uptake as already suggested (23).

In the same way, no significant changes in the solubility coefficient of 2-heptanone for base paper were observed with relative humidity, whereas the solubility coefficient in the coated paper increased by 10 times between 10 and 80% RH. As for permeability, the 2-heptanone solubility coefficient of the wheat gluten layer can be estimated by taking into account the relative coat weight of the layer ( $55 \text{ g m}^{-2}$ ). As shown in **Figure 7**, the WG layer was found to possess a high sorption ability,



**Figure 6.** Diffusivity coefficient of aroma compound as a function of relative humidity: ( $\Delta$ ) 2-heptanone through base paper; ( $\blacktriangle$ ) 2-heptanone through WG coated paper; ( $\square$ ) 2-nonanone through base paper; ( $\blacksquare$ ) 2-nonanone through WG coated paper.



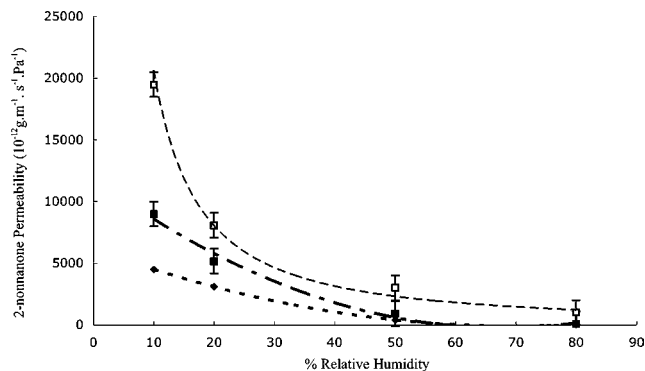
**Figure 7.** 2-Heptanone solubility coefficient as a function of relative humidity in base paper ( $\Delta$ ), WG coated paper ( $\blacktriangle$ ), and gluten layer ( $\circ$ ).

which increased with relative humidity and was largely superior (6 times) to that of the base paper. Experimental determination of 2-heptanone sorption by a self-supported gluten film at 50% RH gave a coefficient of  $23 \times 10^{-3} \text{ kg m}^{-3} \text{ Pa}^{-1}$  versus  $14.5 \times 10^{-3} \text{ kg m}^{-3} \text{ Pa}^{-1}$  by calculation. The ability of the gluten layer to sorb 2-heptanone was confirmed in agreement with literature data; a solubility coefficient of 2-heptanone ( $24 \times 10^{-3} \text{ g m}^{-3} \text{ Pa}^{-1}$ ) was found in a wheat gluten film (26).

It can be supposed that the increase of the 2-heptanone solubility and consequent transfers with relative humidity could be due to the higher water content of the films. However, the solubility of this compound in water is limited to  $4.3 \text{ g L}^{-1}$  at  $22^\circ\text{C}$  (44), and the difference in water content between the base paper and the gluten coated paper for a determined humidity or between two levels of humidity for the same paper could not explain this increase.

For hydrophilic polymers such as EVOH, nylon 6, multilayer polymer, methylcellulose, and proteins films an increase of permeability was observed with increasing relative humidity and was interpreted as a consequence of the plasticizing effect of water (15, 16, 25, 27, 36). High relative humidity could induce a reduction of the glass transition temperature ( $T_g$ ) to values below ambient temperature and consequently an increase of the polymeric chain mobility. More sites were available for the aroma sorption process, and diffusivity of small molecules was favored.

Wheat gluten is a highly amorphous polymer that is water plasticizable. Indeed, the presence of amide groups, which can



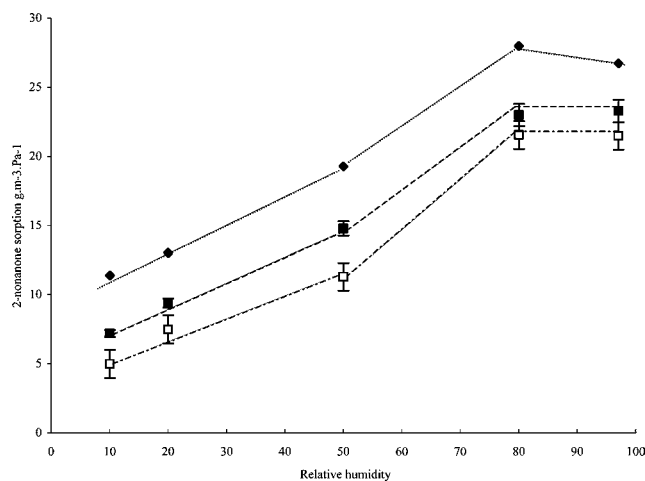
**Figure 8.** 2-Nonanone permeability through base paper ( $\square$ ), WG coated paper ( $\blacksquare$ ), and gluten layer ( $\blacklozenge$ ) as a function of relative humidity.

