

## Changes in Macroscopic Viscosity Do Not Affect the Release of Aroma Aldehydes from a Pectinaceous Food Model System of Low Sucrose Content

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The effects of pectin and viscosity on the release of a systematic series of aldehydes (alkanals, methyl-alkanals, alkenals, and alkandienals) were studied in a food model system of low sucrose content (10% w/w). The viscosity was varied by adding different amounts of  $\text{Ca}^{2+}$  (0, 13.5, and 27 mg/g pectin) to the model system of constant pectin concentration (0.4% w/w). Air–liquid partition coefficients,  $K$  (37 °C), of the aroma compounds were determined in aqueous and pectin-thickened solutions. Diffusivities of the aroma compounds in water and three pectin-thickened solutions were estimated from release rate constants that were obtained via timed collection of volatiles in the gas phase and quantifications by dynamic headspace–gas chromatography. The partition coefficients increased as the carbon chain increased within each homologous series. Overall, no significant difference was found between partition coefficients of aldehydes in water and in pectin solutions except for 2-methyl-propanal and butanal that showed higher  $K$  values when pectin was present. Furthermore, the diffusional properties of the model system with a constant pectin level (0.4% w/w) remained constant when the viscosity was increased from 0.001 to 150 Pa s. It was concluded that neither pectin nor alterations in macroscopic viscosity as such influenced the release of aldehydes from the pectin-thickened food model system.

**KEYWORDS:** Aroma; diffusion; hydrocolloids; partition coefficients; pectin; release rate; thickeners; viscosity; volatiles

### INTRODUCTION

Because of their viscosity-increasing and gel-forming properties, hydrocolloids have become widely used in the food industry as thickeners, stabilizers, or fat substitutes. Several reports have documented that perceived flavor intensity and sweetness decrease with increasing viscosity, i.e., with increasing hydrocolloid concentration in a food system (1–6). The extents of decrease in flavor perception and sweetness have been shown to differ depending on the physicochemical properties and the type of hydrocolloid being employed (7, 8). These effects of hydrocolloids on flavor perception have been interpreted to be due to binding of flavor molecules to the polymers and/or caused by diffusion retarding effects of the hydrocolloids resulting from their formation of a three-dimensional structural network (1, 9–12). Such mechanisms have also been suggested to apply for instrumentally measured flavor release dynamics in different hydrocolloid food model systems, including pectin food model systems (11, 13–15). However, the available hypotheses of viscosity-induced hindrance of molecular migration cannot properly explain why (i) the dynamic flavor release rate of less volatile flavor compounds tends to be less affected by increases

in viscosity than highly volatile compounds (11), (ii) changes in viscosity in the order of ~100-fold only decrease the reported diffusion coefficients of the aroma compounds by ~2–3-fold (13, 16), and (iii) sucrose addition tends to significantly diminish the experimentally measured diffusion coefficients (13).

To better understand the basics of how hydrocolloid addition affects the dynamics of flavor release, a more fundamental, thermodynamic approach appears to be required and the specific effects of molecular diffusion vs the effects of convective or Eddy diffusion must be clarified. Also, to evaluate whether differences exist among different types of aldehydes, a systematic series of aroma compounds needs to be tested. Furthermore, to distinguish between the influences of hydrocolloid polymer concentration vs viscosity increase effects, an ideal system for testing is one where the polymer concentration remains constant while the viscosity changes. Such a system employing a particular,  $\text{Ca}^{2+}$  sensitive, high methoxylated pectin (HMP) was designed for the work to be reported here.

Pectin has become one of the most widely used hydrocolloid thickening and gelling agents. Besides their typical usage to form gels in acidic media of high soluble solids content HMPs are applied in a broad range of products with low sucrose content (<10%), where they act as viscosity enhancers and stabilizers of ketchup, ice cream, yogurt drinks, and other acidified milk

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**Table 1.** Literature Values of Volatile Compounds: Molecular Weights ( $M_w$ ), Boiling Points ( $B_p$ ), Hydrophobic Fragmental Constants ( $\log P$ ), and Odor Descriptors

