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Journal of Chromatography A, 969 (2002) 9–16

JOURNAL OF CHROMATOGRAPHY A

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Use of inverse gas chromatography to determine thermodynamic parameters of aroma–starch interactions

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Abstract

Interactions between aroma compounds (*d*-limonene, ethyl hexanoate, octanal and 1-hexanol) and high amylose cornstarch were studied using inverse gas chromatography. Free energies of adsorption (ΔG_a) and enthalpies of adsorption (ΔH_a) of aroma compounds on starch were measured in the temperature range of 33–40 °C. The results showed existence of interactions between aroma compounds and starch, involving hydrogen bounds and dipole–dipole interactions. Sorption isotherms and Henry's law solubility coefficients (S) were determined at 40 °C. Three different shapes of isotherms were obtained according to the BET classification: type III for *d*-limonene, type II for ethyl hexanoate and linear for octanal and 1-hexanol.

Keywords: Thermodynamic parameters; Inverse gas chromatography; Adsorption isotherms; Aroma compounds; Starch

1. Introduction

Interactions between aroma compounds and other ingredients of the food matrix play an important role in the flavour perception of the food product and consequently its acceptance by the consumer [1]. Starch is an important ingredient in all cereal products. Moreover, starch and starch derivatives are widely used as additives (thickener, stabiliser, texturing agent etc.) or as flavour carriers. A fundamental understanding of aroma–starch interactions is useful to improve food flavouring and to develop new carriers for flavour encapsulation.

Interactions between aroma compounds and polysaccharides at low water content have mostly been studied by static methods. The matrix is exposed to an atmosphere enriched with the aroma compound. When the equilibrium is reached, the amount of aroma compound sorbed in the food matrix is determined by direct analysis of the material [2,3], or by headspace analysis [4,5].

In contrast, the current study used a dynamic technique: inverse gas chromatography (IGC). IGC involves injecting a known amount of individual sorbate (in this case an aroma compound) into a column packed with the material to be tested (in this case starch), placed in the oven of a gas chromatograph. In comparison to static methods, IGC allows access to more thermodynamic parameters (partition coefficient, solubility coefficients, and also enthalpies of adsorption, free energies of adsorption). IGC is

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0021-9673/02/$ – see front matter
PII: S0021-9673(02)00208-X

also a more rapid technique to determine the sorption isotherms of the sorbate on the matrix.

In the last few decades, IGC has become a powerful technique in evaluating the properties of many materials. In addition to thermodynamic parameters, IGC provides access to kinetic parameters such as diffusion coefficients, as well as several physico–chemical properties of materials such as surface energy, phase transitions, crystallinity and specific area. IGC has a wide range of applications: pharmaceuticals, natural and synthetic polymers, food products and ingredients, flavouring and perfume, minerals etc. With the appearance of the first commercial inverse gas chromatographs [6], IGC is becoming increasingly popular. IGC has expanded in the pharmaceutical industry, and may well do the same in the food area.

In food science, IGC has mostly been used to measure the sorption of water in dry food products like cookies [7], soluble coffee [8], starchy products [9,10], pectin [11], or the sorption of aroma compounds on food packaging polymers [12,13]. Few authors have used IGC to study interaction between aroma compounds and food matrices [14–17]. The main drawback of IGC is the dehydration of the stationary phase during the experiment. As water plays an important role in flavour–matrix interactions, it is important to control this parameter. Recently, the IGC technique has been improved by humidifying the carrier gas to reduce matrix dehydration [13,15].

In the current communication, thermodynamic parameters of aroma–starch interactions were determined by IGC. Experiments were performed at different temperatures to measure the enthalpies of adsorption and free energies of adsorption, and with increasing amounts of aroma compounds to determine the sorption isotherms and the solubility coefficients.

2. Materials and methods

2.1. Materials

2.1.1. Aroma compounds

d-Limonene was obtained from René Laurent (Le Cannet, France). Ethyl hexanoate, octanal and 1-hexanol were obtained from Sigma–Aldrich Chimie (Saint-Quentin Fallavier, France). The purity of aroma compounds ranged from 98 to 99%.

