Effect of Thickeners on Aroma Compound Behavior in a Model Dairy Gel

Samuel Lubbers,* Nicolas Decourcelle, Daniel Martinez, Elisabeth Guichard, and Anne Tromelin

Unité Mixte de Recherche FLAVIC, ENESAD-INRA, 17 Rue Sully, Dijon Cedex F21065, France

The effects of thickeners on the headspace release of aroma compounds from a model dairy gel were investigated. Starch, pectin, and locust bean gum (LBG) were introduced separately to the fat-free dairy gel via sugar syrups. The release of nine aroma compounds was analyzed by solid-phase microextraction (SPME), and the partition coefficients of retention were calculated. For an increase in starch concentration, there was an overall decrease in aroma release. Pectin concentrations in gel higher than 0.04% caused an increase in aroma release. For LBG no major effect was observed. A quantitative structure−property relationship (QSPR) approach was used to propose which types of interactions were involved between aroma molecules and thickener macromolecules in the complex foodstuff. Twenty molecular descriptors of volatile compounds appeared to be significant in correlation with the partition coefficients of retention. The surface-weighted negatively charged partial surface area seemed to play a critical role in the behavior of aroma compound.

KEYWORDS: Yogurt; thickeners; flavor release; SPME; QSAR; QSPR

INTRODUCTION

Fat and flavor are important factors in food acceptance, but it is known that fat content affects the partitioning of flavor molecules between the air phase and food matrix. When the fat content of a food system is reduced, there will be imbalances in the flavor release (*1*), perceptions of flavor, appearance, mouthfeel, and structure (*2*). To retain the properties of a product when the fat is removed, fat substitutes are used. Common examples are starch, pectin, guar gum, and locust bean gum (LBG). Viscosity is an important property for quality control, especially for products expected to have a certain consistency in relation to sensory attributes such as mouthfeel and appearance. An increase or decrease in viscosity can have major effects on the acceptance of the product (*3*). It has been found that with an increase in the concentration of pectin and starch in fat-free stirred yogurt there was an increase in viscosity. However, thickeners are also capable of altering the flavor of the product.

Recent works have shown that with an increase in thickeners in a model dairy gel there were effects on both the viscosity and the aroma release for starch and pectin (*4*, *5*). A greater release of hydrophilic compounds was found in pectin gels and for starch; the gels were found to show a greater release of hydrophobic flavor compounds (*6−8*). This could be attributed to the effect of matrix−volatile compound interactions involving starch, pectin, volatiles, and sugars (*1*, *5*, *9*). However, other authors have shown that thickeners had no impact on flavor

release by the study of the headspace in yogurt (*10*, *11*) and by nose-space measurements (*12*). In summary, two phenomena have been proposed to explain the behavior of flavor compounds in these systems. It could be that the nature of the macromolecule is involved either (i) directly by engaging interactions with the aroma compound or (ii) by modifying the conditions of mass transfers within the system. The study of the system, under thermodynamic equilibrium conditions and kinetic conditions, permitted partial differentiation of the phenomena (*2*, *13−16*).

The aim of this work was to specify the effects of different thickeners (starch, pectin, and LBG) on the retention/release of aroma compounds and to propose which type of molecular interactions were involved. The challenge was to lead the experimentation in a system having complexity intermediate between those of the foodstuff and the model system of the laboratory. Thus, the model dairy gel used was composed of fat-free yogurt and thickener sugar syrups. The retentions/releases of aroma compounds from dairy gels were carried out using solid-phase microextraction (SPME) at equilibrium. SPME is a powerful method for sampling aroma compounds, but it is poorly adapted for a true quantification. Therefore, the specific partition coefficient of retention was used to estimate the role of thickener concentration on the retention/release of aroma compounds.

The basis of an alternative research about aroma release mechanisms by means of the computational approach quantitative structure−property relationships (QSPR) method was previously used in the study of the behavior of volatiles in carrageenan gel (*17*). The influence of the chemical structure on retention/release equilibrium of several aroma compounds

Table 1. Composition of the Thickener Preparations (Quantities Shown as Grams per 100 g of Final Mix)

ingredient added	starch preparation			pectin preparation			LBG preparation			ref
sodium citrate	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
calcium citrate	0.07	0.07	0.07	0.02	1.1	1.6	0.07	0.07	0.07	0.07
potassium sorbate	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
starch	0.5	2	3							
pectin				0.2	1	1.5				
LBG							0.25	0.75	1.25	
FOS	9.3	9.3	9.3	9.3	9.3	9.3	9.3	9.3	9.3	9.3
fructose	9.3	9.3	9.3	9.3	9.3	9.3	9.3	9.3	9.3	9.3
water		until 100 g			until 100 g			until 100 g		until 100 g