| aldehyde                       | structure formula  | $M_w$<br>(g/mol) | $B_p$<br>(°C) | $\log P^a$ | odor descriptors <sup>b,c</sup> |
|--------------------------------|--|------------------|---------------|------------|---------------------------------|
| I. branched                    |  |                  |               |            |                                 |
| 2-methyl-propanal              | CH <sub>3</sub> -CHCH <sub>3</sub> -COH  | 72               | 65            | 0.82       | green, pungent                  |
| 3-methyl-butanal               | CH <sub>3</sub> -CHCH <sub>3</sub> -CH <sub>2</sub> -COH                           | 86               | 93            | 1.34       | herbaceous, green, malty        |
| 2-methyl-butanal               | CH <sub>3</sub> -CH <sub>2</sub> -CHCH <sub>3</sub> -COH                           | 86               | 93            | 1.34       | green, cocoa, and coffee        |
| 2-methyl-pentanal              | CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CHCH <sub>3</sub> -COH           | 100              | 117           | 1.86       |                                 |
| saturated                      |  |                  |               |            |                                 |
| butanal                        | CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>2</sub> -COH                              | 72               | 75            | 0.81       | green, pungent                  |
| pentanal                       | CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>3</sub> -COH                              | 86               | 103           | 1.29       | pungent, nutty                  |
| hexanal                        | CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>4</sub> -COH                              | 100              | 128           | 1.80       | grassy, leafy, tallowy          |
| heptanal                       | CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>5</sub> -COH                              | 114              | 153           | 2.32       | fatty, pungent                  |
| octanal                        | CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>6</sub> -COH                              | 128              | 171           | 2.86       | fatty                           |
| nonanal                        | CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>7</sub> -COH                              | 142              | 191           | 3.36       | fatty, fruity, citrus           |
| II. monounsaturated            |  |                  |               |            |                                 |
| ( <i>E</i> )-2-pentenal        | CH <sub>3</sub> -CH <sub>2</sub> -CH=CH-COH  | 84               | 99            | 0.88       | pungent, green, apple, orange   |
| ( <i>E</i> )-2-hexenal         | CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CH=CH-COH                        | 98               | 147           | 1.40       | green, leafy, apple             |
| ( <i>E</i> )-2-heptenal        | CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>3</sub> -CH=CH-COH                        | 112              | 166           | 1.92       | fatty, almond                   |
| ( <i>E</i> )-2-octenal         | CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>4</sub> -CH=CH-COH                        | 126              | ?             | 2.44       | green, fatty, nutty, honey      |
| ( <i>E</i> )-2-nonenal         | CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>5</sub> -CH=CH-COH                        | 140              | ?             | 2.96       | cucumber, tallowy               |
| III. diunsaturated             |  |                  |               |            |                                 |
| ( <i>E,E</i> )-2,4-hexadienal  | CH <sub>3</sub> -(CH=CH) <sub>2</sub> -COH   | 96               | 69            | 0.99       | fresh, green, floral, citrus    |
| ( <i>E,E</i> )-2,4-heptadienal | CH <sub>3</sub> -CH <sub>2</sub> -(CH=CH) <sub>2</sub> -COH                        | 110              | 85            | 1.51       | fatty                           |
| ( <i>E,E</i> )-2,4-octadienal  | CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>2</sub> -(CH=CH) <sub>2</sub> -COH        | 124              | ?             | 2.03       | fatty, green, sour              |
| ( <i>E,E</i> )-2,6-nonadienal  | CH <sub>3</sub> -CH <sub>2</sub> -CH=CH-(CH <sub>2</sub> ) <sub>2</sub> -CH=CH-COH | 138              | ?             | 2.55       | tallowy                         |
| ( <i>E,E</i> )-2,4-nonadienal  | CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>3</sub> -(CH=CH) <sub>2</sub> -COH        | 138              | ?             | 2.55       | fatty, floral                   |

<sup>a</sup> Calculated by the method of Rekker (36). <sup>b</sup> Ref 37. <sup>c</sup> Ref 38.

beverages (17, 18). HMPs were described as calcium sensitive pectins, which can gel in the presence of Ca<sup>2+</sup> without the addition of sucrose as long as blocks of deesterified pectin are present (19, 20). Therefore, such pectins are very useful for low fat or sugarless, acidic food products formulation (21).

The objective of this study was to clarify the influence of pectin and alterations in viscosity on the release of volatiles from pectin-thickened food systems at low sugar content. As already indicated above, a food model system was designed where the effect of viscosity was separated from the polymer concentration by inducing variations in viscosity by adding different levels of Ca<sup>2+</sup> to a system with constant HMP concentration (0.4% w/w). Low sucrose concentration was employed to avoid any confounding effects from a high sugar content, which creates conditions of low water activity and reduced interactions between pectin and water (13). To evaluate possible interactions and diffusion properties of aroma compounds in pectin-thickened viscous solutions, static headspace (SHS) at equilibrium and timed dynamic headspace (DHS) analyses were carried out. To specifically understand the influence of viscosity on molecular diffusion of aroma compounds and thus abolish Eddy diffusion effects, it was decided to avoid any mechanical treatment such as stirring of the pectin-thickened solutions. To investigate the impact of functional group, degree of unsaturation, and carbon chain length of the aroma compounds, a homologous series of saturated, methyl-branched, mono-, and diunsaturated aldehydes were selected for the study.

## MATERIALS AND METHODS

**Sample Preparation.** Three different stock solutions were prepared from 20 chemical compounds: (I) saturated and methyl-branched aldehydes (2-methyl-propanal, 2-methyl-butanal, 3-methyl-butanal, 2-methyl-pentanal, butanal, pentanal, hexanal, heptanal, octanal, and nonanal); (II) monounsaturated aldehydes ((*E*)-2-pentenal, (*E*)-2-hexenal, (*E*)-2-heptenal, (*E*)-2-octenal, and (*E*)-2-nonenal); and (III) diunsaturated

aldehydes ((*E,E*)-2,4-hexadienal, (*E,E*)-2,4-heptadienal, (*E,E*)-2,4-octadienal, (*E,E*)-2,4-nonadienal, and (*E,E*)-2,6-nonadienal), all obtained from Aldrich-Chemie (Steinheim, Germany). Their molecular weights, structural formulas, boiling points, hydrophobic fragmental constants, and odor descriptors are presented in **Table 1**. Saturated and methyl-branched aldehydes (I) were dissolved in ethanol at the concentration of 10 mg/g. Mono- (II) and diunsaturated aldehydes (III) were dissolved at 20 mg/g. Aliquots of each stock solution were further diluted in Milli-Q water to give a final flavor concentration of 20 µg/g in mixture I, and 40 µg/g in mixtures II and III. Diluted solutions were transferred into 22.3 mL gas chromatography (GC) vials for determination of partition coefficients by SHS-GC. Thickened solutions were prepared by using 0.4% (w/w) pectin (HM, sensitive to calcium Genu type H6, unstandardized, DM = 72, CPKelco, Denmark) and 10% (w/w) sucrose (Sigma-Aldrich Chemie). The mixture of pectin and sucrose was added to 90 °C Milli-Q water at pH 3.6. The viscosity of the solutions was varied by adding different levels (0.00, 0.02, and 0.04% w/w) of CaCl<sub>2</sub>·2H<sub>2</sub>O to the pectin-sucrose solution; this calcium addition level corresponded to a range of approximately 0–27 Ca<sup>2+</sup> mg/g pectin. For each group of aldehydes, the stock solution of aroma compounds was added to a preweighed quantity of the viscous solution such that the final concentration of aroma compounds was 20, 40, and 40 ppm for saturated, monounsaturated, and diunsaturated aldehydes mixtures, respectively.

