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Emulsification enhances the retention of esters and aldehydes to a greater extent than changes in the droplet size distribution of the emulsion

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Abstract

The physicochemical and organoleptic properties of an emulsion depend on the way the constituents interact with one another to form emulsion droplets, interfacial region and continuous phase. The objective of this work was to evaluate the respective impact of both the emulsification and the modification of the properties of an emulsion, such as the droplet size distribution, on the partition of aroma compounds. The emulsions were prepared with sodium caseinate and the low melting point fraction of anhydrous milk fat ($\Phi = 0.3$). Their volume-surface mean droplet size ranged from 1.8 to 0.3 μm. Results showed that the measured partition coefficients of ethyl pentanoate, isoamyl acetate, hexanal and *t*-2-hexenal were lower than the calculated ones from values measured separately over continuous and dispersed phases. The droplet size distribution had no significant impact on the partition coefficient of the three esters whereas, for a volume-surface mean diameter below 0.5 μm, the partition coefficients of the two aldehydes were drastically reduced. The greater retention is not related to the sodium caseinate remaining in the continuous phase of the emulsion. The formation of an interfacial area seems to govern the partition of aroma compounds in emulsions.

Keywords: Emulsion; Droplet size; Caseinate; Aroma; Partition

1. Introduction

Aroma is an important part of perceived flavour in food. Aroma release is governed by partition coefficient and mass transfer (Kinsella, 1988; Overbosch, Asterof, & Haring, 1991). Partition coefficient and mass transfer depend on the food matrix composition and/or structure (Kinsella, 1990; McClements, 1999b). Many foods can be described, more or less, as oil-in-water emulsions, characterised by the presence of an oil phase dispersed in an aqueous phase, both being separated by an interface. The bulk physicochemical and organoleptic properties of an emulsion depend on the way the constituents (such as oil and emulsifiers) interact with one another to form emulsion droplets, an interfacial region, and a continuous phase (McClements, 1999a). Proteins, lipids and polysaccharides modify the partition coefficients of aroma compounds in monophasic systems (de Ross, 1997; Fisher & Widder, 1997; Godshall, 1997; Guichard, 2002; Kinsella, 1990; Lübbers, Landy, & Voilley, 1998). Currently, there is no general rule for describing and understanding the effects of the oil–water interface on the partition coefficients of aroma compounds between air and a matrix (Druaux & Voilley, 1997). In addition, modification of the droplet diameter gives contradictory results with regard to partition and release of aroma compounds. Some authors find no effect of the droplet size distribution on the partition

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coefficients of aroma compounds (Druaux, Courthaudon, & Voilley, 1996; Le Thanh, Thibeaudeau, Thibaut, & Voilley, 1992; Miettinen, Tuorila, Piironen, Vehkalahti, & Hyvönen, 2002; Rabe, Krings, & Berger, 2003) while others do find a change in partition or release, depending on droplet size distribution (Carey, Linforth, & Taylor, 2003; Charles, Rosselin, Beck, Sauvageot, & Guichard, 2000a, Charles, Lambert, Brondeur, Courthaudon, & Guichard, 2000b; Doyen, Carey, Linforth, Marin, & Taylor, 2001; van Ruth, King, & Giannouli, 2002a, van Ruth, de Vries, Geary, & Giannouli, 2002b). Our objective was to evaluate the respective impacts of the emulsification and the modification of the droplet size distribution of an emulsion on the partition of aroma compounds. Three esters, isoamyl and amyl acetates and ethyl pentanoate, and two aldehydes, hexanal and *t*-2-hexenal, were added as a blend to give an overall green apple aroma. The emulsions were prepared with sodium caseinate and the low melting point fraction of anhydrous milk fat, with dairy products as target foods.

