Effect of Composition on Release of Aroma Compounds

Samavati, Vahid; Emam-Djomeh, Zahra*⁺

*Department of Food Science and Engineering, Faculty of Agricultural Engineering and Technology,
University of Tehran, I.R. IRAN*

Mehdinia, Ali

Marine Living Science Department, Iranian National Center for Oceanography, Tehran, I.R. IRAN

Mohammadifar, Mohammad Amin

*Department of Food Science, Faculty of Nutrition and Food Science, Shahid Beheshti University of Medical
Sciences, Tehran, I.R. IRAN*

Omid, Mahmoud

*Department of Agricultural Machinery Engineering, Faculty of Agricultural Engineering and Technology,
University of Tehran, I.R. IRAN*

ABSTRACT: *The effect of oleic acid (5 and 10% v/v) and xanthan gum (0.5 and 1% wt) on
partitioning and retention of ethyl acetate and diacetyl from two matrices with a different composition
was investigated by applying static head space gas chromatography. Two matrices with different
composition have been developed: one containing carbohydrates (xanthan gum) and in the second one,
called complex matrix, lipid (oleic acid) was added. The roles of Xanthan Gum (XG) and lipid (oleic acid)
on the retention of aroma compounds were pointed out. Changes in the composition of matrices exhibited
a considerable effect on the air/liquid partition coefficient ($K_{a/l}$) values at equilibrium. The kinetic study
of the release from both matrices had shown a decrease of the initial rate of release (R_i) by reference
with water. The rheological properties of all matrices were investigated and the flow behavior of all
matrices was successfully modeled with power law and cross models. Power law model was found
as the better model to describe the flow behavior of dispersions.*

KEY WORDS: *Aroma release, Complex matrix, Xanthan gum, Partition coefficient.*

INTRODUCTION

The physico-chemical behavior of small molecules such as flavour compounds in food matrices is one of the most important parameters involved in their activity and sensory perception; hence, this behavior can have pronounced effects on the flavour quality of foods which are mostly emulsions, i.e. dispersed systems of oil and aqueous phases.

The volatile compounds are generally lipophilic and, before being released in the vapor state, they have to transfer through several interfaces such as the interface between the lipidic and aqueous phases or between

the liquid and the vapor phases [1]. The mass transfer at the different interfaces in a multicomponent system must be taken into account.

Both thermodynamic and kinetic mechanisms influence the flavor release and into the gas phase at each step of food product preparation and consumption [2]. The thermodynamic component involves the partitioning of flavour compounds between the food matrix and the gaseous phase above it under equilibrium conditions and is described by the partition coefficient, which is the ratio of the concentration of the volatile in the gaseous phase to its concentration in the matrix [3-5]. The rate at which equilibrium is achieved is defined by the kinetic component. In biphasic media two steps are necessary to consider for the perception of the aroma: the transfer from the lipidic phase to the aqueous one and those from the aqueous phase to the vapor one.

The retention of aroma compounds can be affected by physico-chemical interactions between macromolecules such as proteins and carbohydrate, lipids and aromatic compounds [6,7].

Many studies have been carried out in simple systems consisted of water, proteins, lipids and carbohydrates [4, 5, 8-12]. These works indicated that both food components and structure may control flavor partitioning and release from the different phases of food.

The affinity of the volatiles for these phases as well as the nature and the volume of the dispersed phase, the nature and the area of the oil–water interface and the emulsifier/stabilizer used a reconsidered to influence the aroma release from emulsified systems [6, 12-15].

Hydrocolloids are widely used in the food industry due to their thickening and stabilizing properties in food products. Hydrocolloids affect the volatility of the molecules of the aromatic compounds and their partitioning between different phases by two mechanisms: The first one is diffusion decrease as predicted by the Stokes - instein equation where diffusion is inversely proportional to viscosity [16]. The second one involves specific interactions of the aroma compounds molecules with the macromolecule often due to adsorption, entrapment in micro regions, complexation and hydrogen bonding [9, 16].

The reduction of the aroma release in foods containing thickening agents and has attributed this phenomenon to the barrier effect of these macromolecules. The predominant factors playing a role in the release are the composition and the structure of the media [17].

Lipid is one of the main food ingredients that have been shown to have a great effect at the sensorial perception since they are good solvent for the flavour compounds. Nevertheless the retention of the aromatic compounds depends also on their physico-chemical characteristics such as polarity, hydrophobicity and solubility [18]. *Widder & Fischer* (1996) observed that the description of the odour of an emulsion aromatized system with various aroma compounds having different polarity is modified when the lipid content increased from 1% to 20%: this modification was described by the reduction of the release of the non-polar compounds [19].

The study of the influence of food components on the retention or release of an aroma compound usually involves the use of a head space GC technique. Application of static head space techniques has given insight into the partitioning of aromatic compounds between the different phases of system. Trapping of head space volatiles, using porous polymer absorbents, as well as Solid Phase MicroExtraction (SPME) have also been used to investigation of aroma retention [20].

