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# Vapour partition of aroma compounds in strawberry flavoured custard cream and effect of fat content

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## Abstract

Gas–matrix partition coefficients (*k*) of volatile compounds of a strawberry flavour added to a complex model system (custard dessert, COST action 921 recipe) were determined. The influence of fat content on the volatility of the strawberry aroma compounds was investigated using full fat milk- (FFM) and skimmed milk- (SM) custards. For the purpose of this study, the phase ratio variation (PRV) method was used because of its easy application for a mixture of volatiles without requiring any calibration. From the 15 aroma compounds present in the flavouring mixture, seven were volatile enough to be detected and concentrated enough to allow the calculation of *k* values. Gas–matrix partition coefficients were compared to gas–water partition coefficients. For some aroma compounds (ethyl hexanoate, ethyl butanoate, and hexanal) a significantly lower *k* value was observed in FFM-custard than in water, indicating a retention effect caused by the matrix. As expected, the fat content and the hydrophobicity of the volatile compounds were of great importance to explain the differences between partition coefficients in SM custards and in FFM custards: for SM-custard, a higher release in the vapour phase was observed than for FFM-custard; the more hydrophobic the aroma compound, the higher the effect. Moreover, ethyl butanoate and hexanal were less retained in SM-custard than in water. This may be attributed to a salting-out effect due to sucrose.

The results of this study indicate the importance of the interactions between volatiles and non-volatile compounds as well as of the chemical and physical properties of the aroma compounds in affecting the composition of the gas phase at equilibrium with a complex matrix. More than that, they provided a basis for the studies developed within COST action 921 with the flavoured custard model system.

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*Keywords:* Gas/matrix partition coefficient; Phase ratio variation method (PRV); Milk fat; Strawberry aroma compounds; COST action 921; Custard

## 1. Introduction

Flavour quality is one of the most important factors determining the acceptance of foods by the consumer. Flavour is mainly related to the release in the gas phase of volatile aroma compounds present in the food and several are the aspects that influence it and contribute to define the final perception by human sense.

Kinetic and thermodynamic phenomena affect the partition of aroma compounds from a food in the gas phase (Voilley & Souchon, 2006; Guichard, 2002; Druaux & Voilley, 1997). The former are related to the diffusion of volatile compounds in the system and physical and structural properties of the food are relevant for the mass transfer kinetics in the matrix itself as well as in the vapour phase.

The equilibrium distribution of flavour compounds between the different phases (solid–water–oil) and the physicochemical interactions between the aroma compounds and food macromolecules play, on the other hand, an important role in the thermodynamic aspects of the flavour release and may suppress the presence of the aroma compounds in the gas phase.

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The concentration of volatile compounds in one or between several phases of a system depends on the specific properties of the pure compound and on thermodynamic parameters at macroscopic level (vapour pressure, solubility, partition coefficient and activity coefficients) (Voilley & Souchon, 2006).

However, proteins and saccharides (oligo-, poly-) could determine interactions of different nature with aroma molecules reducing their concentration in the vapour phase. As a consequence, a flavouring can generate totally different odour sensations when applied to different foods or if not well optimised, it could also result in an imbalance in the aroma profile (de Roos, 2006; Guyot et al., 1996; Van Ruth & King, 2003).

The knowledge of the way aroma compounds are distributed between food matrix and gas phase allows to understand their perception by consumer in food system.

Giving the importance of flavour performance in food, a large number of studies have been carried out using simple binary (water–aroma) or ternary (water–solute–aroma) model systems, mainly aqueous or at low viscosity to better understand the thermodynamic and kinetic phenomena affecting aroma release. A vast literature related to the effects of hydrocolloids, carbohydrates (e.g. starch, pectins) and proteins on the liquid–gas partition of volatiles have been generated in the past (Druaux & Voilley, 1997; Goubet, Le Quere, & Voilley, 1998; Guichard, 2002). However, in spite of the advances in flavour research, the prediction and control of flavour behaviour in complex food systems is still limited (Conde-Petit & Nuessli, 2006).