interact with water, contributes to the high water content of this polymer at high relative humidity (23). One of the most visible effects of plasticizer is the decrease of glass transition temperature of the polymer. The  $T_g$  value for dry gluten was found to be equal to  $187^\circ\text{C}$  but to decrease significantly with increasing water content to reach ambient temperature (45). It could be supposed that at  $25^\circ\text{C}$  and high humidity, the higher mobility of the gluten proteins chain made the 2-heptanone diffusion in the polymeric network easier and increased the accessibility of the 2-heptanone sorption site, inducing a higher 2-heptanone permeability.

*Transfer of 2-Nonanone.* The effect of relative humidity on 2-nonanone permeability and diffusivity was completely different from that observed on 2-heptanone for both papers. A significant decrease of 2-nonanone permeability with increasing relative humidity was found (Figure 8). From 10 to 50% RH, the permeability of 2-nonanone decreased by 100 times through WG coated paper. Above 80% RH, the permeability was inferior to  $10 \times 10^{-15} \text{ kg m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ . For uncoated paper, changes in 2-nonanone permeability with relative humidity were less marked but were not negligible. Estimation of permeability through the gluten layer clearly showed the impact of coating in the decrease of 2-nonanone permeability. Moreover, experimental determination of 2-nonanone permeability through a self-supported wheat gluten film at 10 and 50% RH showed the same trend of decrease (from  $1542 \times 10^{-15}$  to  $50 \times 10^{-15} \text{ kg m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ ). As previously stated, the experimental values were lower than the calculated values due to the difficult evaluation of layer thickness and the lack of coating homogeneity.

As expected, the diffusivity coefficients through both papers decreased with the relative humidity (Figure 6). In contrast, the sorption behavior of the two papers was surprising: the sorption of 2-nonanone in both papers increased with the moisture content up to reach 80% RH (Figure 9). The aroma uptake of the WG coated paper was slightly higher than that of the base paper. The sorption of 2-nonanone by the WG coating layer was also estimated and reported in Figure 9. Solubility coefficients higher than those of both papers were clearly observed, with, however, the same trend of sorption increase with relative humidity. It has been verified that the increase of moisture content and its effect on 2-nonanone solubility could not explain the increase of solubility. Indeed, the solubility in water of 2-nonanone was particularly weak ( $0.38 \text{ g L}^{-1}$  at  $22^\circ\text{C}$ ).

A decrease of transfer has already been described for esters in PVOH polymers (2). Permeability and solubility of ethyl propionate decreased with increasing relative humidity, but the decrease in diffusivity was observed for only very high relative humidity. The authors explained that the presence of water



**Figure 9.** 2-Nonanone solubility coefficient as a function of relative humidity in base paper (□), WG coated paper (■), and gluten layer (◆).

**Table 1.** Mean Contact Angles of Base Paper and Wheat Gluten (WG) Coated Paper to Water, Oil, and Aroma Compounds Measured at 25 °C and Different Relative Humidities (RH)

material	% RH	contact angle (deg)			
		water	oil	2-heptanone	2-nonanone
base paper	50	109.7 (2.7)	<10	<10	<10
	85	67.4 (2.1)	<10	nd <sup>a</sup>	nd
WG coated paper	50	89.9 (2.1)	30.4 (0.9)	24	20
	85	66.6 (1.8)	37.4 (1.5)	nd	nd

<sup>a</sup> Not determined.

molecules in the polymer matrix occupied “holes” that otherwise would be available for the diffusion of molecules. Consequently, the diffusivity diminished with the increasing of length of the viable diffusion paths. For polymers in the glassy state such as polycarbonate, oxygen transfers were described as decreasing after volatile sorption. The free volume that could be available for the oxygen transfer was already occupied by volatiles, increasing the tortuosity and thus decreasing oxygen diffusion (37).