2.1.2. Starch

Corn starch with an amylose content of 70–80% and less than 1% extractable lipids, was provided by Roquette Frères (Lestrem, France). The starch was sieved to obtain particle sizes between 40 and 63 μm.

2.2. Methods

2.2.1. Inverse gas chromatography

Glass columns (11.5 cm×4.5 mm I.D.) were deactivated with dimethyldichlorosilane (DMCS) before being packed with starch. Column packing was facilitated by combined application of an electric vibrator and a vacuum system. The mass of the stationary phase was 1.14±0.04 g.

The starch column was placed in the oven of a Carlo Erba 6000 Vega II gas chromatograph and connected to the injector and detector with deactivated fused-silica tubing (0.32 mm I.D.). The gas chromatograph, equipped with a flame ionisation detection (FID) system, was operated under isothermal conditions at a temperature of 33, 36 or 40 °C. These low temperatures were chosen in order to preserve the maximum water content in the starch column. The injector and detector temperatures were maintained at 250 °C. The carrier gas was nitrogen. The nitrogen flow rate was regulated at 20 ml min^{-1}. This flow rate provided a pressure of 2.1±0.1 bar at the head of the column. All experiments were performed under humid conditions, the carrier gas being bubbled in water, as described by Boutboul et al. [15]. Prior to the experiments, the starch column was conditioned for a minimum of 8 h with the carrier gas to reach a stable starch–water content, resulting in stable retention times. The water content of starch at equilibrium was 9±1%.

Pure aroma compounds were injected in a splitless mode with a 0.5-μl Hamilton syringe (Supelco, Bellefonte, PA, USA). The amount injected for (ΔH_a) and (ΔG_a) calculations was 0.5 μl, while 0.05, 0.1, 0.2, 0.3, 0.4 or 0.5 μl were injected when determining of sorption isotherms. Retention times were determined using Borwin 1.2 data acquisition

software. All injections of aroma compounds were performed in triplicate. Less than 10% variation was observed in retention times for replicate injections. Column to column variations were less than 10% for *d*-limonene, ethyl hexanoate and octanal and 15% for 1-hexanol.

Under these conditions of low water content (9±1%) and low temperature (36–40 °C), the starch was in the glassy state since the T_g of corn starch is around 140 °C at a water content of 10% [18]. Therefore, we have assumed that our experiments were concerned with the solid–gas chromatography and the following IGC equations could be used.

2.2.2. Specific retention volume

Specific retention volumes, V_g, were calculated using Eq. (1), where t (min) is the retention time of the solute, t_0 (min) is the retention time of a non-retained compound (methane), F (ml min^{-1}) is the carrier gas flow rate, m (g) is the mass of stationary phase and T (K) is the temperature of the column. The James and Martin compressibility factor, j, was calculated using Eq. (2), where P_i and P_0 are the inlet and outlet pressures, respectively:

$$V_g = j \cdot \frac{(t - t_0)}{m} \frac{F \cdot 273}{T} \quad (1)$$

$$j = \frac{3}{2} \cdot \frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1} \quad (2)$$

2.2.3. Enthalpies of adsorption

To determine the enthalpies of adsorption (ΔH_a) of the four aroma compounds on high amylose corn starch, the specific retention volumes (V_g) were measured at three different temperatures (33, 36 and 40 °C) and the retention diagram $\ln V_g = \ln(1/T)$ was plotted for each compound. ΔH_a was calculated from the slope of the retention diagram, which is equal to $(-\Delta H_a/R)$, according to Eq. (3):

$$\Delta H_a = -R \cdot \frac{\partial(\ln V_g)}{\partial(1/T)} \quad (3)$$

2.2.4. Free enthalpies of adsorption

Free enthalpy of adsorption of each aroma compound on high amylose corn starch has been determined at each temperature (33, 36 and 40 °C) using Eqs. (4) and (5):

$$\Delta G_a = -RT \ln K_p \quad (4)$$

where K_p is the partition coefficient of the aroma compound between the stationary phase (starch) and the mobile phase (Eq. (5)):

$$K_p = V_N/V_P \quad (5)$$

where V_N is the net retention volume (Eq. (6) and V_p is the volume of the stationary phase:

$$V_N = jF(t - t_0) \quad (6)$$

K_p has been calculated as follows: (i) according to Eqs. (1) and (6):

$$V_N = jF(t - t_0) = V_g \cdot \frac{T_c m}{273} \quad (7)$$

(ii) according to Eqs. (5) and (7):

$$K_p = V_g \cdot \frac{T_c}{273} \cdot \frac{m}{V_p} = V_g \cdot \frac{T_c}{273} \cdot \rho \quad (8)$$

where T_c is the column temperature and ρ is the density of the stationary phase.