In fact, when this approach is applied to real foods, multi-component and multi-phasic systems, the comprehension of the flavour release could be hindered by the complexity of food. The simultaneous presence of macromolecules of different nature as well as other intrinsic factors (moisture, water activity, pH, physical and structural properties) could act synergistically or in opposite way in affecting the gas–matrix partitioning and making complicated the actual aroma release. This explains the limited studies carried out on gas–matrix partitioning of aroma compounds in complex (model or real) systems. In this case, results obtained in simple models become basic and key elements to be considered to understand the flavour release. (Philippe et al., 2003; Savary, Guichard, Doublier, & Cayot, 2006; Seuvre, Philippe, Rochard, & Voilley, 2006).

Fat is widely present in foods and its presence is of major importance in contributing to their quality and stability (Drewnowski, 1992; Guichard, 2002). Beside the important effects on physical and sensorial properties, fat could act as flavour precursor, flavour carrier and flavour release modulator (Brauss, Linforth, Cayeux, Harvey, & Taylor, 1999). Many are the studies carried out on the effects of the presence of lipids, mainly in biphasic systems (emulsions), on the flavour release due to the ability of fat to act as a solvent phase for aroma compounds depending on their lipophylicity (Doyen, Carey, Linforth, Marin, & Taylor, 2001; Relkin, Fabre, & Guichard, 2004; Van Ruth, Grossmann, & Delahunty, 2001).

When lipids are completely or partially removed from a food (i.e. low-fat foods), relevant changes in the quality properties could occur, including changes in both the rate and intensity at which flavour molecules are released in the gas phase and in the mouth during consumption.

One way of investigating the retention (or release) of aroma compounds in complex matrixes is to measure the gas/matrix partition coefficient $K(= C_g/C_m)$; this parameter describes the distribution of volatile compounds between the gas phase ($C_g$, mass or molar concentration of volatile compounds in the headspace) and the food matrix ($C_m$, mass or molar concentration of volatile compounds in the matrix).

Both static headspace methods (headspace analysis) and dynamic headspace methods (exponential dilution) have been used to measure the partition coefficient. Among the static methods, direct and indirect methods can be distinguished: direct methods require determination of aroma concentrations in both phases when the equilibrium is reached (Arvisenet, Voilley, & Cayot, 2002), while indirect methods such as the PRV method (phase ratio variation) are based on the influence of the sample volume on the concentration in the gas phase. Recently Savary et al. (2006) successfully used the PRV method for determination of $K$ values of a mixture of aroma in complex semi-solid matrices systems.

In the present work, the vapour–matrix partition of aroma compounds of a strawberry flavour added in a complex milk-based semi-gelled food system was studied. To this purpose, a custard dessert was chosen as food model system and prepared according to the recipe and procedure proposed within the COST action no. 921. The influence of fat on the volatility of strawberry aroma used to flavour custard dessert was also investigated by using two model systems prepared with skimmed milk and full fat milk.

## 2. Materials and methods

### 2.1. Strawberry aroma

The composition of the strawberry aroma, produced by Givaudan Schweiz AG (Duebendorf, Switzerland) and used for this study, is reported in Table 1.

### 2.2. Custard dessert preparation

Custard dessert was prepared according to the COST action 921 recipe and procedure using commercial sucrose (Sucrerie d'Erstein, Erstein, France), modified tapioca starch E1442 (Cerestar, Manchester, UK), $\kappa$-carrageenan (Danisco, Copenhagen, Denmark) and full fat milk (3% fat, Désirée, France) in the concentrations reported in Table 2. This procedure was standardised to produce each time a sample of 250 g of custard.

Sucrose, modified tapioca starch and $\kappa$-carrageenan were dissolved in full fat milk under stirring at room temperature.