2. Materials and methods

2.1. Chemical compounds

The purity of amyl acetate, ethyl pentanoate, hexanal, and *t*-2-hexenal was greater than 98%, as determined by GC (Aldrich, Saint Quentin Falavier, France). IFF (Longvic, France) provided the isoamyl acetate. Aroma compounds were dissolved in propylene glycol (Aldrich, Saint Quentin Falavier, France). The physicochemical and thermodynamic constants of the aromas are given in Table 1. Ultrapure water was prepared with a Millipore system. Armor Protéines S.A.S. (Saint-Brice-en-Coglès, France) supplied the sodium caseinate and France Beurre (Quimper, France) the low melting point fraction of anhydrous milk fat (amf), which exhibited a drop point of 20–24 °C. Prior to use, the low melting point fraction of amf was melted at 50 °C for 1 h to erase its thermal history and then maintained at 40 °C before emulsification. At 32 °C, the temperature of the experiments, the fat was totally liquid.

2.2. Experimental design

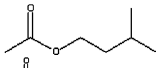
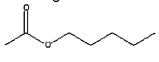
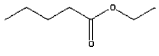
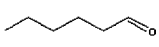
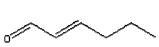
Oil-in-water emulsions, stabilised by sodium caseinate, were prepared at various homogenisation pressures to obtain different volume-surface mean diameters. A decrease in the latter led to an increase in surface area and thus to a reduction of the sodium caseinate remaining in the continuous phase. The partition of aroma over solutions of 10, 20 and 30 g l^{-1} of sodium caseinate was measured to evaluate the effect on partition coefficients of the sodium caseinate concentration remaining in the continuous phase. Partition coefficient over the low point fraction of amf was determined in a separate study (unpublished results).

The stability of emulsions was evaluated by laser granulometry over time, after flavouring and after headspace measurement.

2.3. Emulsion preparation

Preliminary tests revealed that a sodium caseinate concentration of 30 g l^{-1} was required to obtain stable emulsions of the expected droplet size distribution (from 0.5 to 2 μm) and during the time of the experiment (two days). Consequently, an emulsifier solution was prepared by dispersing 30 g l^{-1} of sodium caseinate (Na–Cas) in 80 mM NaCl solution containing 0.2 g l^{-1} of sodium azide (as an antimicrobial). The resulting solution

Table 1
Physicochemical and thermodynamic characteristics of the five aroma compounds

Compound	Structure	MW[a]	BP[a] (°C)	P_{sat}[a] (mm Hg)	S[a] (g l^{-1})	Log P[a]	Henry's constant[a] (Atm m^3 mol^{-1})	γ Calculated (1)
Isoamyl acetate		130	142	5.6	2.0	2.26	5.87×10^{-4}	3673
Amyl acetate		130	149	3.5	1.7	2.3	3.88×10^{-4}	3664
Ethyl pentanoate		130	145	4.8	2.2	2.34	3.72×10^{-4}	5345
Hexanal		100	131	11.3	5.6	1.78	2.13×10^{-4}	82
t-2-Hexenal		98	146	6.6	5.3	1.58	4.89×10^{-5}	173

(1) Calculated according to UNIFAC.
All data were collected at 25 °C (298 K). MW, molecular weight; BP, boiling point; P_{sat}, saturated vapour pressure; S, solubility in water; Log P, log partition coefficient between water and octanol; γ, activity coefficient.
[a] http://esc-plaza.syrres.com/interkow/physdemo.htm.

was stirred overnight at 4 °C to ensure a complete hydration of proteins and then the pH was adjusted to 6.7. Oil-in-water emulsions were then prepared by homogenising 30 wt% of low melting point fraction of amf and 70 wt% of Na–Cas solution at 32 °C. First, a coarse emulsion was prepared with a high-speed blender at 20000 rpm for 45 s (Polytron PT 6100, Kinematica, Littan, Switzerland). Second, the coarse emulsion was passed through a valve homogeniser (Stansted Fluid Power, UK) at pressures of 34, 70 and 250 MPa to generate different droplet size distributions. Nine different emulsions were prepared, characterised and flavoured.