2.2.5. Sorption isotherms

Sorption isotherm data were calculated from the shape of the chromatographic peaks according to the method of Kiselev and Yashin [19], as applied by Gavara et al. [20] to the study of aroma (Fig. 1).

The sorbate uptake by the stationary phase (a) was calculated using Eq. (9):

$$a = \frac{A_{\text{ads}}}{A_{\text{cal}}} \cdot \frac{m_s}{m_p} \quad (9)$$

where m_s (μg) is the mass of the injected compound, m_p (g) is the mass of the stationary phase. A_{cal} is the chromatographic peak area, and A_{ads} is the sum of

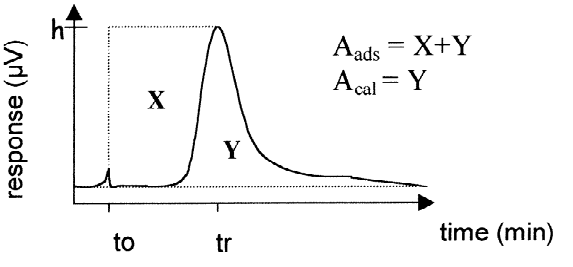

Fig. 1. Chromatographic peak and its exploitation in IGC.

the area bound by the base line, the peak height, the non-retention time and the final peak profile.

The partial pressure of the sorbate (p) was calculated from Eq. (10):

$$p = \frac{n_s R T_c h}{F_c A_{\text{cal}}} \tag{10}$$

where n_s (μmol) is the sorbate moles, R (Pa m^3 K^{-1} mol^{-1}) is the universal gas constant, T_c (K) is the column temperature, F_c (ml min^{-1}) is the corrected flow rate, h (μV) is the peak height.

The flow rate was corrected for temperature and compression drop through the column length. The corrected flow rate (F_c) was calculated from Eq. (11), where F (ml min^{-1}) is the carrier gas flow rate, T_c (K) is the column temperature and T_r (K) is the room temperature (at which the flow rate is measured). P_i and P_0 are the inlet and outlet pressures, respectively:

$$F_c = \frac{F T_c}{T_r} \cdot \frac{[(P_i/P_0)^3 - 1]}{[(P_i/P_0)^2 - 1]} \tag{11}$$

The areas A_{ads} and A_{cal} (Fig. 1) were calculated with Matlab 4 software. Acquisition of the chromatograms was made using Borwin 1.2 software. The data were then exported to a text file, and treated with Matlab 4 software, in order to replot the chromatograms and to calculate the areas.

2.2.6. Solubility coefficients

Solubility coefficients, S (μg g^{-1} Pa^{-1}), were calculated from the sorption isotherms using Henry's law (Eq. (12)):

$$a = Sp \tag{12}$$

where S corresponds to the slope of the sorption isotherm [$a = f(p)$]. S was measured in the initial linear portion of the isotherms, as described by Gavara et al. [20]. At this low sorbate concentration, no interaction between the sorbate molecules themselves occurs.

3. Results and discussion

3.1. Enthalpies of adsorption

To determine the enthalpies of adsorption (ΔH_a) of the four aroma compounds on starch, the specific retention volume (V_g) of each compound was measured at three different temperatures (33, 36 and 40 °C) and the retention diagrams $\ln V_g = f(1/T)$ were plotted (Fig. 2). Straight lines were obtained with a slope equal to ($-\Delta H_a/R$), according to Eq. (3).