Table 1
Chemical and physico-chemical properties of compounds of the strawberry flavour mixture

| Chemical class | Name (molecular formula) | CAS number | Amount in the flavouring mixture (mg/g) | Hydrophobicity ($\log P_{\text{oct-w}}$)[a] | Molecular Weight (g/mol) | Boiling $T$ (°C)[b] | Solubility in water (25 °C) |
|---|---|---|---|---|---|---|---|
| Esters | Ethyl hexanoate ($C_8H_{16}O_2$) | 123-66-0 | 20 | 2.84 | 144.21 | 108 | 0.52 g/l[a] |
| | Ethyl butanoate ($C_6H_{12}O_2$) | 105-54-4 | 90 | 1.78 | 116.16 | 120 | 5.6 g/l[a] |
| | Benzyl acetate ($C_9H_{10}O_2$) | 140-11-5 | 2 | 1.97 | 150.17 | 200 | Not soluble |
| | Methyl benzyl acetate (Styrallyl acetate) ($C_{10}H_{12}O_2$) | 93-92-5 | 1 | 2.33 | 164.20 | 212 | slightly (0.01–0.1%) |
| | Ethyl 3-methyl-butanoate(ethyl iso pentanoate) ($C_7H_{14}O_2$) | 108-64-5 | 10 | 2.19 | 130.19 | 133–135 | Not soluble |
| | *cis*-3-hexen-1-yl acetate ($C_8H_{14}O_2$) | 3681-71-8 | 5 | 2.63 | 142.20 | 156 | Not soluble |
| | Methyl anthranilate ($C_8H_9NO_2$) | 134-20-3 | 1 | 1.87 | 151.16 | 256 | 2.9 g/l (23 °C) |
| | Methyl cinnamate ($C_{10}H_{10}O_2$) | 103-26-4 | 24 | 2.64 | 162.19 | 262 | Not soluble |
| | Methyl dihydrojasmonate ($C_{13}H_{22}O_3$) | 24851-98-7 | 5 | 2.33 | 226.0 | 100–109 | Not soluble |
| Terpens | 2,5-dimethyl-4-hydroxy-3(2H)-furanone Furaneol™ ($C_6H_8O_3$) | 3658-77-3 | 5 | 0.09 | 128.13 | 176 | <10% |
| Furan derivate | γ-decalactone ($C_{10}H_{18}O_2$) | 706-14-9 | 20 | 2.77 | 170.25 | 114–116 | 0.66 |
| Alcohols | *cis*-3-hexen-1-ol($C_6H_{12}O$) | 958-96-1 | 15 | 1.56 | 100.16 | 156–157 | Very slightly (<%) |
| Lactone | 4-hydroxy-3-methoxy-benzaldehyde (Vanillin) ($C_8H_8O_3$) | 121-33-5 | 5 | 1.21 | 152.15 | 252 | 10 g/l |
| Aldehydes | Hexanal ($C_6H_{12}O$) | 66-25-1 | 1 | 1.78 | 100.16 | 119–124 | 4.8 g/l |
| Ketons | β-ionone ($C_{13}H_{20}O$) | 14901-07-6 | 1 | 3.57 | 192.30 | 126–128 | Very slightly |
| | *TRIACETIN (solvent)* | 102-76-1 | 795 | | | | |

[a] Calculated by the Rekker method (Rekker, 1977).

Table 2
Composition of custard-matrices prepared with skimmed milk or full fat milk and with different flavouring concentrations

| Labels | Ingredients (%, w/w) | | | | | |
|---|---|---|---|---|---|---|
| | Skimmed milk | Full fat milk | Sucrose | Starch | κ-Carrageenan | Flavouring |
| SM-I | 90.93 | – | 5 | 4 | 0.01 | 0.06 |
| SM-II | 90.87 | – | 5 | 4 | 0.01 | 0.12 |
| FFM-I | – | 90.93 | 5 | 4 | 0.01 | 0.06 |
| FFM-II | – | 90.49 | 5 | 4 | 0.01 | 0.50 |

The mixture was then heated in a IKA® LR 1000 reactor (IKA®, Staufen, Germany) at 97 °C for 30 min under stirring at 150 rpm. After cooking, strawberry flavouring mixture was added to matrix and flavoured custard was cooled at 25 °C for 15 min under stirring at 150 rpm under standardised conditions. It is noticeable that water and aroma losses unavoidably occurred during this period. To balance weight loss due to evaporation during the heating step, water was added to the custard sample up to the initial weight of the mixture. The exact amount of aroma compounds remaining after cooling was not checked because it was not necessary to know it when using the PRV method.

