

# QUANTITATIVE STRUCTURE-PROPERTY RELATIONSHIPS APPROACH OF AROMA COMPOUNDS BEHAVIOUR IN POLYSACCHARIDE GELS

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## Abstract

Pectin and carrageenan are common used thickeners in fat free foods. The aim of this work was to study separately and to compare their respective effects on the aroma release, in order to investigate the nature of involved interactions. In this way, we studied the influence of the chemical structure of 13 aroma compounds on retention/release equilibrium between vapour phase and gels using QSPR tools. Six descriptors are involved in the best obtained QSPR equations, and three of them appeared to play a critical role in the behaviour of aroma compound. Our results put forward the role of polar effects on the retention of odorant molecules in both *iota*-carrageenan and pectin gels, indicating that *iota*-carrageenan polymer do not change the interaction between aroma compounds and water molecules, whereas pectin causes slightly different interaction involving positive charged surfaces areas in the retention phenomenon.

## Introduction

The demand for fat free food products is constantly increasing, but the reduction of fat content in a food system induces changes in flavour release (1), flavour perception, appearance, mouth-feel, and structure (2). Fat and flavour are important factors in food acceptance and can affect the partitioning of hydrophobic flavour molecules (3). In order to retain the properties of a product when the fat is removed, fat-substitutes as starch, pectin and carrageenans are used. The retention/release equilibrium has been studied most frequently for inhomogeneous products (4; 5), than for thickeners separately (6). Pectin and carrageenan are common used thickeners, and the aim of this work was to study and to compare their respective effects on aroma release. In this way, the amount of 13 aroma compounds released in the headspace was quantified at equilibrium above pure water, *iota*-carrageenan and pectin gels. To evaluate the influence of the chemical structure of aroma compounds on retention/release equilibrium between vapour phase and gels, we used QSPR approach. QSPR methods attempt to find relationships between the properties of molecules and an experimental response; the assumption is that changes in molecular properties elicit different responses. The QSPR study is intended to represent a physico-chemical property into a simple mathematical relationship, the QSPR equation:  $ER = f(p_1, p_2, p_3, \dots, p_n)$ .

Our present aim consists first to propose a qualitative interpretation in order to investigate the nature of involved interactions by identifying some relevant structural properties related to the retention.

## Experimental

All the flavour compounds used were obtained from Sigma-Aldrich (Saint Quentin Fallavier, France). Purity of flavour compounds was evaluated by GC-FID (> 95 %). *iota*-Carrageenan was kindly supplied by Rhodia Food (Aubervilliers, France). The low-methoxyl and low-amidated pectin 102-AS was purchased from CP Kelco (Denmark). The final aromatized gels are respectively composed of (i) 1 % *iota*-carrageenan, 0.3 % sodium chloride and 15  $\mu\text{L L}^{-1}$  for all aroma compounds in water and (ii) 0.36% pectin and 16  $\mu\text{L L}^{-1}$  for all aroma compounds in water.

The partition coefficient  $PC = \frac{[\text{flavour compound}]_{\text{matrix}}}{[\text{flavour compound}]_{\text{vapour}}}$  was determined by PRV method, based on the influence of the volume of the sample on the concentration of volatile in the headspace (7). They established the following Eq. (1):

$$\frac{1}{A} = \frac{1}{f_i \times C_M} \times (PC + \beta) \quad \text{Eq. (1)}$$

where  $A$  is the chromatographic peak area at equilibrium,  $f_i$  is the proportional factor,  $C_M$  is the initial sample concentration in the matrix and  $\beta$  is the ratio  $V_{\text{vapour}}/V_{\text{matrix}}$ . High phase ratio  $\beta$  were used, from 207 to 3.16; each matrix was analysed in triplicate. Headspace analysis was performed after equilibration at 30 °C for at least 2 h 30 on a Trace (Thermoelectron, France) gas chromatograph using a flame ionization detector (FID), and the data were processed using software developed in our laboratory (8; 9).