ΔH_a values ranged from −55 to −92 kJ mol^{-1} (Table 1). By comparing ΔH_a values to the enthalpy of condensation of the compounds ΔH_c (found in tables), it was observed that $|\Delta H_a|$ is greater than $|\Delta H_c|$. This implies that the enthalpies of adsorption measured are not only due to the heat of condensation of the compounds onto the matrix, but also to

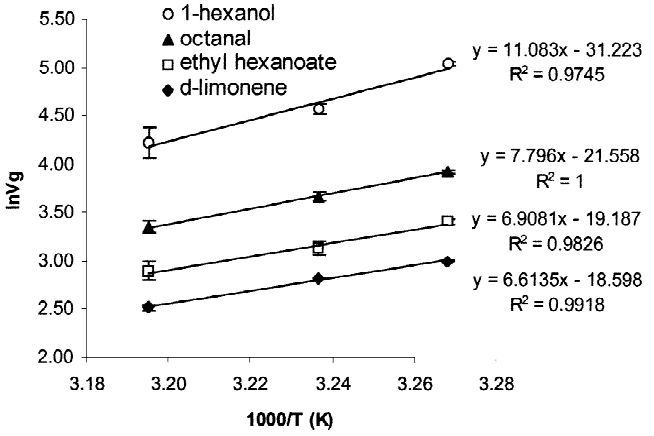

Fig. 2. Retention diagrams of aroma compounds on high amylose corn starch.

Table 1
Enthalpies of adsorption (ΔH_a) of aroma compounds on high amylose corn starch, comparison with enthalpies of condensation (ΔH_c) of the compounds

Aroma compound	ΔH_a (kJ mol^{-1})	ΔH_c (kJ mol^{-1}) [24]	$\lvert\Delta H_a\rvert - \lvert\Delta H_c\rvert$ (kJ mol^{-1})
1-Hexanol	−92.1	−61.6	30.5
Octanal	−64.8	−43.0	21.8
Ethyl hexanoate	−57.4	−51.7	5.7
d-Limonene	−55.0	−44.0	11

physico–chemical interactions between aroma compounds and starch. $\lvert\Delta H_a\rvert - \lvert\Delta H_c\rvert$ ranged from 5.7 to 30.5 kJ mol^{-1} (Table 1). These values correspond to weak energy bounds such as hydrogen bounds and dipole–dipole interactions.

For the more polar compounds (1-hexanol, octanal and ethyl hexanoate), hydrogen bonds (10–40 kJ mol^{-1}) and Van der Waals dipole–dipole interactions (2.1–8.4 kJ mol^{-1}) are likely to be involved. Hydrogen bonds can be formed between the hydroxyl groups of starch and the hydroxyl group of 1-hexanol (donor and acceptor) or the carbonyl group of octanal (acceptor). 1-Hexanol is more likely to interact via hydrogen bonds, because of its donor and acceptor capacity. Presumably this is why 1-hexanol showed a stronger energy (30.5 kJ mol^{-1}) than octanal (21.8 kJ mol^{-1}). Hydrogen bonds could not be involved for ethyl hexanoate, which showed a weak energy (5.7 kJ mol^{-1}) because of the steric hindrance of the molecule. In this case, only dipole–dipole interactions must be involved.

d-Limonene, which is an apolar compound, could not develop such polar interactions with starch. However, its energy was quite important (11 kJ mol^{-1}) in comparison to ethyl hexanoate. One hypothesis would be the existence of hydrophobic interactions between *d*-limonene and non-complexed lipids present in high amylose cornstarch (at a ratio less than 1%).

ΔH_a values determined in this study (from −55.0 to −92.1 kJ mol^{-1}) are within the range of those reported in the literature for polar polymeric matrices, using IGC. Valeri and Demertzis [10] measured enthalpies of adsorption of ethanol on starchy substrate to be from −14.3 to −20.3 kJ mol^{-1}. Enthalpies of adsorption of heptane and octane on cellulose were −47.0 and −57.0 kJ mol^{-1}, respectively [21]. ΔH_a values of −15.5 to −81.2 kJ mol^{-1} were calculated for alcohols (C1–C4) on ethylene–vinyl alcohol copolymer (EVOH) [20].

3.2. Free energy of adsorption

The free energies of adsorption were calculated for each compound at each temperature (33, 36 and 40 °C) (Table 2).