To evaluate the effect of fat content, custard dessert samples were prepared by substitution of the full fat milk with an equal quantity of skimmed milk.

In order to obtain a detectable gas chromatographic response for some aroma compounds of the strawberry flavour, different aroma concentrations were added to the custard dessert and, in particular, 0.06% and 0.5% in FFM-custards and 0.06% and 0.12% in SM-custards.

### 2.3. Head space gas chromatography (HSGC) analysis

#### 2.3.1. Sampling

Different amounts ranging from 50 mg to 3000 mg of each preparation were poured into headspace vials (22 mL, Supelco, Bellefonte, USA). Vials were sealed using silicone septa in metallic caps (VWR International, Wien, Austria). For each custard type (FFM-SM, different aroma concentration) only one batch of product was used to fill the vials due to the highly standardised procedure used in this preparation (Cayot, 2006).

Three repetitions were performed per volume which represented 21 vials for one measurement of the $K$ coefficient for each type of custard. Samples were stored at 10 °C overnight until HSGC analysis.

#### 2.3.2. Gas chromatography (GC) analysis

Analysis was carried out according to Savary et al. (2006). 1 mL of headspace was automatically withdrawn from a vial using a 1 mL gastight syringe (Hamilton, Switzerland), previously equilibrated at 30 °C for 2 h, and analyzed on a Fison MFC 800 gas chromatograph using a flame ionisation detector (FID). Only one headspace injection was made from each vial. The injector temperature was set at 240 °C and injection rate at $200\ \mu L\ s^{-1}$. A $320\ \mu m \times 30\ m$ capillary BD-Wax column (df = 0.5 μm, Chromoptic, France) was used with carrier gas (helium) pressure of 70 bar. Oven temperature program was as follows: 40 °C for 5 min, then to 240 °C at $5\ °C\ min^{-1}$ and then 10 min at 240 °C. Temperature of detector was set to 250 °C.

Assignment of the peaks to the 15 aroma compounds was performed by Retention Index method on the chromatogram obtain by analysis of 1 μL of flavour mixture diluted 1:1000 in dichloromethane directly injected in the GC.

### 2.4. Data analysis

#### 2.4.1. The phase ratio variation method

Increasing quantities (50, 100, 200, 500, 1000, 2000, 3000 mg) of each flavoured matrix (SM and FFM custard) were poured into vials; each vial represented a different phase ratio $\beta$: 465, 232, 115, 46, 22, 11, 7. At equilibrium, 1 mL sample of headspace was withdrawn from each vial and analyzed by gas chromatography.

The phase ratio variation (PRV) method is based on the influence of the volume of sample on the concentration of volatile compounds in the headspace (Ettre, Welter, & Kolb, 1993) described the equation:

$$\frac{1}{A} = \frac{1}{f_i C_\mathrm{m}} K + \frac{\beta}{f_i C_\mathrm{m}},$$

where $A$ is the chromatographic peak area at equilibrium, $f_i$ is the proportional factor, $C_\mathrm{m}$ is the initial sample concentration in the matrix and $\beta$ is the phase ratio among volume of headspace $V_\mathrm{g}$ and volume of the matrix $V_\mathrm{m}$ ($\beta = V_\mathrm{g}/V_\mathrm{m}$).

To transform mass into volume, the density of the different custards was determined using a picnometer.

This previous equation, which has two variables (phase ratio $\beta$ and the peak area $A$), corresponds to a linear equation of the following type:

$$\frac{1}{A} = a\beta + b,$$

where $a = K/f_i C_\mathrm{m}$ and $b = 1/f_i C_\mathrm{m}$.