In accordance with the principle behind the phase variation method (22), four different volumes (0.5, 1.0, 1.5, and 3 mL) of each thickened and flavored solution were transferred to the vials, and the vials were capped and analyzed by SHS-GC to determine partition coefficients.

**Methods of Analysis.** SHS-GC. Aromatized samples were preequilibrated at ambient temperature for 24 h prior to equilibration at 37 °C for 120 min; this equilibration time was used after verification that equilibration of the aroma compounds in both aqueous and pectin-thickened solutions was complete after 100 min. After equilibration, the headspace sample was automatically withdrawn using a Perkin-Elmer HS 40 XL autosampler and injected into a Perkin-Elmer XL gas chromatograph using injection times of 0.06, 0.12, and 0.2 min for the samples with mixtures of saturated, monounsaturated, and diunsaturated aldehydes, respectively. The gas chromatograph was equipped with a DB-5 column (J&W Sci., U.S.A.), 60 m length, 0.25 mm i.d.,

1.0  $\mu\text{m}$  film thickness, and a flame ionization detector (FID) heated at 300 °C. The oven temperature was programmed from 50 (1 min hold) to 275 °C at a rate of 20 °C/min. Liquid–vapor partition coefficients of the aroma compounds in water and thickened solutions were determined using a phase ratio variation method, which does not require the use of internal or external standards and is based on the determination of relationship between the reciprocal peak area and the phase ratio of the vial containing the sample solution (22). Five independent measurements were carried out for each thickened and aqueous system.

**DHS-GC.** For DHS analysis, the aroma compounds were isolated by transferring 5 g of aqueous or pectin-thickened solution to a 125 mL sample flask. The sampling flask was placed in a water bath at 37 °C, and the headspace above the solution was flushed with purified nitrogen gas (100 mL/min) for 15, 30, 60, 90, 120, 240, 360, 600, and 720 s. The released volatiles were collected on traps (Perkin-Elmer, CN, U.S.A.) packed with 225 mg of Tenax TA (Tenax Chrompack, Bergen op Zoom, The Netherlands). Volatiles were desorbed from Tenax by a thermal desorption (250 °C, 3 min)/cold trap (−30/250 °C) device (Perkin-Elmer ATD 400). Through a heated transfer line, compounds were directed and analyzed using a DB-5 column (J&W Sci.), 30 m length, 0.25 mm i.d., and 1.0  $\mu\text{m}$  film thickness, on a Hewlett-Packard Series II 5890 GC equipped with an FID heated at 275 °C. The oven temperature was held at 40 °C for 2 min and then programmed to 275 °C at a rate of 20 °C/min with a final hold of 5 min. For quantification of aroma compounds, six standard solutions of aroma compounds of known concentrations were injected and analyzed ( $n = 3$ ).

**Determination of Release Rate Constants.** Dynamics of the flavor release were revealed during the collection of aroma compounds over 720 s on nine Tenax traps. Release rate constants ( $k$ ) were calculated from the rate of adsorption on the Tenax traps by the method described by Roberts and Acree (23):

$$k = (d[A]/dt)_{\text{trap}}/[A_0]$$

where  $[A]$  = concentration of the volatile in liquid phase (mg/L),  $[A_0]$  = initial concentration of the volatile in liquid phase (mg/L), and  $t$  = time (min).

As the amounts of aroma compounds collected on the traps were negligible as compared to the amounts remaining in the liquid phase, the assumption was made that the concentration of aroma compounds in the liquid phase during the collection of the volatiles was equal to the initial concentration. The slopes of the graphs,  $(d[A]/dt)_{\text{trap}}$ , from plotting micrograms of flavor compound collected from the trap vs time, were then determined.

**Rheological Measurements.** Rheological behavior of thickened solutions was characterized by shear viscosity. The measurements were performed 24 h after preparation of thickened solutions by using a Stress Tech (Reologica, Sweden), a controlled stress rheometer with cone and plate geometry C40 4. Flow curves were recorded at 37 °C by increasing the stress from 0.05 to 12 Pa in 20 logarithmic steps. Measurement delay time was 20 s; integration time was 30 s.

**Statistical Analysis.** Analysis of variance was used to determine significant differences among the air–liquid partition coefficients and release rate constants. Significance was established at  $p < 0.05$ .

## RESULTS AND DISCUSSION

**Viscosity.** The recorded flow curves of the three pectin-thickened solutions and water showed pronounced differences in rheological behavior (Figure 1). The thinnest pectin solution containing no  $\text{Ca}^{2+}$  behaved as a Newtonian fluid within the range of applied stress, while the two solutions with added  $\text{Ca}^{2+}$  exhibited shear thinning behavior. As expected, water had the lowest viscosity. The high apparent viscosity of the thickest solution with 0.04%  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (27 mg/g pectin) at low applied stress indicated some formation of structured zones and incipient gel behavior. Because the previous study (24) showed that adding of  $\text{Ca}^{2+}$  to the solution above 27 mg/g pectin concentration did not enhance solution viscosity anymore, this

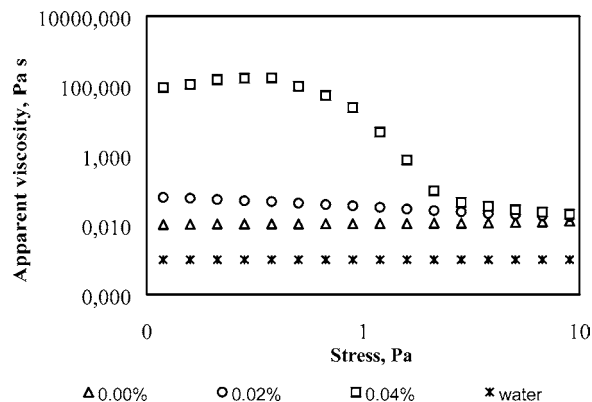


Figure 1. Viscosities curves of 0.4% pectin solutions with different amounts of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (% w/w) added.