3.3. Sorption isotherms and solubility coefficients

3.3.1. Sorption isotherms

The sorption isotherm of each aroma compound was determined at 40 °C (Fig. 3). Increasing amounts of aroma compounds (from 0.05 to 0.5 μl) were injected onto the column and the sorbate uptake by the stationary phase (*a*) was plotted versus the partial pressure of the sorbate (*p*).

Sorption isotherms of 1-hexanol and octanal are linear. They follow Henry's law, from which it is adduced that these sorbates have a high affinity for the matrix.

Sorption isotherm of ethyl hexanoate has an *S* shape; type II according to the BET classification, implying a medium affinity of the molecule for the matrix. This isotherm can be divided in three sections: the first section is concave to the pressure axis (1), the second section is linear (2), and the third section is convex to the pressure axis (3). These three sections correspond to (1) the fixation of flavour molecules onto starch, (2) a saturation phenomenon, where all the binding sites of starch for ethyl hexanoate are taken, and (3) the accumulation of the sorbate molecules on the surface of starch. The exponential shape of this last section shows a cooperative effect.

Table 2
Free energies of adsorption of aroma compounds on high anylose corn starch at 33, 36 and 40 °C

	ΔG_a (kJ mol−1)		
	33°C	36°C	40°C
d-Limonene	−6.88	−6.40	−5.63
Ethyl hexanoate	−7.91	−7.16	−6.61
Octanal	−9.23	−8.56	−7.79
1-Hexanol	−12.06	−10.87	−10.9

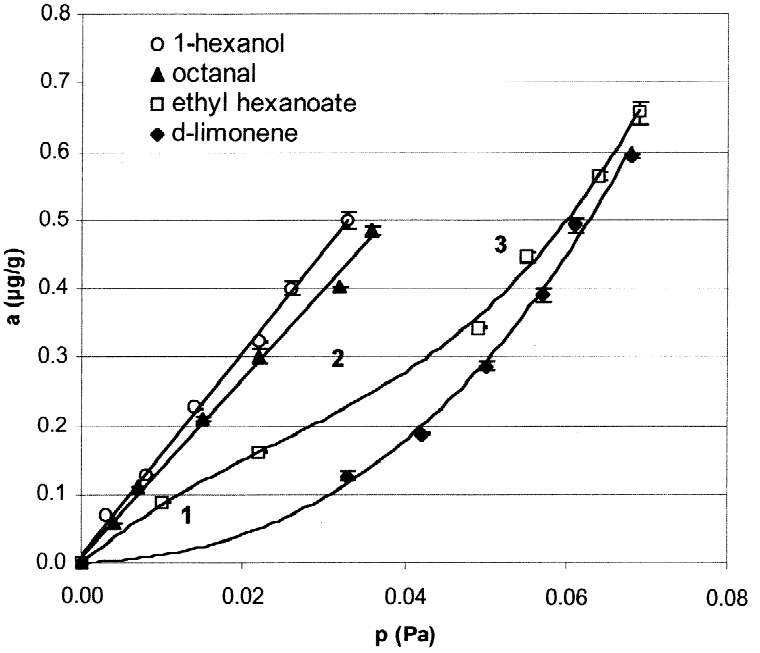

Fig. 3. Sorption isotherms of aroma compounds on high amylose corn starch at 40 °C.

Sorption isotherm of *d*-limonene is type III of BET classification, which means a weak affinity of the sorbate for the matrix. Interactions of sorbate molecules between themselves are stronger than sorbate–matrix interactions. This isotherm is convex to the pressure axis. A strong cooperative effect is observed: at low pressure the sorption is weak, and then sorption of the first molecules of *d*-limonene on starch facilitates the sorption of additional sorbate molecules. Sorption then increases rapidly with the pressure, corresponding to the accumulation of *d*-limonene on the surface of starch.

The shape of the isotherms was correlated to the shape of the chromatographic peaks obtained by injecting increasing amounts of aroma compounds.

For 1-hexanol and octanal, which have linear isotherms, the retention time decreases as the injected volume increases (Fig. 4).