The partition coefficient $K(=a/b)$ is calculated from the values $a$ and $b$ obtained by plotting $1/A$ against $\beta$, when the linear relationship is obeyed ($R^2 > 0.8$).

### 2.5. Statistics

Results for all identified aroma compounds are reported as mean of three series of determinations and their standard deviation. Student's $t$-tests ($p < 0.05$) were used to determine significant differences among $K$ values calculated in custard matrices prepared with skimmed and full fat milk (Statistica 6.0 for Windows software).

## 3. Results and discussion

The custard dessert used as model for the gas–matrix partition is a complex matrix from both compositional and structural point of view. The various ingredients used to prepare this complex food model system contribute to the presence of several biopolymers (i.e. milk proteins, tapioca starch), hydrocolloids (carrageenan), as well as small solutes (milk salts, lactose and sucrose). Fat is present as milk fat globules when full fat milk is used. All these substances could strongly affect the vapour partitioning of a volatile compound added to the matrix. Moreover, water content is quite high (80% ca.) and, due to the limited content of water binding solutes (mainly sucrose and to a limited extend, lactose, starch and milk proteins), a high water activity (0.97 ca.) characterises the custard system.

From a structural point of view, the heat treatment (that induces gelatinisation of starch and carrageenan gelation) and the use of full fat milk lead to a mixed semi-gelled emulsified system (Hernando et al., 2006).

PRV method was here proposed as a reference method to measure the partition of volatile compounds between the gas phase and this complex model system and to build a basis for studies dealing with the kinetics of aroma release.

### 3.1. Performance of the PRV method to measure apparent partition coefficients

Under the experimental conditions of this study (preparation conditions, added amounts and temperature of analysis), only seven out of 15 strawberry aroma compounds were volatile enough and concentrated enough in the custard samples to be detected by headspace-GC: ethyl hexanoate, ethyl butanoate, benzyl acetate, ethyl 3-methyl buthanoate, *cis*-3-hexenyl acetate, *cis*-3-hexenol and hexanal.

The non-detectability of eight out of fifteen volatile compounds (methyl benzyl acetate, benzyl acetate, methyl anthranilate, methyl dihydrojasmonate, methyl cinnamate, γ-decalactone, furaneol, vanillin) could be caused by their relative low concentration in the matrix (in the order of ppm) as well as by their low volatility (Table 1).

However, some other small peaks were present in the chromatogram of the custard dessert samples not assigned to any of the strawberry aroma compounds and likely correspondent to volatile compounds naturally present in the non-flavoured custard.

Moreover, for some volatiles the concentration used in the COST 921 reference model was to low to give detectable HSGC peak and to obtain $K$ data, in both FFM and SM-custards, it was necessary to add higher concentrations of the strawberry flavouring (0.50 and 0.12, respectively, instead of 0.06%).

Partition coefficient, $K$, of the volatile compounds measured by PRV method were obtained by plotting the reciprocal of peak areas against the phase ratio, $\beta$ values. For the detected volatile compounds, linear regression models fitted well to the experimental data: correlation coefficients ($r^2$) were higher than 0.97.

The $K$ values obtained in custard samples are reported in Table 3. For a better discussion of the results, in this Table gas–water partition coefficients of the same compounds as determined by the same methodology (Savary et al., 2006) that, in turn, are reliable and consistent with literature data obtained by other methods (Jouquand, Ducruet, & Giampaoli, 2004; Van Ruth & Villeneuve, 2002), are also reported.