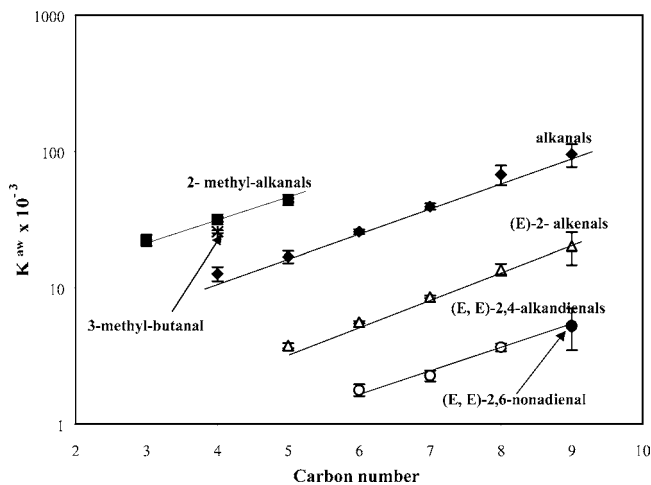


Figure 2. Average air–water partition coefficients,  $K_{aw}$ , of saturated, methyl branched, monounsaturated, and diunsaturated aldehydes homologous at 37 °C ( $n = 5$ ).

study was conducted with 27  $\text{Ca}^{2+}$  mg/g pectin as the upper  $\text{Ca}^{2+}$  concentration. Rega et al. (13) reported that mechanical spectra of HM pectin solutions showed a gel structure already at 0.1% pectin concentration. According to May (25), 27  $\text{Ca}^{2+}$  mg/g pectin is around that value of  $\text{Ca}^{2+}$  concentration when the gel strength reaches the maximum.

**Partitioning of Aldehydes in Different Media.** The measurement of equilibrium concentrations, thus partition coefficients, leads to the estimation of modifications of thermodynamic parameters and the presence of interactions between polymer and aroma compounds. Partitioning of 20 aldehydes with different degrees of unsaturation, different carbon chain length, and functional group was first measured in water and then in the three pectin-thickened solutions. The values of the air–water partition coefficient ( $K_{aw}$ ) measured in water increased with increasing carbon number in the molecules in each of the homologous series of aldehydes (Figure 2). This is in accordance with what was shown in the early work of Buttery et al. (26). The  $\text{C}_6$ – $\text{C}_9$  diunsaturated aldehydes (2,4 hexadienal–2,6 nonadienal) had the lowest  $K_{aw}$  values, ranging from  $1.8 \times 10^{-3}$  to  $5.3 \times 10^{-3}$ , while the short,  $\text{C}_3$ – $\text{C}_5$  methyl-branched alkanals had the highest  $K_{aw}$  values that were in the order of  $22.3 \times 10^{-3}$  to  $43.9 \times 10^{-3}$  among the compounds investigated (Figure 2). The volatility, i.e., the  $K_{aw}$ , gradually decreased with the introduction of each conjugated double bond to alkanals.

The methyl-branched alkanals are the most volatile series, and alkandienals are the least volatile. Respectively, there is a decrease of the logP value from alkanal to alkenal and then to



**Table 2.** Air–Liquid Partition Coefficients of Aldehydes ( $K \times 10^{-3}$ )<sup>a</sup> in Water and in 0.4% Pectin Thickened Solutions with Different Amounts (% w/w) of Added CaCl<sub>2</sub>·2H<sub>2</sub>O

| compound              | water             | 0.4% pectin solution    |                         |                         |
|-----------------------|-------------------|-------------------------|-------------------------|-------------------------|
|                       |                   | 0.00% CaCl <sub>2</sub> | 0.02% CaCl <sub>2</sub> | 0.04% CaCl <sub>2</sub> |
| 2-methyl-propanal     | 22.3 <sup>a</sup> | 28.5 <sup>ab</sup>      | 32.4 <sup>b</sup>       | 30.8 <sup>b</sup>       |
| 2-methyl-butanal      | 31.6 <sup>a</sup> | 32.0 <sup>a</sup>       | 32.9 <sup>a</sup>       | 30.7 <sup>a</sup>       |
| 3-methyl-butanal      | 25.7 <sup>a</sup> | 26.4 <sup>a</sup>       | 27.1 <sup>a</sup>       | 25.4 <sup>a</sup>       |
| 2-methyl-pentanal     | 43.9 <sup>a</sup> | 45.9 <sup>a</sup>       | 48.3 <sup>a</sup>       | 44.4 <sup>a</sup>       |
| butanal               | 12.7 <sup>a</sup> | 16.5 <sup>b</sup>       | 17.5 <sup>b</sup>       | 16.4 <sup>ab</sup>      |
| pentanal              | 16.9 <sup>a</sup> | 15.9 <sup>a</sup>       | 14.6 <sup>a</sup>       | 16.1 <sup>a</sup>       |
| hexanal               | 25.7 <sup>a</sup> | 26.4 <sup>a</sup>       | 27.4 <sup>a</sup>       | 24.9 <sup>a</sup>       |
| heptanal              | 39.4 <sup>a</sup> | 43.5 <sup>a</sup>       | 44.5 <sup>a</sup>       | 35.9 <sup>a</sup>       |
| octanal               | 67.5 <sup>a</sup> | 56.7 <sup>a</sup>       | 52.2 <sup>a</sup>       | 48.3 <sup>a</sup>       |
| nonanal               | 95.0 <sup>a</sup> | 134.8 <sup>a</sup>      | 72.5 <sup>a</sup>       | 99.4 <sup>a</sup>       |
| (E)-2-pentenal        | 3.8 <sup>a</sup>  | 4.2 <sup>a</sup>        | 4.2 <sup>a</sup>        | 4.3 <sup>a</sup>        |
| (E)-2-hexenal         | 5.6 <sup>a</sup>  | 6.2 <sup>a</sup>        | 6.1 <sup>a</sup>        | 6.4 <sup>a</sup>        |
| (E)-2-heptenal        | 8.6 <sup>a</sup>  | 6.5 <sup>b</sup>        | 9.4 <sup>a</sup>        | 9.6 <sup>a</sup>        |
| (E)-2-octenal         | 13.6 <sup>a</sup> | 16.0 <sup>a</sup>       | 16.9 <sup>a</sup>       | 14.1 <sup>a</sup>       |
| (E)-2-nonenal         | 20.1 <sup>a</sup> | 27.1 <sup>a</sup>       | 19.9 <sup>a</sup>       | 24.8 <sup>a</sup>       |
| (E,E)-2,4-hexadienal  | 1.8 <sup>a</sup>  | 1.6 <sup>a</sup>        | 1.6 <sup>a</sup>        | 1.9 <sup>a</sup>        |
| (E,E)-2,4-heptadienal | 2.3 <sup>ab</sup> | 2.5 <sup>a</sup>        | 1.5 <sup>b</sup>        | 3.2 <sup>a</sup>        |
| (E,E)-2,4-octadienal  | 3.7 <sup>a</sup>  | 1.9 <sup>b</sup>        | 1.2 <sup>b</sup>        | 3.2 <sup>a</sup>        |
| (E,E)-2,4-nonadienal  | 5.2 <sup>a</sup>  | 5.1 <sup>a</sup>        | 2.4 <sup>b</sup>        | 4.6 <sup>ab</sup>       |
| (E,E)-2,6-nonadienal  | 5.3 <sup>a</sup>  | 4.5 <sup>a</sup>        | 3.9 <sup>a</sup>        | 4.0 <sup>a</sup>        |
| CV (%)                | 8.5               | 13.1                    | 16.0                    | 19.0                    |