The retention constant ( $K_{\text{ret}}$ ) by the matrix is defined with the following Eq. (2) (10):

$$K_{\text{ret}} = \frac{[\text{flavour compound}]_{\text{matrix}} / 1}{[\text{flavour compound}]_{\text{vapour}} \times R \times T / 1} = \frac{[\text{flavour compound}]_{\text{matrix}}}{[\text{flavour compound}]_{\text{vapour}} \times RT} \quad \text{Eq. (2)}$$

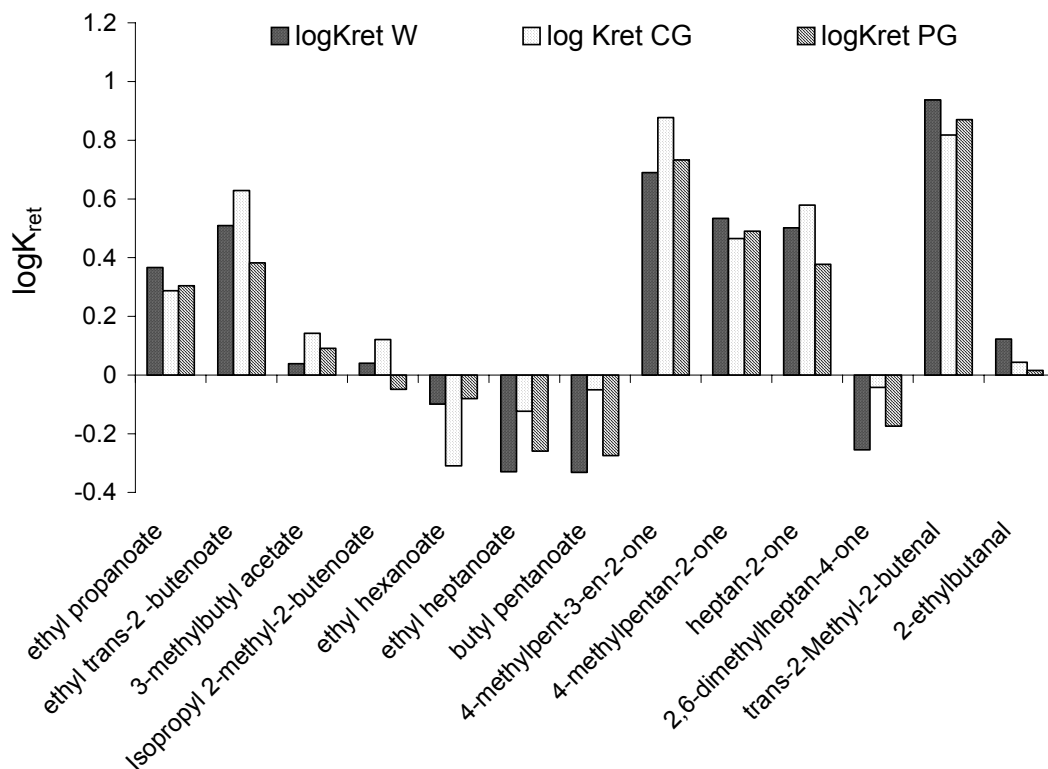
where  $R$  is the perfect gas constant and  $T$  the temperature (K), and  $K_{\text{ret-water}}$ ,  $K_{\text{ret-GC}}$  and  $K_{\text{ret-GP}}$  express the retention constant of flavour compounds between water solution, *iota*-carrageenan and pectin gels respectively;  $\log K_{\text{ret}}$  values were used for regression calculations.

The three-dimensional molecular structures of the 13 aroma compounds were calculated using DS Viewer Pro 6.0 (Accelrys Inc.). The structures were then analysed with Cerius2 software (version 4.10; Accelrys Inc., San Diego, 2005) running on a Silicon Graphics workstation (SGI-O2). The equation generation was performed by GA statistical method available in Cerius2 package (10). Reliability and significance of the equations was estimated by  $r^2$  CV- $r^2$  and Bootstrap- $r^2$  values. For equations obtained with 3 independent variables, validation was carried out by Y-randomization at 95% confidence level (19 randomized trials) and by means of a leave-one-out method.

## Results and Discussion

The values of retention constant obtained for the different flavour compounds are reported in (Figure 3). Globally the retention constants are quite similar for water (W), *iota*-carrageenan (CG) and pectin (PG) gels. We found that the most retained compounds are aldehydes and ketones, and the most released in vapour phase are esters. However, ethyl *trans*-2-butenoate is more retained than 2-ethylbutanal,

showing that the whole structure has a greater importance than only the chemical function.