Table 2. Values of Physiochemical Characteristics of Aroma Compounds[a]

compound	MW	AlogP98	Apol	area	dipole-mag	rad gyration	Jurs FNSA 2	FNSA 3	FPSA 2	PNSA 1	PNSA 2	PNSA 3	RNCG	WNSA 1	WNSA 2	WNSA 3	Shadow WPSA 2	X XY length	XZ	Z length
methyl 2-methyl-butyrate	116.2	1.61	4019.3	174.6	3.5	2.5	−0.52	−0.09	1.5	67.9	−164.1	−29.1	0.24	21.4	−51.8	−9.2	188.6	39.5	8.2	31.2 5.7
ethyl hexanoate	144.2	2.41	5045.8	221.8	4.5	3.4	−0.64	−0.10	2.1	79.2	−247.8	−36.9	0.18	30.7	−95.9	−14.3	372.7	49.4	12.8	46.7 5.2
hexyl acetate	144.2	2.26	5045.8	216.2	5.4	3.5	−0.66	−0.10	2.8	82.2	−256.2	−37.8	0.18	31.7	−98.9	−14.6	365.6	52.9	13.3	48.3 5.2
ethyl octanoate	172.3	3.32	6072.3	270.2	4.9	4.1	−0.57	−0.07	1.9	72.3	−260.8	−33.6	0.15	33.1	−119.4	−15.4	636.7	65.1	14.9	58.2 5.4
ethyl decanoate	200.3	4.23	7098.8	306.6	5.6	4.7	−0.72	−0.07	3.3	82.3	−364.5	−37.8	0.13	41.7	−184.7	−19.2	952.5	72.6	17.0	64.3 5.3
butanol	74.1	0.97	2538.6	128.7	2.7	2.2	−0.32	−0.10	2.5	44.6	−82.1	−26.4	0.38	11.6	−21.4	−6.9	103.4	29.6	8.9	28.4 4.9
hexanol	102.2	1.88	3565.1	173.6	3.2	2.8	−0.37	−0.09	2.5	47.9	−119.0	−27.5	0.28	15.4	−38.2	−8.8	218.3	39.8	11.4	38.5 4.9
octanol	130.2	2.80	4591.6	217.3	3.6	3.5	−0.40	−0.07	3.0	48.7	−153.7	−27.8	0.22	18.6	−58.6	−10.6	401.0	50.7	13.9	49.1 5.2
decanol	158.3	3.71	5618.2	261.4	4.0	4.2	−0.45	−0.07	3.7	52.8	−200.4	−29.2	0.19	23.4	−89.0	−13.0	660.5	63.2	16.3	62.2 5.6

[a] MW, molecular weight; AlogP98, calculated octanol/water partition coefficient; Apol, polarizability; dipole-mag, dipole moment; area, van der Waals area of the molecule; rad gyration, radius of gyration; Jurs and Shadow are defined in **Table 3**.

between the vapor phase and carrageenan gel was evaluated, and relationships between the properties of molecules and experimental responses were found. In previous work, our general assumption was that changes in molecular properties elicit different responses. This approach was proposed in the present study to investigate the nature of the interactions involved among aroma compounds in thickener molecules in complex food matrices.

MATERIALS AND METHODS

Thickener Preparation. In food industrial processes, fruit pulp, thickeners, sugars, and aroma are introduced into a dairy product via a "fruit preparation" to obtain, for example, a strawberry stirred yogurt. In the present study, each thickener studied was prepared in a syrup of sugars. Fructooligosaccharides (Raftilose F60, Orfati) and syrup of fructose (fructuline L95, Cosucra) were heated to 95 °C for 5 min at a constant mixing rate of 250 rpm using a Eurostar IKA-Labortechnik agitator. Sodium dihydrogen citrate, calcium citrate, and potassium sorbate (VWR, Prolabo) were added to the sugars and mixed for 2 min. Then, water was added and mixed for 3 min.

For the LBG preparation, the powder (viscogum, Degussa) was directly added into the sugars and salts mixture with stirring. For starch preparation, modified waxy corn starch/diacetylated diadipate of starch (National Starch and Chemical) was previously mixed with cold water before introduction in the sugars and salts mixture. For pectin preparation an 8% (w/w) aqueous solution of pectin (LM 102, CP Kelco) was prepared in a water bath at 80 °C and finally added and mixed with the sugars and salts mixture. All of the thickener preparations were stored at 10 °C for 24−48 h before use. **Table 1** shows the composition of thickener preparations.

Model Dairy Gel. Twenty grams of thickener preparation and 0.05 g of aroma compounds mixed in propane-1,2-diol were added into a fat-free stirred yogurt supplied by Danone (Vitapole, France) and blended for 30 s at 100 rpm (K anchor Kenwood blender). Products were stocked for 7 days at 10 °C before analysis. The final concentrations of starch in dairy gels were 0.1, 0.4, and 0.6 g per 100 g. For pectin, the final concentrations were 0.04, 0.1, and 0.15 g per 100 g,

and for LBG the final concentrations in dairy gels were 0.25, 0.75, and 1.25 g per 100 g.

A control sample (yogurt, sugars, salts, and aroma compounds, without thickener) was used as the reference product for the headspace analysis.

The aroma used in the mixture was composed of nine aroma compounds each at 0.69×10^{-3} mol L^{-1} in propane-1,2-diol. The physicochemical parameters discussed in this paper are listed in **Table 2**.

Flavoring Content. The aroma compound concentrations in dairy gel were determined by simultaneous steam distillation−solvent extraction using a Likens−Nickerson apparatus to control the flavoring. One hundred grams of the product was introduced into a 250 mL vessel; 36 g of NaCl and 0.5 mL of antifoam (Clerol FBA 3107 Cognis St Fargeau Ponthierry, France) were then added. Two hundred microliters of ethyl heptanoate in ethanol (10 μL L^{-1}) as an internal standard was added into the vessel. The sample was extracted by using 25 mL of dichloromethane for 30 min after the boiling point was reached. These extractions were carried out in triplicate. The variation coefficient obtained was less than 5%.