With regard to the papers studied, the presence of water seemed to open the polymer structure (starch for the base paper and gluten for the coated paper) and favored the sorption of 2-nonanone by increasing the availability of hydrophobic absorption sites. However, the presence of water molecules, which occupied “holes”, hindered the 2-nonanone diffusivity and induced a decrease of permeability with the moisture content increase. The transfer properties of 2-nonanone were clearly influenced by its diffusivity properties rather than solubility properties. This behavior was related not only to the hydrophobic nature of the volatile but also to the characteristics of the base and coated papers.

From a comparison of 2-heptanone and 2-nonanone sorption by the papers, it could be observed that the base paper has a higher affinity with 2-nonanone than with the more polar compound. This preferential affinity is also observed for the coated paper or the gluten layer, but less markedly. This result was related to the more hydrophobic nature of the base paper compared to the wheat gluten coated paper as characterized by surface property and contact angle measurements. Indeed, the contact angle of water for base paper was higher than that of WG coated paper (Table 1). The contact angle of oil for base paper was particularly low and could not be measured. In the same manner, the 2-heptanone and 2-nonanone contact angles

**Table 2.** Values of Permeance (*P*) and Solubility (*S*) Coefficients of 2-Heptanone and 2-Nonanone in Wheat Gluten Coated Paper and LDPE Film Measured at 25 °C and at the Full Vapor Pressure of the Compound

material	aroma compound	% RH	<i>P</i> (10 <sup>-3</sup> kg J <sup>-1</sup> m <sup>-2</sup> Pa <sup>-1</sup> )	<i>S</i> (g m <sup>-3</sup> Pa <sup>-1</sup> )
WG coated paper	2-heptanone	10	0.24 (0.02)	1.16 (0.03)
		80	0.83 (0.04)	11.7 (0.8)
	2-nonanone	10	3.8 (0.43)	7.2 (0.16)
		80	0.032 (0.001)	23.6 (1.9)
LDPE	2-heptanone	indifferent	2.34 (0.51)	30.4 (5.1)
	2-nonanone		0.29 (0.02)	126 (26)

of the base paper could not be measured, whereas low but measurable values were obtained with wheat gluten coated paper. The lower the angle contact is, the higher the affinity between the packaging and the liquid. Thus, it can be concluded that base paper had a hydrophobic character which was higher than that of coated paper. To our knowledge, the base paper was treated and impregnated with calcium carbonate and starch. No data were available with regard to the nature of this starch, but hypotheses can be made about its hydrophobic nature. The hydrophobic character of the base paper was reduced by gluten coating and when the humidity increased. Moreover, the slightly lower angle found with 2-nonanone compared to that with 2-heptanone for wheat gluten coated paper confirmed the preferential affinity for the most hydrophobic volatile.

Whatever the relative humidity and the methyl ketones, the experimental values of solubility coefficient were different from calculated values, suggesting interactions between the volatiles and the different films at the concentration studied. Consequently, it can be assumed that the transfer has a non-Fickian behavior as observed for other edible films (25, 28).

*Comparison of Coated Paper and LDPE for Aroma Barrier Properties.* In Table 2, the permeance and solubility coefficients of the two methyl ketones through LDPE film and WG coated papers are reported. When various types of packaging are compared, the permeance obtained by dividing permeability by the thickness is more adaptable.

The solubility coefficients were higher for LDPE film than those found for the coated paper. Whatever the film, the solubility coefficient of 2-nonanone was found to be higher than that of 2-heptanone, according to the nonpolar nature of the films. LDPE is a typical nonpolar film, and for numerous flavor compound classes, as hydrophobicity increases, the quantity of sorbed flavor compounds by LDPE increases (7, 28). Comparatively, the coated paper possessed a weaker affinity for the hydrophobic compound.

Whatever the humidity, the 2-heptanone permeance through the LDPE film was largely superior to that occurring through the gluten coated paper. Also, in spite of an increase of transfer through the gluten coated paper at high humidity, the 2-heptanone permeance through this material is still lower than that occurring in the plastic film.

At low humidity, the 2-nonanone permeance through the LDPE film was lower than the permeance of coated paper, but the decrease of transfer found with the increasing relative humidity led to the barrier effect of coated paper being up to 10 times more effective than the LDPE film.

These results showed the interesting barrier properties of the wheat gluten coated paper for alkan-2-ones, which can be superior in controlled conditions to those of LDPE, a very commonly used packaging film. Therefore, WG coated paper can be advantageously used to package high-moisture foodstuffs such as cheeses, fruits, and vegetables.

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