**Figure 3.**  $\log K_{ret}$  values for the 13 aroma compounds.

Starting from descriptors belonging to the classical groups of descriptors (conformational, electronic, spatial, structural, thermodynamic and topological descriptors) and on the basis of the highest correlation with the property and the lowest between descriptors, we retained 10 descriptors to be used in the equation generation. All reported equations are generated without constant adding and the best obtained equations are reported in Table 2.

**Table 2.** Best obtained equations with 2 factors eqs. 3 to 5 and with 3 factors eqs. 6 to 8.

Eq	logK <sub>ret</sub>	Factor 1	Factor 2	Factor 3	r <sup>2</sup>	F	CV-r <sup>2</sup>	BS-r <sup>2</sup>
3	water	+ 0.015881 Jurs-WNSA-2	+ 0.01691 Jurs-PNSA-1		0.88	77	0.82	0.88
4	CG	+ 0.01285 Jurs-WNSA-2	+ 0.01523 Jurs-PNSA-1		0.74	29	0.67	0.79
5	PG	+ 3.80674 Jurs-RPSA	- 0.587947 CHI-V-3_P		0.87	71	0.76	0.87
6	water	+ 0.017198 Jurs-PNSA-1	- 0.192219 CHI-V-3_P	+ 0.012865 Jurs-WNSA-2	0.89	41	0.75	0.89
7	CG	+ 0.033951 Jurs-PNSA-1	+ 12.1295 Jurs-FNSA-3	+ 0.016598 Jurs-WNSA-2	0.81	22	0.67	0.82
8	PG	- 0.127817 Jurs-FPSA-2	- 0.367312 CHI-V-3_P	+ 3.94632 Jurs-RPSA	0.85	36	0.56	0.896

Meaning of the descriptors used in equations are reported in the Handbook of Molecular Descriptors (11). We found that Jurs-PNSA-1 and Jurs-WNSA-2 are involved in the two-variables equations obtained for both  $\log K_{\text{ret}}\text{-W}$  and  $\log K_{\text{ret}}\text{-CG}$ . For Jurs-WNSA-2 value, the total solvent accessible surface area value weights the partial negative surface area; Jurs-WNSA-2 values are minimum for small molecules with small negative charged surface area (small aldehydes), and maximum for large molecules with large negative surface areas (large esters). In the three-variable equations, CHI-V-3\_P and Jurs-FNSA-3 descriptors are added for  $\log K_{\text{ret}}\text{ W}$  and  $\log K_{\text{ret}}\text{ CG}$  respectively. The use of Jurs-FNSA-3 in  $\log K_{\text{ret}}\text{-CG}$  equation should suggest that interactions with carrageenan gel are more sensible to negative charges.

The three descriptors involved in  $\log K_{\text{ret}}\text{-PG}$  3 variables equation are Jurs-RPSA, CHI-V-3\_P and Jurs-FPSA-2. The best equation obtained with 2 variables involves Jurs-RPSA, CHI-V-3\_P. Jurs-RPSA involves solvent-accessible polar surfaces areas of atoms with absolute value of partial charges greater or equal to 0.2, which represents both negatively and positively charged surfaces areas. Sign of Jurs-RPSA is positive in the  $\log K_{\text{ret}}\text{-PG}$  equation, that suggest that both negatively and positively charged surfaces areas are involved in the retention interaction. The sign negative of terms CHI-V-3\_P and Jurs-FPSA-2 in the 3 variable equations allows modulating the attractive effect by taking into account the repulsive effect due to carbon chain.

To conclude, we observed that *iota*-carrageenan polymer do not change the interaction of aroma compounds with water molecules, whereas pectin causes slightly different interaction involving positive charged surfaces areas in the retention phenomenon. Our results highlight the role of polar effects on the retention of odorant molecules and put forward that retention/release properties are not determined by the chemical classes, but by some chemical properties together. In this way, QSPR approach constitutes a promising tool for the characterisation of interactions involved in complex food matrices.

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