The aim of this work is the studying of aroma retention from model matrices consisting of Xanthan Gum (XG), oleic acid. The measurements of released compounds from the matrices as a function of time were carried out on non-agitated matrices. The release of aroma compounds is thus due to the phenomenon of diffusion of these compounds within the matrix, then due to the transfer of the matrix towards the gas phase and to the diffusion within the gas phase.

EXPERIMENTAL SECTION
Materials

Xathan gum was purchased from Sigma Chemical Company (St. Louis, MO, USA). Oleic acid ($C_{18}H_{34}O_2$, purity 65-88%, ρ=0.889-0.895 kg/m^3) were purchased from Merck Company (Merck, shuchardt OHG 85662, Hohenbrunn, Germany). Aroma compounds (ethyl acetate and diacetyl) were obtained from Merck Company (Hohenbrunn, Germany). Physico-chemical characteristics of both aroma compounds are shown in Table 1.

Matrix preparation

The carbohydrate matrices were prepared by dissolving suitable amounts XG (0.5 and 1% wt) powders into distilled water at 40° C, followed by stirring for

Table 1: Physico-chemical characteristics of aroma compounds.

	Ethyl acetate	Diacetyl
Chemical formula	$C_4H_8O_2$	$C_4H_6O_2$
Molar mass [a]	88.105 g/mol	86.0892 g/mol
Odor	Ether smell	Butter smell
Boiling point	77.1 °C	88 °C
Solubility in water	8.3 g/100 mL (20 °C)	Soluble in 4 parts
Log P (20^{0}C) [b]	0.70	-1.34
Saturated pressure vapour, [c] P^S_i (Pa; 20^{0}C)	24527	16129
Solubility in ethanol, acetone, diethyl ether, benzene	Miscible	Miscible

a: Reid et al. (1987). b:Hansch and Leo (1979). c: Seuvre et al., (2006).

Table 2: Composition of each matrix.

Matrix	Composition	
	XG (wt %)	Oleic acid (v/v %)
W	0	0
H_1	0.5	0
H_2	1	0
C_1	0.5	5
C_2	0.5	10
C_3	1	5
C_4	1	10

30 min in 8000 rpm to ensure complete dispersion. Then, solutions were kept 24 h at room temperature (20°C) to allow full hydration. The complex matrices were obtained by slowly addition of oleic acid (5 and 10 % v/v) into carbohydrate matrices; oleic acid/XG solution mixture was finally emulsified with stirring by Ultra Turrax (IKA T25 Digital, Germany) in 12000 rpm for 15 min. Final matrices were 1-distilled water (medium W) taken as the reference medium, 2-Carbohydrate matrices containing only XG (medium H) and 3-complex matrices (oleic acid in water emulsions consist of XG) (medium C). The Composition of each sample presented in Table 2.

Viscosity measurements

Steady shear viscosity was conducted using a dynamic rheometer (MCR 301, Anton Para Co., Germany). Emulsion viscosity was measured at 0.1-500 1/s. Couette geometry with a cup (33.93mm diameter) and a bob system (32.05 mm diameter, 33.29mm length) was used.

All measurements were performed in 20°C. Power-law model was used to model the matrices flow curves:

$$\text{Power-law model} \qquad \tau = k\,\gamma^n \qquad (1)$$

where τ is shear stress, k is consistency coefficient, γ is shear rate, n is flow behavior index.

Static head space analysis

The different matrices were aromatized with the ethyl acetate (purity > 97%) and diacetyl (purity > 98%) (Merck, shuchardt OHG 85662, Hohenbrunn, Germany) at concentration of 300 ppm. The two aroma compounds were chosen because their physico-chemical properties are different to each other. As can be seen in Table 1, ethyl acetate has lower water solubility and is more hydrophobic (higher n-octanol/water partition coefficient, log P) than diacethyl.

The head space flavour concentrations of the matrices were evaluated by head space solid- phase micro extraction (HS–SPME) with a 50/30 lm DVB/Car/PDMS fiber (Supelco, Bornem, Belgium) followed by GC–MS analysis. A short sampling time of one minute was applied, since this was shown to represent equilibrium head space concentrations [21].