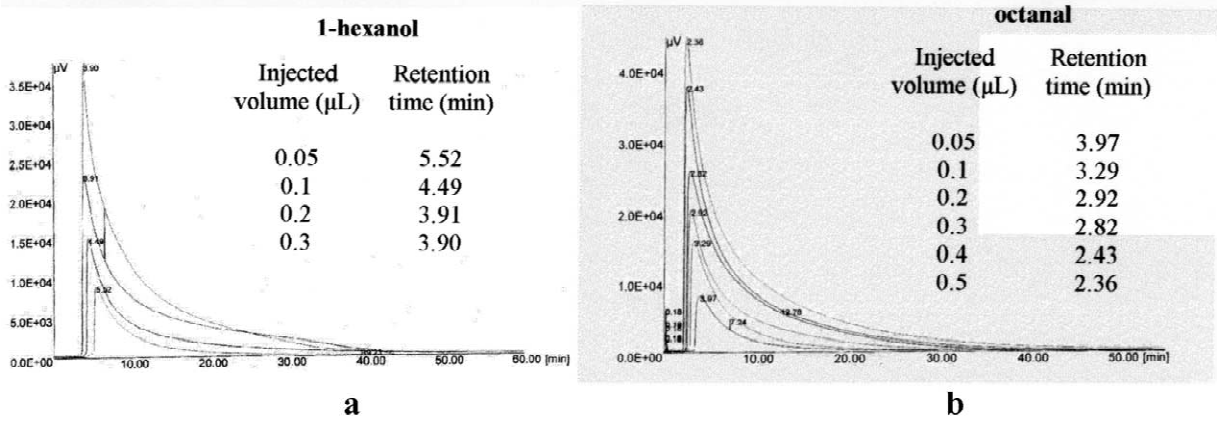

Fig. 4. Chromatographic peaks obtained for injection of increasing volumes of pure 1-hexanol (a) and octanal (b).

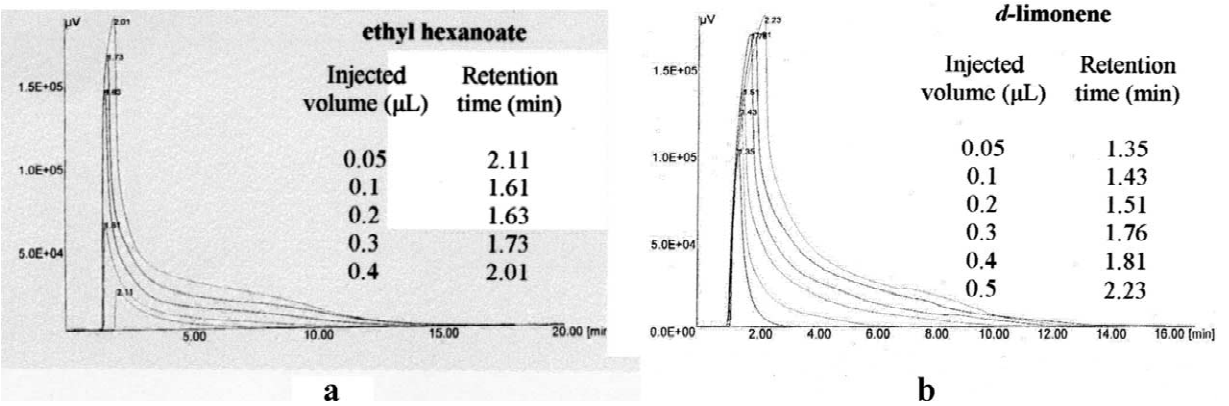

Fig. 5. Chromatographic peaks obtained for injection volumes of pure ethyl hexanoate (a) and *d*-limonene (b).

For ethyl hexanoate (Fig. 5a), which has a BET type II isotherm, the retention time begins to decrease; this corresponds to the fixation step. The retention time becomes constant, which corresponds to the saturation step, and finally increases, which corresponds to the accumulation step.

For *d*-limonene (Fig. 5b), which has a BET type III isotherm, the retention time increases with the injected volume, corresponding to an accumulation phenomenon.