2.4. Droplet size distribution

The droplet size distribution of the emulsions was measured using a laser diffraction instrument (Saturn DigiSizer 5200, Micrometrics, Creil, France). Calculations were performed with the following refractive indices: 1.458, for dispersed phase (low melting point fraction of amf), 1.331 for continuous phase (water), and an absorbance value of the emulsion particle of 0.01 (based on the Mie theory). Flocculation or aggregation of droplets was revealed by a comparison of distribution with and without sodium dodecyl sulphate (0.1% w/w). Results were expressed as volume-surface mean diameter, d_{32}, in μm. The distributions of the nine emulsions are shown in Fig. 1.

2.5. Flavouring of emulsions

Stock solutions of aromas were prepared by accurately weighing each aroma in propylene glycol at room temperature. Each of the nine emulsions was flavoured with four different amounts of the stock solution and then equilibrated overnight at 32 °C under mild stirring. The concentration of aroma compounds ranged from 200 mg kg^{-1} for the highest concentration to 1.5 mg kg^{-1} for the lowest.

2.6. Determination of air–media partition coefficients

Partition coefficients are defined as the ratio of the concentration of each aroma in the gaseous phase (ng ml^{-1}) to its concentration in the liquid phase (ng ml^{-1}). The former concentration was measured by headspace analysis, which was carried out with a Perkin–Elmer HS 40XL automatic sampler paired with a HP 5890 gas chromatograph. The detailed procedure has been given elsewhere (Meynier, Garillon, Lethuaut, & Genot, 2003). Each partition coefficient value was the mean of eight determinations.

To evaluate the effect of the interface on the partition over an emulsion, the experimental partition coefficients were compared to those calculated according to the model proposed by Buttery, Guadagni, and Ling (1973).

$$K_{\mathrm{aem}} = \frac{1}{((\Phi_{\mathrm{cp}}/K_{\mathrm{acp}}) + (\Phi_{\mathrm{dp}}/K_{\mathrm{adp}}))}, \quad (1)$$

where K_{aem} is the partition coefficient between air and emulsion, Φ_{cp}, the mass fraction of continuous phase, Φ_{dp}, the mass fraction of dispersed phase, K_{acp}, the partition coefficient between air and continuous phase, K_{adp}, the partition coefficient between air and dispersed phase.

The partition coefficients of the five aroma compounds over emulsions were calculated according to Eq. (1), considering the measured air–sodium caseinate partition coefficients (see Table 3) and the coefficients measured over the low melting point fraction of amf.

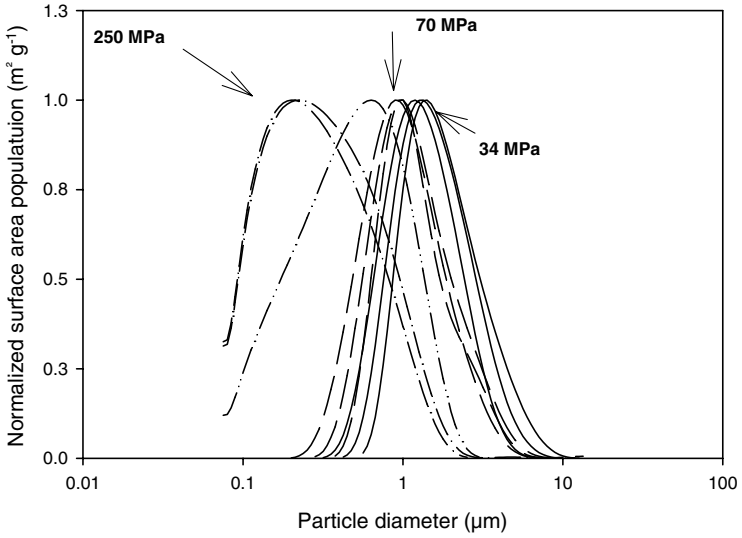


Fig. 1. Droplet size distribution of the emulsions prepared at various pressures with sodium caseinate (30 g l^{-1}, Φ = 0.7 w/w) and low melting point fraction of anhydrous milk fat (Φ = 0.3 w/w). Dash-dotted line: emulsions prepared at 250 MPa; long dashed line: emulsions prepared at 70 MPa; solid line: emulsions prepared at 34 MPa.