Aroma compounds were analysed on an Agilent HP6890 series gas chromatograph equipped with PTV injector, an MPS-2 Multipurpose Sampler (Gerstel, Germany), a HP5973 MSD detector (Mass Selective Detector-Quadrupole type) and an EC–5 MS capillary column (50m × 0.25mm ×0.25 µm i.d.; coating thickness 0.25 µm). For equilibrium measurements the matrices were incubated at 20°C until thermodynamic

equilibration of the samples (25 mL vials containing 10 mL of the aromatized model system) was reached. Preliminary experiments at different equilibrium times were conducted to ensure that the analysis for each sample was performed at equilibrium. A time period of 3 h was sufficient to reach equilibrium for each matrix and flavour compound. For kinetic measurements the samples (25 mL vials containing 10 mL of the flavoured model system) were incubated at $20^{\circ}C$ for 60, 120, 300, 600, 900, 1800, 3600, 5800, 7200 and 10800 second and then head space analysis was done. Head space SPME extracts were taken and desorbed automatically using following MPS-2 parameters: incubation temperature $20^{\circ}C$; extraction time 1 min; desorption time 5 min. GC-MS operating conditions were injector $250^{\circ}C$; transfer line to MSD $260^{\circ}C$; oven temperature start $40^{\circ}C$, hold 5 min, programmed from $35^{\circ}C$ to $150^{\circ}C$ at $5^{\circ}C/min$, from $150^{\circ}C$ to $250^{\circ}C$ at $20^{\circ}C/min$, hold 2 min; carrier gas He 1.2 mL/min; splitless injection, ionization EI 70 eV. Controlled experiments testing the stability and repeatability of the SPME fibre were also carried out.

Peak areas obtained by static head space analysis were converted to concentrations using calibration curves. For the construction of each curve, ethanol solutions containing the aroma compound at five different concentrations were prepared for each sample and analyzed five times applying the same conditions as described previously for the samples. Linear correlation coefficients were found to range from 0.98 to 0.99 for both analytes. The mass partition coefficient between gaseous phase and matrix was calculated

$$K_{mass} = C^{\infty}_{g}/C^{\infty}_{m,} \tag{2}$$

where C_g and C_m are, respectively, the flavour mass fractions (w/w) in the gas and in the matrix phase.

Statistical analysis

SAS software (SAS, 9.1, Inc., USA) was used to evaluate the data. Analysis of variance (ANOVA) was used to determine if the means of responses were significant (P<0.05). All experiments were performed in triplicate.

RESULTS AND DISCUSSION
Rheological investigation

Table 3 shows the parameters obtained with power law model for all matrices. The consistency index (K)

value in power law model increased with increase in oleic acid volume fraction and XG concentration, which indicated that increasing oleic acid volume fraction and XG concentration induced droplet interactions and the complex matrices were more structured.

The flow behavior index (n) decreased when oleic acid volume fraction and XG concentration increased indicating a noticeable shear thinning effect at higher concentration of oleic acid phase and XG with prominent effect of XG concentration, which suggested that shear thinning behavior was mainly due to the presence of XG.

Aroma retention measurement
Aroma compounds partitioning

The behavior of diacetyl and ethyl acetate was different in various matrices and was studied in terms of degree of retention at $20^{\circ}C$ under equilibrium conditions. The percentage of retention (R %) of both aroma compounds in the different matrices was determined using the following equation:

$$R\% = \frac{K^{water}_{a/l} - K^{matrix}_{a/l}}{K^{matrix}_{a/l}} \times 100(\%) \tag{3}$$

Where $K^{water}_{a/l}$ is the partition coefficients of aroma compounds between gaseous phase and water, and $K^{matrix}_{a/l}$ is the partition coefficients of aroma compounds between gaseous phase and different matrix. Any variation of $K^{matrix}a/l$ with respect to the reference $K^{water}a/l$ is an indication of interaction between the aroma compound molecules and the matrix components. A positive percentage value indicates an aroma compound retained by the matrix and a negative value a compound released by the matrix [5]. All of the percentages of retention for both aroma compounds were positive values that indicated an aroma compound retention by the matrices. The partition coefficients (K_{mass}) of both aroma compounds between gaseous phase and matrices for two aroma compounds are displayed in Table 4. Both of aroma compounds did show the same behaviour. The more lipophilic copmpound, ethyl acetate, showed the higher retention in all matrices. The retention of both aroma compounds increased with XG concentration in carbohydrate and complex matrices (Figs. 1 and 2). The difference in retention between the two aroma compounds was attributed to their different physico-chemical

Table 3: Rheological characteristics of each medium (20$^\bullet$C).

Rheological properties				
Matrix	Viscosity (γ=1 1/s) (Pa.s)	Flow Index (n)	Consistency Index (K)	R^2
W	0.001	1.000	0.001	0.99
H_1	0.025	0.716	0.036	0.99
H_2	0.108	0.473	0.296	0.99
C_1	0.037	0.649	0.065	0.99
C_2	0.055	0.621	0.090	0.99
C_3	0.115	0.467	0.304	0.99
C_4	0.141	0.421	0.457	0.99

Table 4: Partition coefficient (Ka/l) of flavour compounds between gaseous phase and different matrices (20$^\bullet$C).