Moreover, for ethyl hexanoate and *d*-limonene, the peaks maxima have a pronounced shoulder on the right-hand side. This corresponds to a saturation phenomenon. For ethyl hexanoate, this phenomenon appears for high amounts of injected compound. For *d*-limonene, it appears from the beginning. This saturation phenomenon is not observed for octanal and 1-hexanol, showing a better affinity for the starch.

It can be observed that the shape of the peaks does not follow the law of ideal chromatography, which presumes that sorbates only interact with the surface of the matrix. In ideal chromatography, a linear isotherm corresponds to a series of symmetrical peaks, a convex isotherm to a series of fronting peaks, and a concave isotherm to a series of tailing peaks. Here, all the peaks are tailing, but the tails are not superposed, as they would have been in ideal chromatography. Moreover, some peaks exhibit both tailing and fronting (*d*-limonene, ethyl hexanoate). For octanal and 1-hexanol, the fronts of the peaks are nearly vertical and shift to the left as in ideal chromatography, but the tails are not superposed. The same types of peaks were observed by Steinberg and Kreamer [22] when injecting volatile organic compounds onto calcareous soils, using humidified IGC. Consequently, as explained by the authors, the shape of the peaks cannot be ascribed only to equilibrium phenomena. This is valid in our case as well. Kinetic phenomena must also be involved, like the diffusion of the aroma compounds inside the starch granules. For most compounds (1-hexanol, octanal, ethyl hexanoate), the maxima of the peaks become more rounded when low amounts are injected, indicating that a diffusion phenomenon can contribute to the peak morphology.

These results are in accordance with our previous studies [15,23], where it was shown that aroma retention on high amylose corn starch mainly results from an adsorption phenomenon, and that diffusion and partitioning phenomena could also be involved in presence of water (at a content of 8–10% in the starch). Water facilitates the diffusion of aroma compounds into the starch granules, and allows the partitioning of the aroma compounds between the gas phase and the water weakly bounded to the granules.

The deviation from the ideal chromatography law can be explained by the heterogeneity of the starch matrix. Starch is a biopolymer made of amorphous and crystalline zones. Starch is also a hygroscopic material containing water. This water facilitates the diffusion of the aroma compounds in the amorphous regions of the starch granules. Moreover, in the system, water is present in the stationary phase but also in the gas phase, which is consequently not

inert. This is not a case of infinite dilution where the probe molecules do not interact with each other. Water molecules present in the gas phase can interact with aroma compounds, thereby complicating the system.

In spite of the deviation from the ideal chromatography law, IGC has proved to be a reliable technique to study biomaterials (food matrices) or hygroscopic polymers (EVOH) [13], where humidity is an important factor.

3.3.2. Solubility coefficients

Solubility coefficients S were calculated from the sorption isotherms using Henry's law (Eq. (12)) at low aroma concentration.

S was calculated from the initial linear portion of the isotherms. S values were representative of the three different behaviours of aroma compounds: S was high for 1-hexanol and octanal (17.5 and 15.8 $\mu g\ g^{-1}\ Pa^{-1}$, respectively), intermediate for ethyl hexanoate (8.7 $\mu g\ g^{-1}\ Pa^{-1}$) and weak for *d*-limonene (1.1 $\mu g\ g^{-1}\ Pa^{-1}$).

S values determined in this work are similar to those determined by Aucejo et al. [13] in EVOH, which is a polar polymer like starch. The authors found a value around 1 $\mu g\ g^{-1}\ Pa^{-1}$ for the solubility coefficient of *d*-limomene and ethyl hexanoate in EVOH at 25 °C.

4. Conclusion

This work has shown that IGC is an efficient tool to study aroma–starch interactions. IGC is also a new technique to determine thermodynamic parameters of aroma–macromolecule interactions, in comparison to classic methods like static headspace. This study allowed us to evaluate the nature of aroma–starch interactions (hydrogen bounds, dipole–dipole interactions) and to understand the different behaviours of aroma compounds with starch considering their chemical structure and function.

Acknowledgements

The authors are grateful to Dr Bertrand Head (ENSIA) for his help on the realisation of the Matlab computer program and to Professor Robert Gauthier from CNRS in Lyon for expert view on IGC applied to polymers.

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