2.7. Statistical analysis

Variance analysis (ANOVA) was used to determine the effect of volume-surface mean diameter on partition coefficients. If significant effects were found, Newman–Keuls tests were performed. Differences between measured and calculated partition coefficients were statistically evaluated using hypothesis tests. The significance level was $p < 0.05$ throughout the study. Statistical analyses were performed with Statgraphics Plus 3.0.

3. Results

3.1. Properties of the emulsions

Prepared emulsions were monomodal and droplet size distributions largely overlapped one another, as shown in Fig. 1. The emulsions were physically stable over the time of the experiments; no coalescence, no flocculation and no droplet size variations were observed upon storage or after flavouring and determination of partition coefficients.

The properties of the emulsions are summarised in Table 2. Modification of the volume-surface mean diameter ($d_{32} = \sum n_i d_i^3 / \sum n_i d_i^2$) induced other changes in the emulsion characteristics. Thus, the surface area of the droplets and the quantity of adsorbed proteins increased when volume-surface mean diameter decreased, whereas the quantity of proteins remaining in the continuous phase of the emulsion decreased. Under our experimental conditions, the volume-surface mean diameter ranged from 0.3 μm for the smallest droplet size distribution to 1.8 μm for the largest ones. This corresponded to an interfacial area ranging from 3.4 to 20 $m^2\,cm^{-3}$ of oil. Assuming that 1.63 mg of sodium caseinate covers 1 m^2 of surface (Courthaudon et al., 1999), the quantity of protein adsorbed at the interface was calculated as well as the quantity of protein remaining in the continuous phase by difference. The concentration of adsorbed caseinate ranged from 1.64×10^{-3} g cm^{-3} of emulsion for the largest droplets to 9.78×10^{-3} g cm^{-3} of emulsion for the smallest ones. The concentration of sodium caseinate in the continuous phase ranged from 19.4×10^{-3} g cm^{-3} of emulsion for the largest droplets to 11.2×10^{-3} g cm^{-3} of emulsion for the smallest ones.

3.2. Partition of the five aroma compounds in solution as a function of sodium caseinate concentration

Partition coefficients of the five aroma compounds were measured over sodium caseinate solutions at 10, 20 and 30 g l^{-1} to evaluate the impact of the protein concentration in the continuous phase on the partition coefficients. The results are shown in Table 3. Among the esters, isoamyl acetate exhibited the highest partition coefficient, amyl acetate had the lowest partition coefficient while ethyl pentanoate had an intermediate value. The unsaturated aldehyde, *t*-2-hexenal, was far more retained in sodium caseinate solution than the saturated one, hexanal (1.0×10^{-4} instead of 1.5×10^{-3}). Air–media partition coefficients of the three esters and hexanal did not change significantly in the presence of 10 or 20 g l^{-1} of sodium caseinate, but were reduced in solutions containing 30 g l^{-1} of protein. In contrast, partition coefficients of *t*-2-hexenal were reduced when protein concentration increased. As shown in Table 2, the concentration of sodium caseinate in the continuous phase of the emulsions varied from 11 to 20 g l^{-1} and such changes in protein concentration only modified the partition coefficient of *t*-2-hexenal.

3.3. Comparison of air–emulsion partition coefficients

3.3.1. Biphasic vs. emulsion

Equation (1) allows the partition coefficient of aroma compounds over a biphasic system to be calculated. Experimental and calculated partition coefficients are given in Table 4. The measured partition coefficients over

Table 2
Properties of oil-in-water emulsions prepared with Na–Cas 30 g l^{-1} at pH 6.7 (ϕ: 0.7) and low melting point fraction of anhydrous milk fat (ϕ: 0.3)

Homogenisation pressure MPa	d_{32} μm	Specific surface area[a] $m^2\,cm^{-3}$ oil	$[Na–Cas]_{ads}$[b] g cm^{-3} emulsion (×1000)	$[Na–Cas]_{c\phi}$[c] g cm^{-3} emulsion (×1000)
34	1.8	3.4	1.6	19.4
34	1.6	3.9	1.9	19.1
34	1.3	4.7	2.3	18.7
70	1.2	5.1	2.5	18.5
70	1.2	5.1	2.5	18.5
70	1.0	5.9	2.9	18.1
250	0.4	13.6	6.7	14.3
250	0.3	18.8	9.2	11.8
250	0.3	20.0	9.8	11.2