Medium	$K_{a/l}$	
	Ethyl acetate	Diacetyl
W[#]	$0.077\pm0.003^{a*}$	0.094 ± 0.004^a
H_1	0.066 ± 0.003^b	0.083 ± 0.003^b
H_2	0.059 ± 0.002^{cd}	0.076 ± 0.003^{cd}
C_1	0.064 ± 0.002^{bc}	0.081 ± 0.002^{bc}
C_2	0.062 ± 0.002^{bc}	0.080 ± 0.003^{bcd}
C_3	0.057 ± 0.002^d	0.075 ± 0.003^{cd}
C_4	0.054 ± 0.002^d	0.073 ± 0.003^{cd}

*a-b: For each column, same letters indicate no significant differences (P<0.05).
#: Keys for the matrices are in Table1.

properties. Eethyl acetate is a non polar compound (log P =0.7) whereas diacetyl is polar (log P = -1.5).

Polar compounds are more soluble in water and can also diffuse easily through the matrix, which can explain the significant lower retention of diacetyl from the matrices [24]. Besides, as many authors report, the higher relative volatility is, the lower the retention [5, 21]. Since the experiments were done in equilibrium conditions, the viscosity effect often involved in aroma retention by affecting diffusion was restricted and the results mainly highlighted physico-chemical interactions between aroma compounds and polysaccharides [5]. It is stated that increase in polysaccharide content influenced the diffusion of aroma molecules in the liquid phase probably through binding and/or physico-chemical interactions between them and the polysaccharide [5]. The same trend was reported by many investigators who detected that the polar compounds exhibited in their solutions lower partition coefficients than the less polar due to their greater water solubility [25]. Whereas air/liquid partition coefficient for pure water system increased for compounds possessing a longer carbon

chain because of the increased hydrophobicity of the molecule [13].

As has been described by *Landy et al.* (1998), aldehydes (ethyl acetate) were entrapped to a lower degree in freeze-dried maltodextrins and β-cyclodextrins than alcohols and esters [2]. *Bylaite et al.* (2005) have proposed that the ordered conformation of some polysaccharide giving a structure may create a ''hydrophobic cavity'' which can entrap flavour compounds [26].

The retention of ethyl acetate in matrices appeared to be linked to their hydrophobicity; this result could be described by the present of hydrophobic interaction between non-polar compound (ethyl acetate) and polymer chains. In the case of more polar compound, diacetyl, the addition of XG has less influence on its retention. Likewise, according to *Secouard et al.* (2003), some flavour compounds were mainly retained by the polysaccharide solutions via steric interaction [4].

Some authors studied the retention of different aroma compounds with various model matrices and stated an effect of the viscosity on aroma release and perception [27-28]. *Decourcelle et al.* (2004) had found that

the existence of pectin gum in fat free stirred yoghurts tended to reduce the concentration of flavour compounds in the head space [18].

To clarify the influence of viscosity on retention of both aroma compounds the calculated values of retention were plotted against increasing viscosity of matrices. Fig. 3 shows the effect of viscosity on both aroma compounds retention. More specifically, a comparison of aroma compounds content in headspace samples indicated that the degree of retention was increased with increasing XG concentration in the matrices. The viscosity dependency of ethyl acetate retention is higher than that of diacetyl (Fig. 3). Carbohydrate and complex matrices were more viscous than water and therefore the diffusion of aroma compound molecules was reduced. This effect was more important on the ethyl acetate. These results are in agreement with those reported by *Roberts et al.* (1996) who observed that non-polar compounds were most affected by a change in viscosity [11].

It is reported that aroma and taste perception decreases with increasing viscosity but other factors such as binding, mouth coating and fresh surface generation also play an important role [29].

With the purpose of investigate the influence of the components of the matrices and that of the rheological behavior on the release and/or the retention of aroma compounds, the two matrices have been developed having the same rheological behavior with different composition (matrices B_2 and C_1).

Fig. 1 and 2, show that the degree of both aroma compounds retention in B_2 and C_1 matrices was not significantly different indicating that the viscosity was the predominant factor for its retention in matrices. On the other hand, the matrices with similar viscosity, XG (1 % wt) and XG/oleic acid mixture (XG 0.5% wt/oleic acid 5% v/v), showed the same aroma retention. This observation revealed that diacetyl and ethyl acetate release was strongly governed by steric phenomena.

The effect of the different components could be pointed out by calculating the ratio between two partition coefficients (Table 5), especially the influence of lipids and carbohydrates. The ratio between water K_{mass} and carbohydrate matrix K_{mass} demonstrations the effect of carbohydrates; the ratio between water K_{mass} and complex matrix K_{mass} indicates both the carbohydrate and lipid effects; the ratio between carbohydrate matrix K_{mass} and
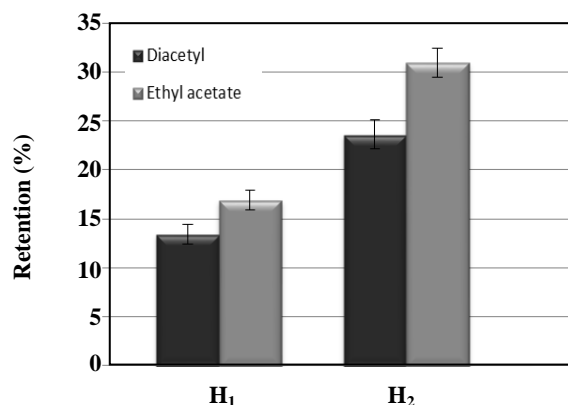