<sup>a</sup> Mean value of 5 measurements. Different superscript letters row wise indicate significance at  $p < 0.05$ .

alkandienal, because a polarity of compound is increasing due to double bonds (Table 1). The logP value describes the partitioning between water and octanol and represents the hydrophobicity of the volatile compound; a negative value implies hydrophilicity.

On the contrary to the effect of the double bond, a substitution of an H atom by a methyl group,  $-\text{CH}_3$ , in straight chain aldehydes results in higher volatility and hydrophobicity of methyl-branched aldehydes as compared to those with a straight chain. The results indicate that the position of methyl group  $-\text{CH}_3$  in the molecule chain also has an effect on the volatility, i.e., the  $K_{\text{aw}}$ , for the short chain aldehydes: 2-methyl-butanal and 3-methyl-butanal have significant different  $K_{\text{aw}}$  values,  $31.6 \times 10^{-3}$  and  $25.7 \times 10^{-3}$ , respectively. However, a significant difference of  $K_{\text{aw}}$  between C<sub>9</sub> alkandienals (E,E)-2,4-nonadienal and (E,E)-2,6-nonadienal was not found regarding the position of second conjugated bound in the molecule. The available literature data show rather big variations in values of reported partition coefficients for individual organic compounds due to the different analytical procedures applied in the studies. The most comprehensive study on partitioning of aldehydes from water and other media, such as vegetable oil, dioctyl phthalate, and paraffin oil, was carried out by Hall and Andersson (27). Their data proved that partition coefficients are highly dependent on temperature and that this dependence is different for different compounds in a certain medium. Their study reported values of partition coefficients at temperatures of 20, 30, and 40 °C. The data obtained in our study are in good agreement with the  $K_{\text{aw}}$  values of saturated and monounsaturated aldehydes at 37 °C interpolated from the data of Hall and Andersson (27).

Air–liquid partition coefficients ( $K$ ) were also measured in three pectin-thickened viscous solutions. Except for the highly volatile aldehydes, 2-methyl-propanal and butanal, the  $K$  of each individual aldehyde compound remained at the same level in water and in the three pectin-thickened solutions of different viscosities (Table 2). That the addition of pectin as such resulted in an increased  $K$  value as compared to that in water for the

most volatile compounds, 2-methyl-propanal and butanal, is presumably ascribable to a “salting out” effect of pectin. Such an effect was recorded previously for the release of highly volatile aldehydes 3-methyl-butanal and pentanal in the presence of HMP (9). This explanation is corroborated by the findings that addition of 0.02 and 0.04% CaCl<sub>2</sub>·2H<sub>2</sub>O to the pectin solution, and hence increased viscosity, did not further affect the  $K$  values of 2-methyl-propanal and butanal in our study (Table 2). The few, decreased values of  $K$  recorded for (E,E)-2,4-alkandienals at 0.02% CaCl<sub>2</sub>·2H<sub>2</sub>O concentration (13.5 Ca<sup>2+</sup> mg/g pectin) are considered as unsystematic fluctuations resulting from unavoidable experimental inaccuracies in the quantifications of these mischievous compounds most probably due to their low vapor pressure; it has thus previously been documented that the pectin structure possesses hydrophobic ester groups that can participate in forming hydrophobic micelles that might cause weak interactions with unsaturated aldehydes of higher carbon chain length. Thus, 2-ketones with chain lengths greater than C<sub>6</sub> were found to bind to LMP pectin via van der Waals interactions between alkyl groups of the 2-ketone and hydrophobic regions of pectinate (28). Nevertheless, the present data document that neither addition of pectin per se nor increased viscosity—induced by Ca<sup>2+</sup> addition—generally suppressed the aroma release. Measured air–liquid partition coefficients  $K$  in pectin-thickened solutions show an absence of interactions between pectin and aroma compounds. Addition of HMP was previously found to result in modification of aroma and taste of typical jam aroma (9), and in pectin systems of high sugar content, a decreased headspace concentration of aroma compounds of up to 59% has been reported, although the extent of this effect varied with different volatiles (9, 13, 14).