[a] Surface = $6/d_{32}$.
[b] $[Na–Cas]_{ads}$ = Surface × (ϕ oil) × protein surface coverage [1.63×10^{-3} g m^{-2} (Courthaudon et al., 1999)].
[c] $[Na–Cas]_{c\phi} = [Na–Cas]_{initial} \times \phi_{c\phi} – [Na–Cas]_{ads}$.

Table 3
Partition coefficients ($\times 10^3$) of aroma compounds at 32 °C between air and sodium caseinate solutions

[Na–Cas] g l^{-1}	Isoamyl acetate	Amyl acetate	Ethyl pentanoate	Hexanal	*t*-2-Hexenal
10	**3.61** ± 0.03[a]	**1.35** ± 0.01[a]	**2.53** ± 0.02[a]	**1.57** ± 0.01[a]	**0.106** ± 0.001[a]
20	**3.63** ± 0.05[a]	**1.35** ± 0.03[a]	**2.55** ± 0.04[a]	**1.50** ± 0.02[a]	**0.086** ± 0.002[b]
30	**3.34** ± 0.03[b]	**1.22** ± 0.01[b]	**2.33** ± 0.02[b]	**1.21** ± 0.02[b]	**0.058** ± 0.001[c]

Values are the means of eight measurements (4 concentrations in duplicate); (bold, mean; plain, standard deviation). Within a column, values with different superscript letters differ significantly ($p < 0.05$).

Table 4
Comparison between calculated and measured air–oil-in-water emulsion (ϕ:0.3) partition coefficients ($\times 10^4$) of aroma compounds at 32 °C

	Isoamyl acetate	Amyl acetate	Ethyl pentanoate	Hexanal	*t*-2-Hexenal
Calculated (1)	**1.31** ± 0.07[a]	**0.39** ± 0.03[a]	**0.80** ± 0.06[a]	**2.01** ± 0.07[a]	**0.45** ± 0.02[a]
Measured (1)	**1.06** ± 0.04[b]	**0.31** ± 0.02[b]	**0.63** ± 0.03[b]	**0.66** ± 0.01[b]	**0.11** ± 0.01[b]
Calculated (2)	**1.31** ± 0.08[a]	**0.39** ± 0.04[a]	**0.80** ± 0.06[a]	**2.00** ± 0.08[a]	**0.42** ± 0.02[a]
Measured (2)	**1.17** ± 0.08[b]	**0.36** ± 0.04[a]	**0.70** ± 0.06[b]	**1.61** ± 0.04[b]	**0.31** ± 0.02[b]

Values are the means of eight measurements (4 concentrations in duplicate); (bold, mean; plain, standard deviation).
Calculated value according to Eq. (1).
Calculated (1) K_{acp}: air–sodium caseinate 10 g l^{-1} partition coefficient (see Table 3).
Calculated (2) K_{acp}: air–sodium caseinate 20 g l^{-1} partition coefficient (see Table 3).
Measured (1): lowest value of air–emulsion partition coefficient.
Measured (2): highest value of air–emulsion partition coefficient.
Statistics: paired comparison calculated (1) vs. measured (1); values with different superscript letters differ significantly.

emulsions were significantly lower than the calculated ones. The only exception was noticed for amyl acetate over large droplet emulsions. The tabulated results show that the modification of the sodium caseinate remaining in the continuous phase did not significantly affect the values of calculated partition coefficients. The discrepancy between measured and calculated coefficients was larger for hexanal and *t*-2-hexenal (differences ranged from 52% to 200%, and from 150% to 310%, respectively) than for isoamyl acetate and ethyl pentanoate (approximately 20%). The lowest partition coefficient measured for hexanal was 6.63×10^{-5} and corresponded to the lowest droplet size and the lowest sodium caseinate concentration in the continuous phase. The partition coefficient calculated with the corresponding partition coefficient over a solution of 10 g l^{-1} of sodium caseinate was 2.0×10^{-4}. It can be concluded that the partition coefficient over an emulsion cannot be accurately predicted from the knowledge of the partition coefficient over the constitutive phases, even if the exact compositions of the continuous and dispersed phases are included in the model.