Fig. 1: Retention of diacetyl and ethyl acetate in carbohydrate matrix ($20^{o}C$). (H_1= 0.5% (wt), XG, H_1= 1% (wt) XG).
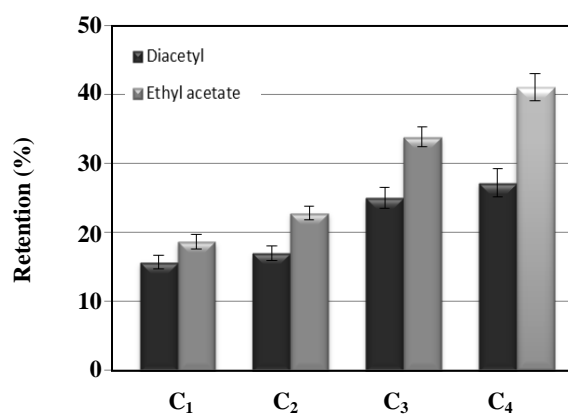

Fig. 2: Effect of complex matrices on the retention of diacetyl and ethyl acetate ($20^{o}C$). (C_1=0.5% (wt) XG + 5% (v/v) oleic acid, C_2= 0.5% (wt) XG + 10% (v/v) oleic acid, C_3= 1% (wt) XG + 5% (v/v) oleic acid, C_4= 1% (wt) XG + 10% (v/v) oleic acid).
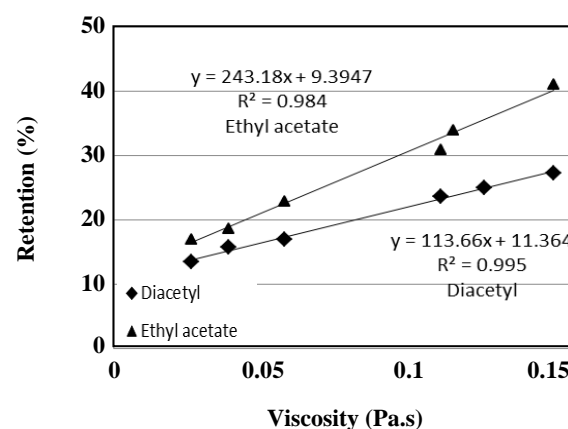

Fig. 3: Aroma retention of diacetyl and ethyl acetate as function of matrix viscosity at $20^{o}C$ at equilibrium condition.

Table 5: Ratio of partition coefficients, K_{mass}, for flavour compounds in the different matrices at 20°C.

K_{mass} matrix/K_{mass} matrix	Diacetyl	Ethyl acetate
W/H$_1$[#]	1.17±0.02[cd]	1.13±0.03[c]
W/H$_2$	1.30±0.03[b]	1.24±0.03[ab]
W/C$_1$	1.19±0.02[cd]	1.15±0.02[c]
W/C$_2$	1.22±0.02[c]	1.17±0.02[c]
W/C$_3$	1.33±0.03[b]	1.25±0.03[ab]
W/C$_4$	1.41±0.03[a]	1.27±0.03[a]
H1/C$_1$	1.01±0.03[f]	1.02±0.02[d]
H1/C$_2$	1.05±0.03[e]	1.03±0.02[d]
H2/C$_3$	1.02±0.03[ef]	1.01±0.03[d]
H2/C$_4$	1.07±0.03[e]	1.02±0.02[d]

a-b: For each column, same letters indicate no significant differences (P 0.05).
#: Keys for the matrices are in Table1.

complex matrix K_{mass} shows the role of the lipids. When the ratio value is >1, a significant component effect on aroma retention is pointed out [6]. The ratio water K_{mass}/carbohydrate matrix K_{mass} presented a value higher than unity. The values were attributed to the establishment of interactions (or possible complexation) between XG and aroma compounds. *Guichard et al.* (1991) described that polyssacharide play an important role on the retention with their thickening and gelling power [30].

The evaluation of both aroma compounds release from carbohydrate and complex matrices indicated the role of oleic acid and the comparison of the release rates from water and complex matrix showed the combined effects of carbohydrate and oleic acid. The most important reduction was observed with the more hydrophobic compound (ethyl acetate).