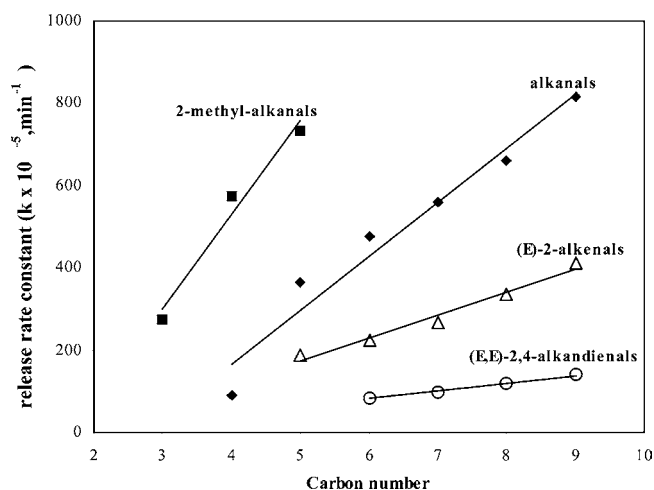
**DHS Release of Aldehydes.** To evaluate if rates of aroma release changed with viscosity, the transfer kinetics of aroma compounds through the stagnant liquid to the gas phase were measured in water and in the three pectin solutions of different viscosities. When boundary layers at the interface are stagnant, mass transport through these layers is by molecular diffusion (29). Collection of the volatiles in the gas phase as a function of time led to the calculation of release rates constants, hence estimation of mass transfer of volatiles in water and viscous pectin solutions. The values of the release rate constants ranged from  $\sim 76$  to  $817$  ( $k \times 10^{-5}$ , min<sup>-1</sup>), and apart from the increasing effects of pectin addition on the release of 2-methyl-propanal and butanal, no pronounced differences in release rate constants were recorded in the different test systems (Table 3). As might be expected, the recorded release dynamics varied in response to the different physicochemical properties of the compounds: carbon chain length, presence of function group, and degree of unsaturation (Figure 3). Thus, the release rate constants vs carbon number in the different homologous series showed similar trends as those found for the partition coefficient values under static conditions: in a homologous series, the release rates were generally lowest for the low carbon number molecules and increased with carbon number; furthermore, methyl-branched aldehydes gave the highest release rates, followed by straight chain alkanals, alkenals, and alkandienals (Figure 3). The obtained data show that partitioning still remained as the main influencing factor for aroma release under dynamic conditions.

The release rate constants for a range of compounds in water have previously been reported using a “retronasal aroma simulator” (23) and a mouth model system (30), where it was demonstrated that in water, the hydrophobic compounds had larger release rate constants than the smaller, more hydrophilic

**Table 3.** Linear Release Rate Constants<sup>a</sup> ( $k \times 10^{-5}$ ,  $\text{min}^{-1}$ ) and Correlation Coefficients<sup>b</sup> ( $r^2$ ) of Aldehydes Released in Water and 0.4% Pectin Solutions with Different Amounts of Added  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (% w/w)