Table 3
Gas/matrix partition coefficients of aroma compounds in custard dessert prepared with full fat milk (FFM) and skimmed milk (SM) (PRV method, 30 °C, 2 h)

| Volatile compounds | $K_i^{\infty}(\times 10^3)$ | | |
|---|---|---|---|
| | Water[a] | FFM[b] | SM[b] |
| Ethyl butanoate | 18.30 | $9.28^a \pm 0.61^{(FF\text{-}I)}$ | $22.80^b \pm 3.36^{(SM\text{-}I)}$ |
| Ethyl hexanoate | 30.20 | $1.73^a \pm 0.12^{(FF\text{-}I)}$ | $17.40^b \pm 2.46^{(SM\text{-}I)}$ |
| *cis*-3-hexenyl acetate | – | $1.28^a \pm 0.17^{(FF\text{-}I)}$ | $9.30\ ^b \pm 1.28^{(SM\text{-}I)}$ |
| Ethyl 3-methyl butanoate | – | $6.90^a \pm 0.80^{(FF\text{-}I)}$ | $33.10^b \pm 6.82^{(SM\text{-}I)}$ |
| Benzyl acetate | – | n.d.[c] | $1.39 \pm 0.26^{(SM\text{-}II)}$ |
| Hexanal | 11.60 | $5.96^a \pm 0.75^{(FF\text{-}II)}$ | $24.60^b \pm 5.18^{(SM\text{-}II)}$ |
| *cis*-3-hexen-1-ol | 0.54 | $0.57 \pm 0.07^{(FF\text{-}II)}$ | n.d.[c] |

[a] Data from Savary et al. (2006).

[b] Experimental $k$ values (means ± s.d.) determined in custards with different flavouring concentrations: SM-I and FF-I, 0.06% (w/w), SM-II, 0.12% (w/w), FF-II, 0.5% (w/w); mean data of FFM and SM with different superscript letter are significantly different ($t$-test, $p < 0{,}05$).

[c] n.d. not detectable, saturated chromatographic peak.

*K* values of volatile compounds in FFM-custard showed a good repeatability as showed by the low standard deviation in particular for ethyl hexanoate and ethyl butanoate. In the case of the SM-custard, on the contrary, a higher dispersion of the *K* data occurred (variation coefficient $\geqslant$ for ethyl 3-methyl butanoate and hexanal) likely due to the different thermodynamic equilibrium of these volatile compounds in this low-fat matrix.

### *3.2. Aroma retention in FFM custard*

Partition coefficients measured in FFM custard were quite low, ranking from 0.00057 for *cis*-3-hexen-1-ol to 0.00928 for ethyl butanoate (Table 3). No direct relationship between these *K* data and the chemical and physical properties (i.e. solubility, hydrophobicity, volatility, saturated vapour pressure) of each individual aroma compound could be defined.

To better understand the partitioning behaviour of these aroma compounds, *K* data in custard were compared with those determined in a simple model system like an aqueous solution (i.e. the gas–water partition coefficient) where physico-chemical interactions are negligible and volatile compounds present at infinite dilution. It should be stressed that if a significant reduction of the gas–matrix partition coefficient occurs it indicates the presence of interactions between aroma compounds and non-volatiles substances. Quantification of the retention effect of matrix on the liquid-vapour partition of the volatiles could be obtained computing R, retention percentage, according to the following Eq. (1) (Seuvre et al., 2006):

$$R(\%) = (k_{H_2O} - -k_{\text{matrix}})/k_{H_2O} \times 100, \tag{1}$$

where $k_{H_2O}$ are the vapour–water partition coefficients and $k_{\text{matrix}}$ are the vapour–matrix partition coefficients. For sake of clarity, positive $R$ values correspond to a retention effect whilst negative $R$ values indicate a release effect by the matrix. Retention percentages of the volatiles are reported in Fig. 1. In our conditions, the highest retention is observed for ethyl hexanoate, followed by ethyl butanoate and hexanal. No meaningful effect by the matrix is, on the contrary, noticed for *cis*-3-hexen-1-ol which *K* value in water and custard are not significantly different ($p > 0.05$).

The decreased volatility observed for the two esters and hexanal in the FFM-custard could be attributed to the interactions between each of these volatiles with the various non-volatile compounds of this very complex matrix. The simultaneous presence of various macromolecular components (i.e. milk proteins, starch and carrageenan), as well as fat is to be considered as the main factor all components that these compound have with and the observed result could be a sum of effects.