Headspace Analysis of the Aroma Compounds. Headspace analysis was performed by SPME with a 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber (Supelco). The choices of the nature of the fiber, the time of exposure, and the time of desorption were discussed in a previous work (*18*). Before sampling, dairy matrices were homogenized by hand with a spoon, and then an aliquot of 20 g was introduced into the flask (40 mL closed-septum headspace vials). An equilibration time of 30 min at 25 °C was used before SPME sampling. This time was chosen to reach the equilibrium between gel and vapor phases.

The aroma compounds were analyzed by gas chromatography (Hewlett-Packard 6890) using a splitless mode (injection port at 250 °C) with a flame ionization detector (FID). A fused-silica capillary column, DB-Wax, 30 m, 0.32 mm i.d., 0.5 μm film thickness (J&W Scientific), was used with helium as the carrier gas (velocity 42 cm s^{-1}). The temperature was programmed to increase from 40 to 120 °C at a rate of 3 °C min^{-1} and then at a rate of 10 °C min^{-1} to 220 °C.

Effect of Thickeners on Flavor Release

J. Agric. Food Chem., Vol. 55, No. 12, 2007 **4837**

Partition Coefficient Calculation. According to our aim of estimating the retention by increasing the amount of thickeners, the theoretical equilibrium between the reference (ref), yogurt + thickener preparation (th), and respective vapor phases corresponding to the two equilibria was considered:

$$[A]_{ref} \leftrightarrows A_{vap-ref} \quad K_1 = \frac{[A]_{vap-ref}}{[A]_{ref}} \quad (1)$$

$$[A]_{th} \leftrightarrows A_{vap-th} \quad K_2 = \frac{[A]_{vap-th}}{[A]_{th}} \quad (2)$$

In this way, a partition coefficient of retention is calculated:

$$K_{ret} = \frac{K_1}{K_2} = \frac{[A]_{vap-ref}}{[A]_{ref}} \cdot \frac{[A]_{th}}{[A]_{vap-th}} \quad (3)$$

The partition coefficient can be used only if the quantity of aroma released in the headspace is negligible compared to the initial quantity of aroma in the product. Therefore, the concentrations of aroma compounds in the sample after SPME measurements, $[A]_{ref}$ for the reference and $[A]_{th}$ for the thickener, with the initial concentration of aroma introduced in the gel $[A]_0$ were compared respectively. The aroma compound concentrations in the samples were determined by simultaneous steam distillation−solvent extraction; taking into account the experimental error, no difference was found before and after the SPME experiment.

Assuming that $n(A)_{vap} \ll n(A)_{liq}$, $[A]_{ref} \# [A]_0$ and $[A]_{th} \# [A]_0$, so that $[A]_{ref} \# [A]_{th}$, and eq 3 becomes

$$K_{ret} = \frac{K_1}{K_2} = \frac{[A]_{vap-ref}}{[A]_{vap-th}}$$

Because $[A]_{vap} \propto$ chromatographic area (A), K_{ret} can be written as

$$K_{ret} = \frac{\text{chromatographic area reference}}{\text{chromatographic area thickeners}}$$

so following K_{ret} for each thickener at each concentration, the log K_{ret} determined for starch and pectin can be used for activity values in QSPR calculations.

QSPR Study. The three-dimensional molecular structures of the nine aroma compound constructions and their structure alignment were performed using DS Viewer Pro6.0. Alignment was done by superimposition of chemical groups, based on electrostatic field fit in order to have a similar orientation of dipole moment and further improved by steric field fit.

The aligned structures were then analyzed with Cerius^2 software (version 4.10; Accelrys Inc., San Diego, CA, 2005) running on a Silicon Graphics workstation (SGI-O2). The modules QSAR$^+$ and Descriptors$^+$ were used for generating the descriptor collection and simple linear regressions. In the present work, 20 descriptors belonging to the classical groups of descriptors (electronic, spatial, structural, and thermodynamical descriptors) were retained. Simple linear regressions of activity versus molecular descriptor values were considered.

RESULTS AND DISCUSSION

The quantities of aroma compounds released into the headspace from gels were determined by SPME. Each thickener was studied separately. Data presented are the ratios between peak area of aroma from reference sample (yogurt without thickener) and from yogurt containing starch, pectin, or LGB, which constituted the partition coefficients of retention (K_{ret}). If no difference in the flavor release was obtained in the presence of thickener versus reference, the value of K_{ret} is equal to 1. Below this value, flavor release increased with the thickener. On the contrary, a value of $K_{ret} > 1$ means that the retention of aroma compound in the gel increased.
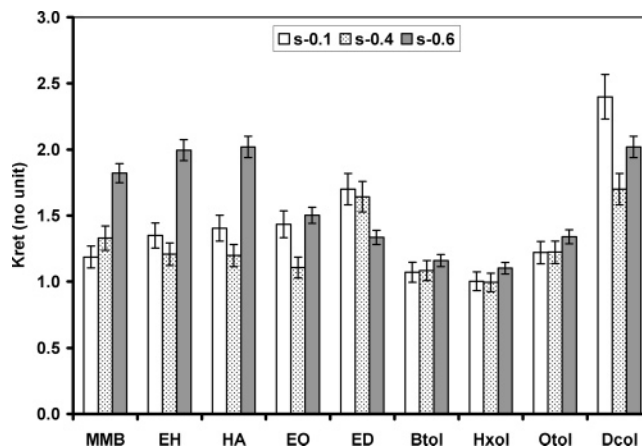

Figure 1. Flavor release of the aroma compounds from dairy gels containing different starch concentrations (0.1, 0.4, and 0.6 g per 100 g in final product). MMB, methyl 2-methylbutanoate; EH, ethyl hexanoate; HA, hexyl acetate; EO, ethyl octanoate; ED, ethyl decanoate; Btol, butanol; Hxol, hexanol; Otol, octanol; Dcol, decanol. Error bars correspond to the 95% confidence intervals.