3.3.2. Changes in the droplet size

The air–emulsion partition coefficients as a function of d_{32} are shown in Table 5. It is clear that the partition coefficients of the three esters were not significantly different, whatever the volume-surface mean diameter. Conversely, partition coefficients of aldehydes were significantly affected by modification of the droplet size distribution. Thus, retention of hexanal increased drastically when the volume-surface mean diameter of the droplet size was below 0.5 μm. For *t*-2-hexenal, values of partition coefficients were scattered even for

Table 5
Measured air–oil-in-water emulsion (ϕ: 0.3) partition coefficients ($\times 10^4$) of aroma compounds at 32 °C

Droplet size d_{32} (μm)	Isoamyl acetate	Amyl acetate	Ethyl pentanoate	Hexanal	*t*-2-Hexenal
1.8	**1.17** ± 0.09[b]	**0.36** ± 0.04[a]	**0.70** ± 0.06[b]	**1.44** ± 0.04[d]	**0.14** ± 0.02[a]
1.6	**1.12** ± 0.09[ab]	**0.33** ± 0.04[a]	**0.67** ± 0.06[ab]	**1.62** ± 0.04[e]	**0.25** ± 0.05[b]
1.3	**1.12** ± 0.06[ab]	**0.33** ± 0.03[a]	**0.67** ± 0.04[ab]	**1.47** ± 0.04[d]	**0.15** ± 0.02[a]
1.2	**1.07** ± 0.09[ab]	**0.31** ± 0.03[a]	**0.64** ± 0.06[ab]	**1.59** ± 0.04[e]	**0.31** ± 0.06[b]
1.2	**1.15** ± 0. 06[ab]	**0.35** ± 0.03[a]	**0.69** ± 0.05[ab]	**1.48** ± 0.04[d]	**0.18** ± 0.03[a]
1.0	**1.09** ± 0.06[ab]	**0.33** ± 0.03[a]	**0.65** ± 0.04[ab]	**1.52** ± 0.03[e]	**0.22** ± 0.03[b]
0.4	**1.11** ± 0.03[ab]	**0.33** ± 0.02[a]	**0.66** ± 0.02[ab]	**1.15** ± 0.01[c]	**0.11** ± 0.01[a]
0.3	**1.09** ± 0.04[ab]	**0.33** ± 0.02[a]	**0.65** ± 0.03[ab]	**0.97** ± 0.01[b]	**0.11** ± 0.02[a]
0.3	**1.06** ± 0.04[a]	**0.32** ± 0.02[a]	**0.63** ± 0.03[a]	**0.66** ± 0.01[a]	**0.11** ± 0.02[a]

Values are the means of eight measurements (4 concentrations in duplicate); (bold, mean; plain, standard deviation). Within a column, values with different superscript letters differ significantly.

similar volume-surface mean diameters (e.g. 0.31 and 0.18×10^{-4} for d_{32} of 1.2 μm). Nevertheless, partition coefficients over the emulsions of the smallest droplet diameter were significantly lower than for the larger ones.