Several studies carried out in simple model systems showed that both ethyl butanoate and ethyl hexanoate are able to interact with many food biopolymers such as present in our custard. In particular, a reduced vapour partitioning has been observed in presence of starch (Arvisenet, Le Bail, Voilley, & Cayot, 2002; Arvisenet, Voilley, et al., 2002; Van Ruth & King, 2003) milk proteins (Fabre, Aubry, & Guichard, 2002; Pelletier, Sostmann, & Guichard, 1998; Van Ruth & Villeneuve, 2002), and carrageenans (Juteau, Tournier, & Guichard, 2004).

The higher hydrophobic nature of the ethyl hexanoate could explain its higher retention in this complex matrix. For many compounds, in fact, the interactions between biopolymers (i.e. proteins, starch) and aroma compounds are due to hydrophobic interactions and clearly are favoured for the less polar compounds. Moreover, the presence of milk fat in the FFM-custard dessert could further increase the retention of this ester in the matrix in respect with the more polar one (ethyl butanoate).

A lower gas chromatography area of ethyl hexanoate than ethyl butanoate added as strawberry flavour in custard dessert in respect to that observed in water was also noticed by Perez-Juan, Flores, and Toldrà (2006) in their study carried out using a SPME technique. Their results, in particular, showed that, in comparison with the data obtained in aqueous solutions, a retention effect by the custard dessert, prepared according the same procedure, was mainly observed for ethyl hexanoate as well as for hexanal.

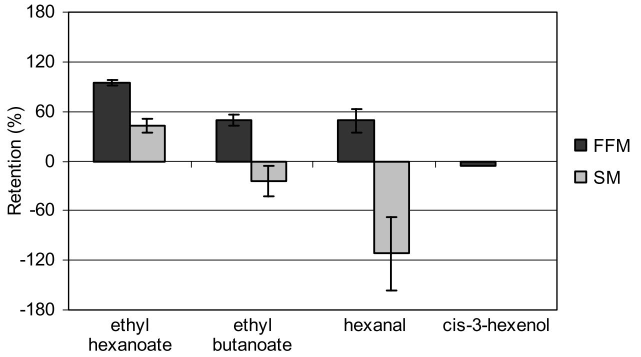

Fig. 1. Retention percentages of some strawberry aroma compounds in custard dessert made with full fat milk (FFM) and skimmed milk (SM).

On the contrary, no meaningful difference between the GC-area of ethyl butyrate in water and in custard was evidenced, likely due to the specific analytical conditions adopted by the authors. In respect with a Head Space Gas Chromatography like that used in the PRV methodology, the results obtained by SPME technique is, in fact, affected by many analytical factors (fiber nature, time and temperature of exposure, etc.).

In the case of *cis*-3-hexenol, the vapour–liquid partition coefficient obtained with the matrix is very similar to the one obtained with water. Matrix seems not to play a marked role in this case. Different results has been observed for this relatively polar aroma compound by other authors with an increase of the vapour–liquid partition coefficient with simple and complex model systems containing small sugars like sucrose (Rabe, Krings, & Berger, 2003; Seuvre et al., 2006). This behaviour could be attributed to the presence of these solutes and/or to an effect of the presence of several solutes that globally reduce water activity and, thus, favour the vapour partitioning of polar volatiles.

### 3.3. Effect of fat content on partition coefficients

The PVR method was also used to measure partition coefficients for the same volatile compounds flavouring a custard cream prepared with skimmed milk. $K$ data are reported in Table 3 and evidence that fat affected the gas/matrix partition coefficients of individual aroma compounds on the basis of their specific affinity for the lipid and aqueous phase. In general, higher $k$ were observed in the volatile compounds detected in the headspace when strawberry aroma was added in SM-custards in respect to the results obtained in the FFM-milk ones, and the difference reflected the specific hydrophobicity of the aroma.

Retention percentages of the aroma compounds in SM custard in respect to water evidence the meaningful importance of fat in the retention of the volatiles with higher affinity for the lipid phase (Fig. 1). In particular, the meaningful reduction of the fat content in the custard reduced the affinity for the matrix and favoured the release in the vapour phase of ethyl butyrate and hexanal. The only compound, among the ones considered, still retained in the custard dessert is ethyl hexanoate.