| compound                       | water            |                       | 0.4% pectin solution  |                       |                       |                       |                       |                       |
|--------------------------------|------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|                                | <i>k</i>         | <i>r</i> <sup>2</sup> | 0.00% $\text{CaCl}_2$ |                       | 0.02% $\text{CaCl}_2$ |                       | 0.04% $\text{CaCl}_2$ |                       |
|                                |                  |                       | <i>k</i>              | <i>r</i> <sup>2</sup> | <i>k</i>              | <i>r</i> <sup>2</sup> | <i>k</i>              | <i>r</i> <sup>2</sup> |
| 2-methyl-propanal              | 274 <sup>a</sup> | 0.97                  | 432 <sup>b</sup>      | 0.90                  | 397 <sup>b</sup>      | 0.96                  | 528 <sup>b</sup>      | 0.97                  |
| 2-methyl-butanal               | 575 <sup>a</sup> | 0.96                  | 641 <sup>a</sup>      | 0.97                  | 584 <sup>a</sup>      | 0.96                  | 630 <sup>a</sup>      | 0.98                  |
| 3-methyl-butanal               | 795 <sup>a</sup> | 0.96                  | 853 <sup>a</sup>      | 0.97                  | 487 <sup>a</sup>      | 0.96                  | 811 <sup>a</sup>      | 0.97                  |
| 2-methyl-pentanal              | 734 <sup>a</sup> | 0.96                  | 748 <sup>a</sup>      | 0.97                  | 669 <sup>a</sup>      | 0.96                  | 688 <sup>a</sup>      | 0.96                  |
| butanal                        | 90 <sup>a</sup>  | 0.98                  | 282 <sup>b</sup>      | 0.98                  | 263 <sup>b</sup>      | 0.96                  | 315 <sup>b</sup>      | 0.97                  |
| pentanal                       | 364 <sup>a</sup> | 0.97                  | 425 <sup>a</sup>      | 0.98                  | 389 <sup>a</sup>      | 0.96                  | 420 <sup>a</sup>      | 0.96                  |
| hexanal                        | 476 <sup>a</sup> | 0.97                  | 526 <sup>a</sup>      | 0.98                  | 483 <sup>a</sup>      | 0.96                  | 502 <sup>a</sup>      | 0.96                  |
| heptanal                       | 559 <sup>a</sup> | 0.97                  | 602 <sup>a</sup>      | 0.98                  | 545 <sup>a</sup>      | 0.96                  | 564 <sup>a</sup>      | 0.96                  |
| octanal                        | 660 <sup>a</sup> | 0.96                  | 689 <sup>a</sup>      | 0.98                  | 610 <sup>a</sup>      | 0.96                  | 662 <sup>a</sup>      | 0.97                  |
| nonanal                        | 817 <sup>a</sup> | 0.96                  | 834 <sup>a</sup>      | 0.96                  | 773 <sup>a</sup>      | 0.97                  | 756 <sup>a</sup>      | 0.98                  |
| ( <i>E</i> )-2-pentenal        | 187 <sup>a</sup> | 0.97                  | 162 <sup>a</sup>      | 0.99                  | 188 <sup>a</sup>      | 0.99                  | 162 <sup>a</sup>      | 0.98                  |
| ( <i>E</i> )-2-hexenal         | 224 <sup>a</sup> | 0.97                  | 190 <sup>a</sup>      | 0.99                  | 223 <sup>a</sup>      | 0.99                  | 189 <sup>b</sup>      | 0.97                  |
| ( <i>E</i> )-2-heptenal        | 268 <sup>a</sup> | 0.97                  | 214 <sup>b</sup>      | 0.98                  | 258 <sup>a</sup>      | 0.99                  | 223 <sup>a</sup>      | 0.98                  |
| ( <i>E</i> )-2-octenal         | 334 <sup>a</sup> | 0.96                  | 245 <sup>a</sup>      | 0.97                  | 319 <sup>a</sup>      | 0.99                  | 274 <sup>a</sup>      | 0.99                  |
| ( <i>E</i> )-2-nonenal         | 412 <sup>a</sup> | 0.95                  | 272 <sup>b</sup>      | 0.96                  | 387 <sup>a</sup>      | 0.99                  | 337 <sup>a</sup>      | 0.98                  |
| ( <i>E,E</i> )-2,4-hexadienal  | 76 <sup>a</sup>  | 0.97                  | 96 <sup>a</sup>       | 0.99                  | 89 <sup>a</sup>       | 1.00                  | 93 <sup>a</sup>       | 0.99                  |
| ( <i>E,E</i> )-2,4-heptadienal | 99 <sup>a</sup>  | 0.97                  | 118 <sup>a</sup>      | 0.99                  | 104 <sup>a</sup>      | 1.00                  | 94 <sup>a</sup>       | 0.99                  |
| ( <i>E,E</i> )-2,4-octadienal  | 120 <sup>a</sup> | 0.94                  | 156 <sup>b</sup>      | 0.95                  | 134 <sup>a</sup>      | 0.99                  | 128 <sup>a</sup>      | 0.98                  |
| ( <i>E,E</i> )-2,4-nonadienal  | 140 <sup>a</sup> | 0.96                  | 173 <sup>a</sup>      | 0.99                  | 151 <sup>a</sup>      | 0.99                  | 147 <sup>a</sup>      | 0.97                  |
| ( <i>E,E</i> )-2,6-nonadienal  | 276 <sup>a</sup> | 0.94                  | 332 <sup>a</sup>      | 0.98                  | 276 <sup>a</sup>      | 0.98                  | 284 <sup>a</sup>      | 0.94                  |
| CV (%)                         | 13.3             |                       | 9.7                   |                       | 8.9                   |                       | 9.2                   |                       |

<sup>a</sup> Mean value of three independent measurements. <sup>b</sup>  $r^2$  correlation coefficient for release curve. Different superscript letters row wise indicate significance at  $p < 0.05$ .



**Figure 3.** Average release rate constants ( $k \times 10^{-5}$ ,  $\text{min}^{-1}$ ) of saturated, methyl branched, monounsaturated, and diunsaturated aldehydes from water at 37 °C ( $n = 3$ ).

compounds. Even though experimental setups and analytical procedures differ among research groups, the available data for 2-heptanone, ethyl butyrate, 1,8-cineole, and 2-methoxy-3-methyl-pyrazine obtained in above-mentioned systems are in the same range as the release rate constants obtained in this study. In our work, the release rate constant found for butanal seems low. Our present assumption is that this may be a result of high solubility and retainment of small molecules in solvent (water) during volatilization, but other mechanisms may also apply.

In the three pectin-thickened solutions of different viscosities, the release rate constants for the individual aldehydes did not differ significantly from those obtained in water, except for 2-methyl-propanal and butanal, which showed higher release rates in pectin-thickened solutions than in water (**Table 3**). Although pectin addition per se increased the release rates of 2-methyl-propanal and butanal, increases in viscosity by calcium addition did not affect the release rates of these or of any of

the other compounds (**Table 3**). Increased diffusivities of volatiles after addition of pectin to aqueous solutions were earlier recorded for *trans*-2-hexenal, linalool, mesifurane, and 2-methyl-butyric acid (16). The increased release rates of 2-methyl-propanal and butanal in the presence of pectin in our system are presumably due to a salting out effect of pectin, which may expel volatiles from liquid to the air phase by interacting with water. It is important to note that this effect appears to be unrelated to the formation of a structural pectin network. If it was, a further increase in release rates would occur with calcium addition and hence viscosity increase, which was not the case. The breakthrough during the trapping of volatiles on the Tenax could not be the explanation for the findings regarding increased release rate of 2-methyl-propanal and butanal in the presence of pectin, because increased release of these particular compounds was also recorded in the measurements by SHS-GC. Definitely, the increase in macroscopic viscosity did not decrease the release rates of any of the compounds tested.