The addition of 0.1% (w/w) of starch in the yogurt induced a significant decrease in the release of aroma compounds into the headspace of the sample. The flavor releases of butanol and hexanol were weakly affected by the presence of starch (**Figure 1**). With a starch concentration of 0.4% (w/w), the values of retention were comparable with those obtained for 0.1% of starch. However, decanol showed a different behavior. The retention was weaker in the matrix, but no explanation can be submitted.

For starch concentration of 0.6% in the dairy gel, there was an overall decrease in the release of esters into the headspace, except for ethyl decanoate, for which the retention was weaker than with lower starch concentrations (0.1 and 0.4%).

The model of macromolecular organization in a stirred dairy gel such as yogurt shows a continuous phase of milk proteins forming a network and aqueous region where the sugars and starch are distributed. Macromolecules of starch are involved in the reinforcement of the protein network. The presence of this network may explain in part the decrease in the flavor release in kinetic studies. It is also known that the effect of increasing the amount of thickeners inhibits the release of aroma compounds (*1*, *2*, *14*, *15*).

In the present study, the values of retention were obtained from coefficients of partition at the thermodynamic equilibrium between the gel phase and the vapor phase. Only the molecular interactions should be thus considered. The nature of the aroma compounds and starch plays a role in the retention of aroma in starch-based matrices (*19*, *20*). The interactions between starch and volatiles are classified into two categories; the first is an inclusion complex, where the aroma compound becomes surrounded by the amylose helix through hydrophobic bonding, and the second and most probable mechanism for the volatile aroma retention in starch gels involves hydrogen bonding between the hydroxyl groups of starch and the aroma compounds (*4*). Moreover, it has been found that the interactions between the amylopectin in the starch and the aroma compounds in the sample should be considered (*21*).

Figure 2 shows the effect of pectin on the aroma release. The samples containing 0.04% of pectin presented a significant retention of overall aroma compounds in the matrix. Hence, the low concentration in pectin seemed to reduce the quantity of aroma compounds in the headspace, especially for ester
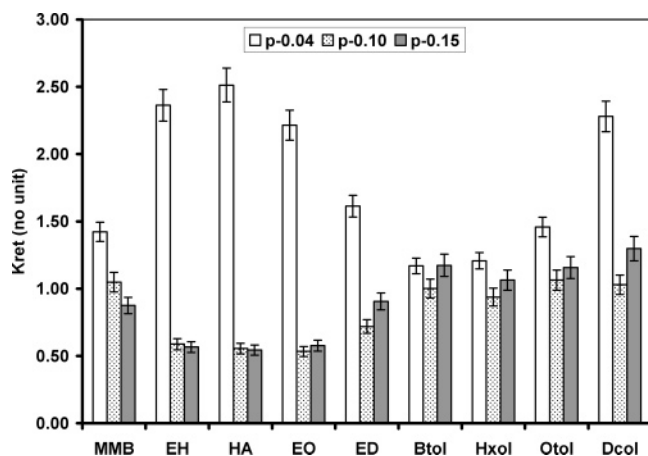
Figure 2. Flavor release of the aroma compounds from dairy gels containing different pectin concentrations (0.04, 0.10, and 0.15 g per 100 g in final product). MMB, methyl 2-methylbutanoate; EH, ethyl hexanoate; HA, hexyl acetate; EO, ethyl octanoate; ED, ethyl decanoate; Btol, butanol; Hxol, hexanol; Otol, octanol; Dcol, decanol. Error bars correspond to the 95% confidence intervals.
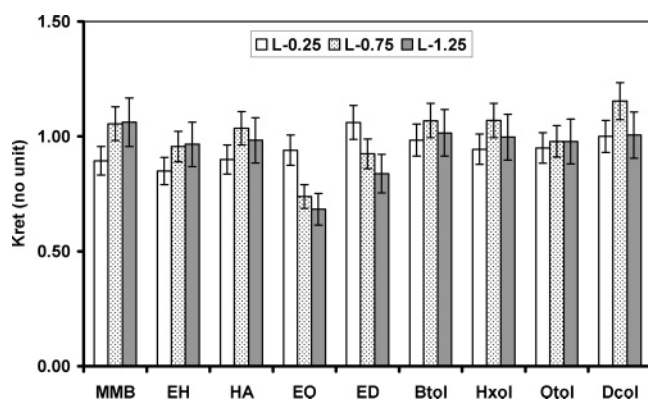

Figure 3. Flavor release of the aroma compounds from dairy gels containing different locust bean gum concentrations (0.25, 0.75, and 1.25 g per 100 g in final product). MMB, methyl 2-methylbutanoate; EH, ethyl hexanoate; HA, hexyl acetate; EO, ethyl octanoate; ED, ethyl decanoate; Btol, butanol; Hxol, hexanol; Otol, octanol; Dcol, decanol. Error bars correspond to the 95% confidence intervals.

molecules. However, for an increase in pectin concentration from 0.04 and 0.15%, a significant increase in aroma release was observed. For alcohols, the impact of the increase in the pectin concentration was not significant.