4. Discussion

4.1. Effect of protein concentration on aroma compound retention

Except for *t*-2-hexenal, the retention of aroma compounds by sodium caseinate became significant above 20 $g\,l^{-1}$. For esters, decreases in partition coefficients were similar (8% for ethyl pentanoate or isoamyl acetate, 10% for amyl acetate) whereas they reached 30% for hexanal and 83% for *t*-2-hexenal. Retention of aroma compounds by proteins has been subjected to several studies and reviews (Guichard & Langourieux, 2000; Guichard, 2002; Kinsella, 1990; Lübbers et al., 1998). Nevertheless, few of these studies dealt with the modification of interactions with increasing quantities of proteins. Widder and Fisher (1996) observed a slight but continuous decrease in the volatility of esters (ethyl butyrate, ethyl-2-methyl-butyrate and ethyl hexanoate) when sodium caseinate concentration increased from 0 to 60 $g\,l^{-1}$. The authors attributed the retention to hydrophobic interactions between esters and proteins. Unlike the esters, the concentration of aldehyde in the headspace was greatly reduced in the presence of a low concentration of sodium caseinate. This behaviour can be explained by the possible reactions of aldehydes with the proteins, leading to covalent bonds (Le Guen & Vreeker, 2003; Widder & Fisher, 1996). Covalent bonds of *t*-2-hexenal were formed with histidyl and lysyl residues of proteins (sodium caseinate and whey proteins) while hexanal only reacted with lysyl residues of proteins (Meynier, Rampon, Dalgalarrondo, & Genot, 2004). In the present study, the concentration of sodium caseinate remaining in the continuous phase of the emulsion did not exceed 20 $g\,l^{-1}$, so the discrepancy between calculated and measured partition coefficients cannot be attributed to interaction between sodium caseinate in the continuous phase and aroma compounds.

4.2. Effect of emulsifications and droplet size

Under our experimental conditions, measured partition coefficients were significantly lower than the calculated ones for four of the five aroma compounds studied. This means that the partition coefficient of aroma compounds cannot be accurately predicted from the coefficient measured in the constitutive phases. Indeed, Eq. (1) does not take into account the presence of an interfacial layer, in which adsorbed proteins were concentrated, nor the consequences of the droplet size distribution (McClements, 1999b). Contradictory results were found in the literature related to the effect of emulsification. When agreement was found between measured and calculated coefficients, it concerned esters such as isoamyl acetate (Seuvre, Espinosa-Diaz, & Voilley, 2000), amyl acetate (Meynier et al., 2003), ethyl butyrate and ethyl hexanoate (Landy, Courthaudon, Dubois, & Voilley, 1996). In two studies, a higher partition coefficient was measured in an emulsion than in biphasic systems (Seuvre et al., 2000; van Ruth et al., 2002a). Finally, as for four of the five studied aroma compounds, measured partition coefficients were lower than the calculated ones (Meynier et al., 2003; van Ruth et al., 2002a; Voilley, Espinosa-Diaz, Druaux, & Landy, 2000). The discrepancy between measured and calculated coefficients cannot be explained by interactions that possibly take place between aroma compounds and sodium caseinate in the continuous phase as no change in partition coefficient occurred at the considered concentration in solution. The concentration of adsorbed sodium caseinate ranged from 1.6 to 9.8 $g\,l^{-1}$. Such concentrations did not per se change the partition coefficient of aroma compounds in solution, except that of *t*-2-hexenal, but modification of the interactions between sodium caseinate and aroma compounds can occur upon the adsorption of protein at the interface, as suggested for 2-nonanone (Voilley et al., 2000). A last hypothesis is to imply the spherical interface of the emulsion in the modifications of molecular organisation when compared to planar interfaces and emulsification itself.

The results clearly show that modification of the droplet size distribution, from 1.8 to 0.3 μm, did not significantly change the partition coefficients of amyl and isoamyl acetate and ethyl pentanoate. We have already mentioned that a reduction of the droplet size volume-surface mean diameter induced an increase in the interface area and thus in the quantity of adsorbed sodium caseinate. Unchanged values of partition coefficients mean that the interactions between adsorbed protein and esters have no significant impact on the partition. The behaviour of aldehydes was different. It seems that, above 5 $g\,m^{-3}$ of adsorbed protein, covalent binding leads to specific binding of these aldehydes at the interface and to a subsequent reduction in their partition coefficients.

5. Conclusions

This work clearly shows that the formation of an spherical interface is a key step governing the partition behaviour of aroma compounds in emulsion. The partition behaviour of esters is not modified by further changes, such as a decrease in the volume-surface mean

diameter, probably due to the nature of the interaction between esters and proteins. Conversely, the possible covalent binding of aldehydes with proteins can modify their partition behaviour when the concentration of adsorbed protein increases (small droplets).

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