To evidence the effect exerted by the fat on aroma release in the custard, the ratio of the vapour–matrix coefficient partition in the SM- on that in FFM-custard of the five out of seven aroma compounds under study was computed and results are reported in Fig. 2. In the same figure for each aroma compound, the correspondent hydrophobicity in terms of $\log P$ is also reported. It could be observed that the reduction of fat content in the matrix induced a higher release in the vapour phase for the compounds with higher affinity with the lipid phase. This behaviour is in agreement with the results of other authors (Amoore & Buttery, 1978; Jouquand et al., 2004; Lubbers, Decourcelle, Vallet, & Guichard, 2004; Savary et al., 2006) investigating partition coefficient in other matrices as well as in emulsified model systems as a function of fat content.

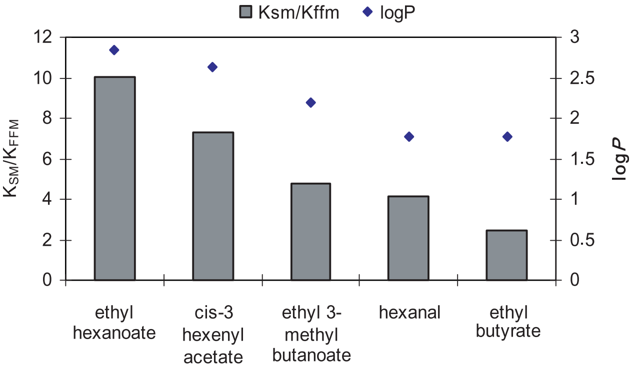

Fig. 2. $K_{SM}/K_{FFM}$ ratio of strawberry aroma compounds in custard made with full fat milk (FFM) and skimmed milk (SM) and the effect of hydrophobicity ($\log P$).

In Fig. 2 it is possible to notice that hexanal and ethyl butyrate are volatiles characterised by a similar $\log P$ but the former resulted less retained in the SM-custard than the latter. This result could be attributed to the different solubility of these compounds. Hexanal, in fact, is less water soluble than ethyl butyrate.

Aroma release from SM-custard may also be attributed to a 'salting-out' effect due to the presence of solutes in the matrix (Taylor, 1998). Mono- and di-saccarides affect the volatility by altering the activity coefficients of aroma compounds (Land, 1978). Moreover, at relatively high concentration, solutes reduce the amount of bulk free water by binding, which increases the relative concentration of some compounds (and in particular of the more polar ones) and therefore can enhance their volatility and release in the vapour phase (Navar, 1971; Pittia, Nicoli, & Lerici, 1998; Rabe et al., 2003).

## 4. Conclusions

PRV method was found an easy and accurate method to measure the partition coefficients of aroma compounds in mixture in complex food systems despite the fact that in our experimental conditions it was not possible to detect all the compounds.

The applied method proved differences in partitioning of aroma compounds dependent on the matrix composition only. Specific binding at the molecular level cannot be proven by this method. However, results reflect the different affinity of individual strawberry aroma compound for the lipid and aqueous phase as well as interactions with the non-volatile compounds of the custard affecting the release in the vapour phase.

The variation of the milk type in the custard dessert would, thus, induce relevant modification of the composition of the vapour phase in equilibrium with the custard dessert. In particular, a reduction of the milk fat as a consequence of the use of the skimmed milk, resulted in an increased concentration of the more lipophilic and volatile compounds (i.e. esters, hexanal) whilst the more polar will be retained in the matrix. Specific interactions between ethyl hexanoate and other non-volatile compounds (proteins, starch, carrageenans) are implied in its retention in the SM-custard.

Beside the quantitative effect of the higher release of some volatiles, the modification of fat concentration in the matrix could also lead to a qualitative modification of the overall strawberry flavour and, likely, to a change in its acceptance by the consumer during its consumption.

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