The major factors determining the extent and the rate of the flavor release from a food matrix are partitioning between air-product phases and mass transport (31). Partitioning of flavor compounds between phases can be expressed by the partition coefficient  $K_{ap} = C_a/C_p$ , which describes the ratio between flavor concentration in the air phase above a given product ( $C_a$ ) and the flavor concentration in the product phase ( $C_p$ ) at equilibrium. The  $K_{ap}$  thus defines the maximum potential extent of flavor release, as determined by the volatility and solubility of the flavor compound at equilibrium. Because the nature of the product matrix components may impact the release of volatiles, the analysis of headspace concentration above a product at equilibrium can help to estimate the level of interaction between flavors and matrix. However, it is important to note that equilibrium conditions do not reflect a real flavor release situation when food is eaten where both aqueous and gas phases are undergoing dilution and where the holding time in the mouth is usually not long enough to reach equilibrium. Hence, when food is eaten, flavor release equilibrium is usually not achieved and the mass transfer factor therefore also plays a role along

with partition in generating the chemical signal that is perceived as flavor (32). The mass transfer coefficient is a measure of the rate of release considering nonequilibrium as a main driving force and is determined by the diffusion coefficient that may or may not be influenced by viscosity changes (33). Hence, in stagnant systems, molecular diffusion applies, and this diffusion mechanism is a result only of random movement of the present molecules. In contrast, with mastication or other mechanical treatments such as stirring, the rate of surface renewal affects the mass transfer, and convective diffusion, or "Eddy diffusion", applies (29). The existing literature data on aroma release from pectin matrixes show that the type of diffusion employed in the studies plays an important role in the release mechanism of volatiles and thus in drawing up the conclusions on the influence of pectin as such. When Eddy diffusion was implemented to the procedure of the volatiles collection from strawberry jam, no more significant differences were found between the system without pectin and the system containing 0.4% HM pectin (9). Authors suggested that the mechanical treatment in the pectin containing system led to the breakage of the pectin network and liberation of aroma molecules. Meanwhile, the outcomes on the weak interactions between pectin and aroma compounds were made on the basis of molecular diffusion (9). Recent works of Hansson et al. (15, 34) on aroma release from pectin gels in mouth model system with mimicked mastication movements corroborate the observation that viscosity or gel strength does not play such a significant role for the aroma release from pectin gels under conditions of Eddy diffusion as it does in the case of molecular diffusion.

Because the calculated release rate constants can be directly related to interfacial mass transfer, thus diffusion coefficient, the data obtained indicate that no change in diffusion rate of an aroma compound takes place over the range of studied viscosities, e.g., from 0.001 to 150 Pa s. In general terms, the diffusion  $D$  of the flavor molecule is reduced as solution viscosity increases as predicted by the Stokes–Einstein equation:

$$D = kT/6\eta\pi a$$

where  $k$  = Boltzman's constant,  $T$  = temperature,  $\eta$  = viscosity, and  $a$  = radius of the molecule. Because the viscosity term is included in the equation for  $D$ , the obtained data immediately appear paradoxical. According to the Stokes–Einstein equation, even a small increase in viscosity, e.g., 2–3-fold, should result in a corresponding decrease in diffusion rate of aroma molecules. However, we did not observe any decrease in aroma diffusivity in pectin-thickened systems even though the viscosity was increased 1000-fold. The explanation for this phenomenon is that in a pectin-thickened solution, the hydrocolloid is still very dilute (0.4% w/w) and that the immobilized water is only loosely bound, even at high "macroscopic" viscosities. Therefore, the water mobility remains nearly unchanged. The volatile aroma compounds are characterized by a comparatively small molecular weight and are thus capable of diffusing without barriers through the water phase around the branches of the pectin chain. In this way, the macro viscosity of the bulk solution has no effect on the diffusion of aroma molecules in the water phase of a thickened solution. In contrast, if water is thickened by adding small, molecular weight thickener such as sucrose, a much greater molar concentration of thickener is required to achieve the same viscosity as compared to adding a high molecular weight hydrocolloid. In this case, the water activity, and thus water mobility, is reduced at the molecular level and thus follows the Stokes–Einstein equation. The impact of both types of viscosities on diffusivity and partitioning of isopentyl

acetate from sucrose and galactomannan (GM) solutions is well-illustrated in the work of Darling et al. (35), which proves that there is no difference on measured diffusion coefficients of isopentyl acetate up to 0.75% w/w concentrations of GM, while in a sugar solution the diffusion coefficient fell with increased viscosity as predicted by the Stokes–Einstein relation.

The recent data of Rega et al. (13) also support this hypothesis, even though their interpretations do not include these thermodynamic considerations. Nevertheless, their results show that the diffusivity of aroma compounds decreases by approximately 8–10-fold in concentrated sucrose solution, followed by only a decrease of 2–3-fold after adding a pectin hydrocolloid to the system, where the measured viscosity increased up to 100 times. Moreover, an increase of the pectin concentration from 0.1 to 0.4 wt % did not affect the diffusivity values (13). In a separate study, addition of 0.4% w/w HMP to a model system gave similar diffusivities as those obtained in aqueous solution for all volatiles (16). However, both studies confirm the same tendency, namely, that diffusivities of aroma volatiles decrease when pectin is added to an aqueous solution of high sugar content. Hence, in contrast to what we believe is the case in low sugar systems, it thus appears certain that in pectin-gelled systems of high sucrose concentration, both diffusivity values and equilibrium headspace concentrations of volatiles are lowered, although the extent of this effect varies with different volatiles (9, 14). The explanation above regarding the effect of sucrose on water may provide a thermodynamic mechanism that explains this phenomenon.

## CONCLUSIONS

The results of this work showed that neither addition of HM pectin per se nor increased macroscopic viscosity, as induced by addition of  $\text{Ca}^{2+}$  ions to the pectin, affected the released levels of aroma aldehydes from pectin-thickened viscous solutions at low sugar content. Moreover, it was found that also the release rate constants of individual aldehydes remained unaltered at a wide range of viscosities. In contrast to the prevailing assumptions, these results thus signify that no binding, molecular interactions, nor diffusion retarding effects occur between aldehydes and pectin alone during the formation of a hydrocolloid network in pectin-thickened solutions. The only exceptions were that 2-methyl-propanal and butanal exhibited increased release in the presence of pectin, presumably due to a salting out effect of pectin. The model employing a calcium sensitive pectin at constant pectin concentration might be useful in further research studies on aroma release or in product development work, where it is desirable to produce viscosity without affecting its physicochemical properties of flavor release.

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