The addition of oleic acid in complex matrices resulted in higher retention of both aroma compounds. However, diacetyl is a polar compound and its interaction with oleic acid (a non-polar compound) is not considerable, but, its retention is affected by oleic acid in complex matrices. This effect could be described by this fact that the viscosity of matrices is affected by presence of oleic acid and increase in viscosity result in higher aroma retention. In general, the effect of matrices on retention

of both aroma compounds is the combination of physical and chemical phenomena. In addition, the viscosity enhancement with increasing XG and oleic acid contents decreases the diffusion rate of both aroma compounds through the interface of the solution.

Effect of carbohydrate on partition coefficient

The product–air partition coefficient determines the quantity of the aroma compounds which can be released [31]. Partition coefficients ($K_{a/1}$) of both aroma compounds between gaseous phase and polysaccharide solutions were determined using Eq. 2. The results are given in Table 4. For both aroma compounds, partition coefficient values were lower in the presence of XG (carbohydrate matrix) than in water alone.

The higher solubility of diacetyl explains its lower affinity for the gaseous phase and therefore a lower partition coefficient ($K_{a/1}$=0.077) compared to ethyl acetate ($K_{a/1}$=0.094). The same trend was stated by many investigators who observed that the polar compounds exhibited in their solutions lower partition coefficients than the less polar due to their higher water solubility whereas air/liquid partition coefficient for pure water system increased for compounds possessing a longer carbon chain because of the increased hydrophobicity of the molecule [13, 25].

Aroma compounds with high air/liquid partition coefficient ($K_{a/1}$) are distributed easier in the gaseous phase and exhibit a relatively low threshold value while the volatiles with low $K_{a/1}$ values tend to distribute more slowly in the air phase and have a high threshold value. This has as a consequence higher $K_{a/1}$ values to account for higher concentrations of aroma compounds in the headspace [5].

The local hydrophobic zones formation may then be favoured by the over-lapping of high polymer chains, thus explaining the greater retention of aroma compounds via hydrophobic interactions. The formation of such hydrophobic zones was proposed to describe the reduction of aroma compound volatility in guar gum and carboxymethylcellulose solutions [11].

Bakker et al. (1996) have considered aroma release from gelatin gels using time intensity assessment. They observed that the rate of release was slower in the gels with higher gelatin concentrations and suggested that the rate of release was governed by the rate at which the gels

were broken down through melting and chewing [11]. *Malkki et al.* (1990) have claimed that binding of tastes and aroma compound moecules to biopolymers and the mouth coating behavior of such thickeners influence aroma perception, and in some condition may have a higher effect than viscosity [32].

Bylaite et al. (2005) have suggested that the ordered conformation of xanthan giving a structure analogous to a double helix may create a ''hydrophobic cavity'' which can entrap aroma compounds. This proposition seems to corroborate our results because a more flexible conformation could provide a larger cavity or a more accessible cavity to ethyl hexanoate. Such a mechanism could be compared with the well-known mechanism of inclusion complexes with starch [26].

Effect of oil volume fraction on partition coefficient

All the ratios water K_{mass}/complex matrix K_{mass} and carbohydrate matrix K_{mass}/complex matrix K_{mass} were > 1. The first ratio presented the effect of both XG and oleic acid and the second ratio the influence of oleic acid. Oleic acid was implicated in the retention: the ratio increased with the hydrophobicity of aroma compounds, similar results was observed before [31, 33].

As can be seen in Table 4, the oleic acid content significantly influenced the volatility of the two aroma compounds. Both aroma compounds showed an increase in retention with increased oleic acid volume fraction, which was more pronounced in the case of the non-polar compound, ethyl acetate. The partition coefficient of ethyl acetate exhibited its highest value for water followed by the values for carbohydrate matrices (16-30% reduction) and complex matrices (20-42% reduction).

Similarly, the partition coefficient of diacetyl seemed to be greatest from water while a decrease of 13-23% and 16-28% was evident for carbohydrate and complex matrices, respectively. The hydrophobicity of the volatile compound molecules in addition to their solubility seems to be the key factors for the equilibrium between the matrices and the air phase. The lipid/water phase ratio affected the distribution of the aromatic compounds over the continuous phase, dispersed phase and, consequently, the air phase. The observed effect of the oleic acid is in accordance with other studies on a number of alcohols, ketones, sters, aldehydes etc., which confirmed a profound effect of the lipid content of foods on aroma compounds release [12, 15].

The hydrophobic medium could induce a decrease of aroma compounds not only because of the affinity of aroma compounds for lipids but also because of the consistency of the lipidic medium [34]. Oleic acid with its fatty acid chains could form interactions with more hydrophobic compounds and retains the aroma compounds.

The difference in behavior of aroma compounds could be explained by the differences of polarity and the chemical functions of their molecules. For ethyl acetate, the influence of retention by the complex matrix was more noticeable, arising from its affinity for lipid phase.

Hansson et al. (2003) observed that the air/pectin gum gel partition of the flavour compounds was probably affected by two mechanisms; one depending on the polarity of the aroma compound and one from the pectin that retained the molecules in the network either by sterical hindrance or by formation on non-polar micelles [35].