This result is surprising compared to the data on the behavior of pectin in model solution with volatile compounds. Thus, several authors showed that pectin induces a reduction in the flavor release with an increase in concentration (*18, 22, 23*). Our result was reproduced five times. For pectin concentrations of 0.1 and 0.15%, the peak areas are very close and not significantly different, showing the validity of the data. The distribution of pectin in the stirred dairy gel was proposed by Tromp et al.: only 20% of molecules of pectin interact with the protein network, and the other 80% of the pectin molecules are in the aqueous phase and do not interact with the casein network (*24*). The great increase in concentration of pectin in the aqueous phase could involve an effect of salting out for the aroma compounds, which are also in this aqueous phase. More investigation will be necessary to confirm this hypothesis.

Figure 3 shows the effect of locust bean gum on the aroma release. The greatest aroma release was obtained when there was a LBG concentration of 0.25% in a stirred gel. The increase
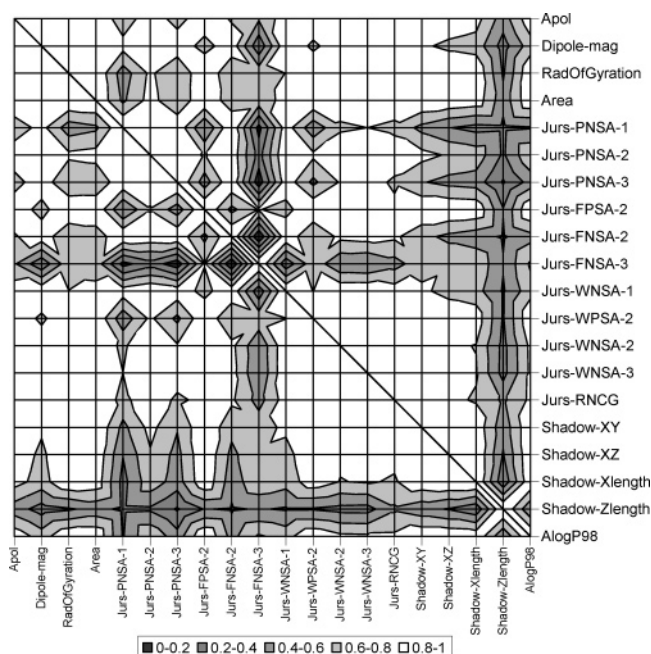

Figure 4. Graphical representation of correlation matrix of the 20 descriptors selected (absolute values). Abbreviations of descriptors are presented in **Table 3**.

in concentration of LBG from 0.75 to 1.25% showed little difference in the flavor release. The quantities of methyl 2-methylbutyrate, ethyl hexanoate, and hexyl acetate in the headspace showed slight increases in aroma retention for an increase in LBG concentration. On the contrary the quantity of ethyl octanoate and ethyl decanoate showed an increase in flavor release. No significant difference was observed for the alcohols. Thus, for most of the aroma compounds studied, the impact of LGB on flavor release was weak.

Effect of Aroma Compounds. Results from the headspace analysis on the thickened dairy gels have shown us so far that for an increase in the concentration in the thickeners there was a decrease in the flavor release with starch or an increase with pectin, and no major effect with LBG. However, we cannot go any further in explaining why or how this has happened. Therefore, by using a QSPR approach available in the Cerius[2] package, we have attempted to show a relationship in the interactions between the aroma compounds and the thickeners in the matrix by correlating them to structural or property descriptors of the aroma molecules. The QSPR study is intended to represent an experimental response (denoted ER) in a simple mathematical relationship, the QSPR equation: $ER = f(p_1, p_2, p_3, ..., p_n)$, where ER is in the present work of the logarithm of coefficient partition (log K_{ret}). Starting from 58 molecular indices, 20 descriptors were selected, which present at least a dependable correlation with the partition coefficient values, but the descriptors selected were not to be perfectly correlated together. The values and definitions of the 20 descriptors are reported in **Tables 2** and **3**. The correlation matrix of the 20 descriptors is graphically reported in **Figure 4**. The spatial descriptors were correctly correlated together (correlation coefficient at 0.99): area, shadow *XY*, shadow *XZ*, and radius of gyration. The hydrophobic constant AlogP98 was highly correlated with the above group. Some Jurs descriptions were correlated together with a high value of the correlation coefficient. High values of coefficient of correlation were obtained also between the Jurs WPSA 2, Jurs FPSA 2, and the group area, shadow *XY*, and radius of gyration.