The oleic acid had a significant effect on aroma release as with adding oleic acid in complex matrices the rates of release of both aroma compounds decreased (Table 4). This reduction was expected since oleic acid addition was accompanied by an increase in the viscosity of the matrices (Table 3). The viscosity of the medium is an important factor that influences the diffusion of aromatic molecules since the Stokes–Einstein equation predicts that the diffusion is dependent on the square root of the viscosity. For diacetyl the influence of oleic acid was noticeable with a mean decrease of 16-28% for all matrices containing oleic acid.

Oleic acid seemed to be as critical in the rate of release of non-polar aroma compound, ethyl acetate, as it is in the case of diacetyl, indicated that even a small amount of oleic acid led to drastic shifts (20-42% decrease) in phase partitioning and, correspondingly, to smaller concentrations released in to the head space.

Seuvre et al. (2006) have revealed that one means of reducing aroma release in low fat systems was to incorporate the oil droplets into biopolymer gel particles that were termed microstructured emulsions. In these microstructures the oil droplets are enclosed in a gel phase, creating a static diffusion layer around the oil droplets. This increases the path-length through which the aroma must diffuse before exiting from matrix. The result of these structures was to hinder the rate at which the lipophillic aromas replenish the continuous phase and reduce the rate of aroma release in to the headspace [6].
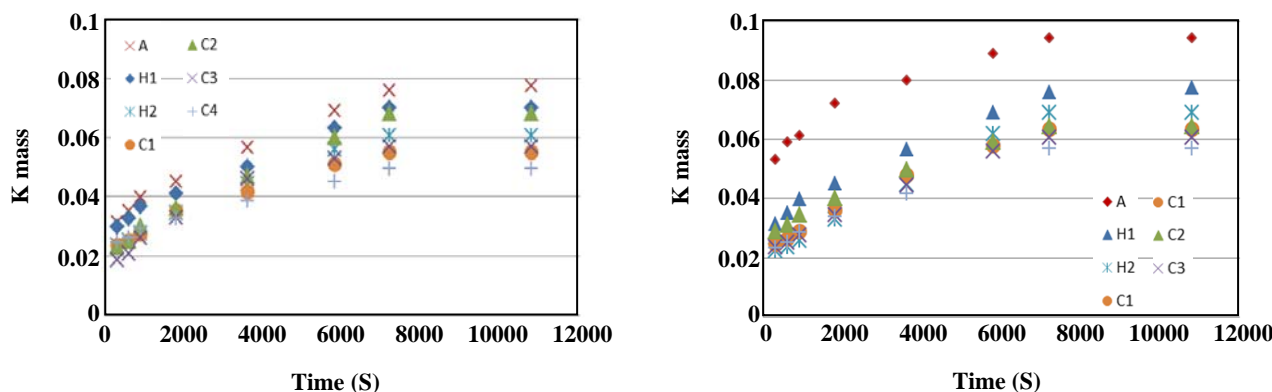
Fig.4: Release of aroma compounds from various matrices at 20°C: a) ethyl acetate, b) diacetyl (A= Distiled water without XG and oleic acid, H₁= 0.5% (wt) XG, H₂= 1% (wt) XG, C₁=0.5% (wt) XG + 5% (v/v) oleic acid, C₂= 0.5% (wt) XG + 10% (v/v) oleic acid, C₃= 1% (wt) XG + 5% (v/v) oleic acid, C₄= 1% (wt) XG + 10% (v/v) oleic acid).

Lipids decrease the vapour pressure of numerous volatile compounds and then influence the aromatic perceived profile [19, 36].

It is observed that emulsions suppress the release of lipophillic molecules such as ethyl hexanoate but have no influence on the hydrophillic aroma compounds such as butanone [6]. The lipophillic aroma compounds are more affected by the complex matrices because they predominantly partitionin to the oil phase whereas the hydrophilic aromas are not affected since they are predominantly present in the aqueous phase.

Kinetic release of the aroma compounds

To investigate the release of the aromatic compounds from the matrices, measurements have been performed on non-agitated matrices during time. Then the release is only the result of diffusion phenomenon through the matrices and of the transfer of the aroma compounds towards the gaseous phase and of diffusion in the gaseous phase. To study the influence of the nature of the aroma compound and the effect of the matrix components on the kinetic of release, the K_{mass} kinetic curves were drawn (Fig. 4).

These measurements are realized in the three media (water, carbohydrate matrix and complex matrix). From water, the more hydrophobic aroma compound, ethyl acetate, presented the higher amount of releasing. The same order of quantities of released aroma compounds from the carbohydrate and complex matrices was detected. For the two compounds the influence of the complex matrix (containing oleic acid) was significant but with a higher retention for ethyl acetate.