Effect of Thickeners on Flavor Release

J. Agric. Food Chem., Vol. 55, No. 12, 2007 **4839**

Table 3. Definition of the Descriptors Selected for the Study

descriptor	definition
AlogP98	calculated octanol/water partition coefficient (Ghose and Crippen AlogP, parameters 1998)
Apol	polarizability
Area	van der Waals area of the molecule (molecular surface area)
dipole-mag	dipole moment; indicates strength and orientation of a molecule in an electrostatic field
Jurs FNSA 2	fractional charged partial surface area: total charge weighted negative surface area: partial negative solvent-accessible surface area multiplied by the total negative charge divided by the total molecular solvent-accessible surface area
Jurs FNSA 3	fractional negative charged partial surface areas: atomic charge weighted negative surface area: sum of the product of solvent-accessible surface area × partial charge for all negatively charged atoms
Jurs FPSA 2	fractional charged partial surface area: total charge weighted positive surface area (partial positive solvent-accessible surface area multiplied by the total positive charge) divided by the total molecular solvent-accessible surface area
Jurs PNSA 1	partial negative surface area: sum of the solvent-accessible surface areas of all negatively charged atoms
Jurs PNSA 2	total charge weighted negative surface area: partial negative solvent-accessible surface area multiplied by the total negative charge
Jurs PNSA 3	atomic charge weighted negative surface area: sum of the product of solvent-accessible surface area × partial charge for all negatively charged atoms
Jurs RNCG	relative negative charge: charge of the most negative atom divided by the total negative charge
Jurs WNSA 1	surface-weighted charged partial negative surface area: Jurs-PNSA-1 multiplied by the total molecular solvent-accessible area and divided by 1000
Jurs WNSA 2	surface-weighted charged partial negative surface area: Jurs PNSA-2 multiplied by the total molecular solvent-accessible area and divided by 1000
Jurs WNSA 3	surface-weighted charged partial negative surface area: Jurs PNSA-3 (sum of the product of solvent-accessible surface area × partial charge of all negatively charged atoms) multiplied by the total molecular solvent accessible area and divided by 1000
Jurs WPSA 2	surface-weighted charged partial positive surface area: total charge weighted positive surface area: partial positive solvent-accessible surface area multiplied by the total positive charge multiplied by the total molecular solvent-accessible area and divided by 1000
rad gyration	radius of gyration
Shadow *X* length	length of molecule about *X* axis
Shadow *XY*	area of the molecule in the *XY* plane
Shadow *XZ*	area of the molecule in the *XZ* plane
Shadow *Z* length	length of molecule about *Z* axis

Table 4. Correlation Matrix of log K_{ret} Values for Yogurts Containing Different Thickener Concentrations (in Grams per 100 g in Final Product)

	starch 0.1%	starch 0.4%	starch 0.6%	pectin 0.04%	pectin 0.1%	pectin 0.15%
starch 0.1%	1					
starch 0.4%	0.63	1				
starch 0.6%	0.32	0.44	1			
pectin 0.04%	**0.61**	0.32	**0.82**	1		
pectin 0.1%	−0.56	0.15	−0.34	−0.71	1	
pectin 0.15%	−0.36	0.25	−0.47	−0.65	**0.92**	1

Using statistical tools available in the QSAR$^+$ module, the correlation matrix of the log K_{ret} values obtained with the different amounts of starch and pectin was calculated (**Table 4**). Retentions observed by increasing the amount of starch were positively correlated together, but there was a strongly decreasing correlation from 0.4 to 0.6% and this was also weak between 0.1 and 0.6%. Intriguingly, there was a good correlation between the retention of 0.6% starch and 0.04% pectin. On the other hand, the retention with 0.04% pectin was negatively correlated with the retention at the other concentrations; this showed that dramatic changes in the involved interactions should be supposed.

Involved Descriptors Significance. Most of the 20 selected descriptors were correlated with $K_{ret(Starch0.1\%)}$. Only Shadow *Z* length did not present correlation ($R^2 = 0.14$; $F_{test} = 1.09$).

The only one negatively correlated descriptor was Jurs RNCG, whereas Jurs PNSA 2 and FNSA 2, Jurs WNSA 2, and Jurs WNSA 3, assuming negative values, were in absolute values positively correlated with retention in gel containing starch 0.1%. All others (Apol, dipole-mag, area, Jurs FPSA 2, Jurs WNSA

1, Jurs WPSA 2, Shadow *XY*, Shadow *X*, Shadow *X* length, and AlogP98) were positively correlated.

Apol, area, Shadow *XZ*, Shadow *X* length, and AlogP98 are related to the shape of the molecule and its capacity to involve van der Waals apolar interactions (London dispersion forces); this means that the higher the surface of a molecule in the plane, the higher these interactions.

The Jurs descriptors are charged partial area descriptors that encode the spatial charges and surface distribution (*25*). Jurs RNCG encodes electronic properties of charges repartitioned on the molecule. It is equal to relative negative charge and more precisely to the charge of the most negative atom divided by the total negative charges. Its value increases with polarity of the molecule, and this effect appeared to be unfavorable on the retention by the matrix.

All other Jurs descriptors involve charged surface areas and are in fact correlated with area and Apol. From all of these observations, it appeared that retention in diary gel containing 0.1% starch was favored by hydrophobic interactions, and the existence of strong polarity disfavored retention in this matrix. However, the role of some negative surface Jurs descriptors pointed out the possible establishment of the three types of van der Waals interactions: dispersion forces (London) and dipole−dipole interactions (Keesom and Debye).

For both higher amounts of starch (0.4 and 0.6%) and pectin (0.04, 0.1, and 0.15%), all of the previous correlations were severely disturbed; no reliable correlation arose between the descriptors and log K_{ret} values.

Interestingly, the retention of the smallest and most hydrophobic alcohols weakly depended on the nature and amounts of thickener used. In addition, methyl 2-methylbutanoate exhibited the same retention tendency as the alcohols, and the observed retention for the most hydrophobic ester (ethyl
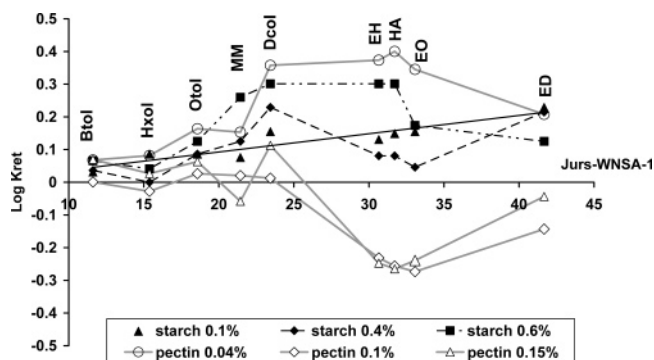
4840 *J. Agric. Food Chem.,* Vol. 55, No. 12, 2007

Lubbers et al.

Figure 5. Variations of relationships between Jurs WNSA 1 and Log K_{ret} values according to the amounts of thickeners. Btol, butanol; Hxol, hexanol; Otol, octanol; MMB, methyl 2-methylbutanoate; Dcol, decanol; EH, ethyl hexanoate; HA, hexyl acetate; EO, ethyl octanoate; ED, ethyl decanoate.

decanoate) was less affected by the nature of thickener than the other esters. Thus, it is strongly suggested that retention/release properties were not determined by the chemical classes, but by a set of chemical properties.

Graphical analysis of plots log K_{ret} versus descriptor pointed out the descriptor Jurs WNSA 1 as a particular interest for qualitative interpretation (**Figure 5**). It appeared that two subsets could be distinguished from the training set, according to their values. The Jurs WNSA 1 values highlighted the existence of two groups: (i) ethyl hexanoate, hexyl acetate, ethyl octoanoate, and ethyl decanoate, which corresponded to the higher absolute values; and (ii) the alcohols butanol, hexanol, octanol, and decanol and the ester methyl 2-methylbutanoate, which correspond to lower absolute values. This approach is only qualitative, but allowed us to appreciate some common behavior for each group showing relationships between Jurs WNSA 1 and K_{ret} values according to the amounts of thickeners used.

As previously mentioned, Jurs descriptors encode charge distribution at the surface of the molecule. Negatively charged areas were similar for the same chemical class (alcohols, one oxygen; and esters, two oxygens). Then in the same chemical class, lower values were related to the smallest molecules, whereas higher values were related to the biggest molecules. Taking into account this status, the smaller values should be associated with low hydrophobicity and, inversely, higher values to high hydrophobicity. That was in good accordance with correlation observed between log $K_{ret(Starch0.1\%)}$ and Jurs WNSA 1 values. Thus in this case, hydrophobic interactions between macromolecules of starch and aroma compounds were evoked. The increase in the amount of starch seemed to disrupt this "hydrophobic effect" in favor of other natures of interactions. The presence of at least two interaction types inside the matrix, involving several different and competitive interactions between the aroma compounds and dairy gel and hydrophobic and polar binding, was suggested. These two antagonistic interactions would be compensated for both the most hydrophilic and the most hydrophobic compounds, whereas, on the one hand, for the retention (starch 0.4 and 0.6%, pectin 0.04%) they would act as synergy and, on the other hand, for the release (pectin 0.1 and 0.15%) of the compounds having intermediate Jurs WNSA 1 values.

To elucidate the impact of different thickeners on flavor release, they were used separately in a model dairy gel. With 0.1% starch, the retention was explained by hydrophobic interactions, but the existence of strong polarity disfavored the retention. With the highest concentration of starch this hydrophobic effect was disrupted, and the presence of several different

and competitive interactions, hydrophobic and polar binding, should be evoked. The increase in pectin concentration caused an increase in the flavor release, but the nature of interactions involved will have to be specified.

The QSPR study showed an intricate role is due to adding both starch at concentrations higher than 0.1% and pectin and put forward the power of negatively charged surface areas. The present QSPR approach constituted a promising tool for characterizing the interactions involved in complex food matrices. To be able to propose a more accurate hypothesis, experiments will soon be performed to obtain true partition coefficient values involving a larger range of chemical structures.