From the release curves, a linear correlation exists between time and aroma compounds concentration in the gas phase for the initial parts of the kinetic release curves. By calculating the slope of this initial part of the curves, information on the aroma compound diffusion through the liquid-gas interface can be achieved (Table 5). The determination coefficient (R^2) values were ranged from 0.97 to 0.99 indicating a good fitness.

The behavior of diacetyl was different from ethyl acetate. The release curves of diacetyl from water and from both the carbohydrate and complex matrices are nearer than that from release curves of ethyl acetate. In other word, the effect of XG and oleic acid for ethyl acetate is higher than diacethyl. Diacetyl has a great affinity for water (high water solubility) and a low log P (= -1.5).

Ethyl acetate displayed the shorter equilibrium time whereas diacetyl took a long time to reach the equilibrium. The hydrophilic compound (diacetyl) which presents affinity for the water molecules was the compound with the slower rate of release (R_i) and the faster equilibrium time. These compounds establish interactions with the water molecules which must be broken to allow the release of the aroma compounds in the gas phase. This describes the slow initial rate of release (R_i) of these compounds. For the hydrophobic compound, the repulsion by the water molecules is immediate, from where a high initial rate of release. But the release is progressive in time, thus the time to reach the equilibrium is longer. Similar results have been reported by *Seuvre et al.* (2007) [34].

With respect to the difference between the aroma

compounds, from the data of Table 4 is shown that diacetyl had a faster rate of release (R_i) than ethyl acetate as this is reflected by the slope of initial parts of the release curves which was attributed to the different physico-chemical properties of the compounds (Table 5).

In the case of diacetyl, when comparing the slopes of initial part of release curve for water and matrix containing only XG, a significant decrease was observed while a further decrease following the addition of oleic acid was noticed. This could be clarified by the presence of XG, which even at a low level induces a transition from a macromolecular solution to a structured system. This system affects the diffusion rate of diacetyl molecules and, consequently, the initial slopes of the release curve.

The effect of the complex matrix (containing oleic acid) on the both aroma compounds was significant but with a higher retention for ethyl acetate.

From experiments carried out on matices containing only XG, decrease of the slope of initial part of release curve was evidenced (26-72%), which was probably the result of hydrogen bond formation between the diacetyl and the matrix. Similar result was stated by *Karaiskou et al.* (2008) [12].

Similarly, in compare with water the release rate of ethyl acetate was slower in carbohydrate matrices (Table 5). Furthermore, addition of oleic acid in carbohydrate matrix (5% v/v) (C_1) resulted in a 35% slope decrease, which was further continued with increasing carbohydrate content to 89% for the maximum XG added matrix C_4.

The oleic acid in complex matrices stabilizes the molecules of ethyl acetate by forming a protective film around them contributing, in this way, to their retention in the complex matrices.

The values of R_i in complex matrices were lower than those from water. This reduction was mostly due to the retention of flavour compounds by the oleic acid present in the complex matrices: indeed, the more hydrophobic compound, ethyl acetate, presented the slower rate (Table 5). The equilibrium time of both aroma compounds were a little longer than those in water. These observations were partially in agreement with *Haahr et al.* (2000) who investigated the release of aroma compounds as a function of time from water, from colza oil emulsions with different concentrations and from pure colza oil.

Table 6: Slope values calculated from the initial part of the release curves of diacetyl and ethyl acetate in different matrices (20^oC).

Matrix	Slope ($\times 10^{-3}$)	
	Diacetyl	Ethyl acetate
$W^\#$	0.19 ± 0.001^a	0.11 ± 0.001^a
H_1	0.15 ± 0.001^{bc}	0.08 ± 0.001^{bc}
H_2	0.11 ± 0.001^c	0.06 ± 0.001^c
C_1	0.14 ± 0.001^d	0.06 ± 0.001^{cd}
C_2	0.12 ± 0.001^e	0.04 ± 0.001^e
C_3	0.09 ± 0.001^d	0.03 ± 0.001^d
C_4	0.06 ± 0.001^e	0.01 ± 0.001^d

For the studied aroma compounds, they found that the fastest release was this from the water and the slowest was this from the colza oil [37].

CONCLUSIONS

The degree of retention of ethyl acetate and diacetyl in matrices containing increasing levels of oleic acid and/or xanthan gum was affected by their physico-chemical characteristics and the nature and concentration of the hydrocolloid. For both model matrices (carbohydrate and complex) the aromatic compounds were retained but with a greater retention in complex matrix which contained oleic acid. Ethyl acetate was mainly affected by xanthan gum addition. Two factors can affect their transfer to gaseous phase. The first refers to the fact that release of aroma compounds from matrices reduces their quantity, which is available for release in the headspace. This lower concentration of available aroma affects both the release rate, as well as their concentration in the headspace under equilibrium, as expressed by the partition coefficient. In addition, the viscosity enhancement with increasing XG and oleic acid contents decreases the diffusion rate of both aromatic compounds through the interface of the system.

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