LITERATURE CITED

(1) Forss, D. A. Role of lipids in flavours. *J. Agric. Food Chem.* **1969**, *17*, 681−685.
(2) Wendin, K.; Solheim, R.; Alimere, T.; Johansson, L. Flavour and texture in sourmilk affected by thickeners and fat content. *Food Qual. Pref.* **1997**, *8* (4), 281−291.
(3) Ünal, B.; Metin, S.; Isikli, N. Use of response surface methodolgy to describe the combined effect of storage time, locust bean gum and dry matter of milk on the physical properties of low-fat set yoghurt. *Int. Dairy J.* **2003**, *13* (11), 909−916.
(4) Boland, A. B.; Buhr, K.; Giannouli, P.; van Ruth, S. M. Influence of gelatin, starch, pectin and artificial saliva on the release of 11 flavour compounds from model gel systems. *Food Chem.* **2004**, *86* (3), 401−411.
(5) Decourcelle, N.; Lubbers, S.; Vallet, N.; Rondeau, P.; Guichard, E. Effect of thickeners and sweeteners on the release of blended aroma compounds in fat-free stirred yoghurt during shear conditions. *Int. Dairy J.* **2004**, *14* (9), 783−789.
(6) Baines, Z. V.; Morris, E. R. Flavour/taste perception in thickened systems: the effect of guar gum above and below c. *Food Hydrocolloids* **1987**, *1* (3), 197−205.
(7) Pangborn, R. M.; Misaghi, Gibbs, Z.; Tassan, C. Effect of hydrocolloids on apparent viscosity and sensory properties of selected beverages. *J. Texture Stud.* **1978**, *9*, 416−436.
(8) Pangborn, R. M.; Szczesniak, A. S. Effect of hydrocolloids and viscosity on flavor and odor intensities of aromatic flavor compounds. *J. Texture Stud.* **1974**, *4*, 467−482.
(9) Buettner, A.; Schieberle, P. Influence of mastication on the concentrations of aroma volatiles—some aspects of flavor release and flavor perception. *Food Chem.* **2000**, *71*, 347−354.
(10) Mei, J. B.; Reineccius, G. A.; Knighton, W. B.; Grimsrud, E. P. Influence of strawberry yogurt composition on aroma release. *J. Agric. Food Chem.* **2004**, *52*, 6267−6270.
(11) Nongonierma, A. B.; Springett, M.; Le Quere, J. L.; Cayot, P.; Voilley, A. Flavour release at gas/matrix interfaces of stirred yoghurt models. *Int. Dairy J.* **2006**, *16* (2), 102−110.
(12) Paci Kora, E.; Souchon, I.; Latrille, E.; Martin, N.; Marin, M. Composition rather than viscosity modifies the aroma compound retention of flavored stirred yogurt. *J. Agric. Food Chem.* **2004**, *52*, 3048−3056.
(13) Solms, J.; Guggenbuehl, B. Physical aspects of flavor applications in food systems. In *Flavour Science and Technology*; Wiley: New York, 1991; pp 319−335.
(14) Roberts, D. D.; Elmore, J. S.; Langley, K. R.; Bakker, J. The effect of viscosity on dynamic flavour release. In *Bioflavour 95*; Etievant, P., Schreier, P., Eds.; INRA: Dijon, France, 1995; pp 35−38.
(15) De Roos, K. Effect of texture and microstructure on flavor retention and release. *Int. Dairy J.* **2003**, *13* (8), 593−605.
(16) Lubbers, S. Texture−aroma interactions. In *Flavour in Food*; Voilley, A., Etiévant, P., Eds.; Woodhead Publishing and CRC Press: Cambridge, U.K., 2006; Vol. Part 3, pp 327−344.

Effect of Thickeners on Flavor Release

J. Agric. Food Chem., Vol. 55, No. 12, 2007 **4841**

(17) Chana, A.; Tromelin, A.; Andriot, I.; Guichard, E. Flavor release from iota-carrageenan matrix: a quantitative structure−property relationships approach. *J. Agric. Food Chem.* **2006**, *54*, 3679−3685.

(18) Lubbers, S.; Decourcelle, N.; Vallet, N.; Guichard, E. Flavor release and rheology behavior of strawberry fatfree stirred yogurt during storage. *J. Agric. Food Chem.* **2004**, *52*, 3077−3082.

(19) Cayot, N.; Taisant, C.; Arvisenet, G.; Meunier, J. M.; Voilley, A. Flavouring ratios and partition coefficients for isoamyl acetate in various starch-based food matrices. *Sci. Aliment.* **2000**, *20* (6), 561−574.

(20) Arvisenet, G.; Le Bail, P.; Voilley, A.; Cayot, N. Influence of physicochemical interactions between amylose and aroma compounds on the retention of aroma in food-like matrices. *J. Agric. Food Chem.* **2002**, *50*, 7088−7093.

(21) Arvisenet, G.; Voilley, A.; Cayot, N. Retention of aroma compounds in starch matrices: competitions between aroma compounds towerd amylose and amylopectin. *J. Agric. Food Chem.* **2002**, *50*, 7345−7349.

(22) Hansson, A.; Leufven, A.; van Ruth, S. M. The influence of composition and storage on aroma headspace concentration of pectin gels. In *Proceedings of the 10th Weurman Flavour Research Symposium*; Le Quere, J. P., Etievant, P. X., Eds.; Intercept: Paris, France, 2002; pp 95−98.

(23) Rega, B.; Guichard, E.; Voilley, A. Flavour release from pectin gels: effects of texture, molecular interactions and aroma compounds diffusion. *Sci. Aliment.* **2002**, *22*, 235−248.

(24) Tromp, R. H.; de Kruif, C. G.; van Eijk, M.; Rolin, C. On the mechanism of stabilisation of acidified milk drinks by pectin. *Food Hydrocolloids* **2004**, *18* (4), 565−572.

(25) Stanton, D. T.; Jurs, P. C. Development and use of charged partial surface area structural descriptors in computer-assisted quantitative structure−property relationship studies. *Anal. Chem.* **1990**, *62*, 2323−2329.