

Effect of Xanthan on Flavor Release from Thickened Viscous Food Model Systems

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The influence of xanthan concentration (0, 0.02, 0.1, 0.4, and 0.8% w/w) and bulk viscosity on the release of 20 aroma compounds of different chemical classes (5 aldehydes, 4 esters, 5 ketones, 3 alcohols, and 3 terpenes) was evaluated in xanthan-thickened food model systems having different viscosities. Interactions between flavor compounds and xanthan were assessed by measuring air–liquid partition coefficients, K , of aroma compounds in pure water and in the xanthan solutions by static headspace gas chromatography. Mass transfer of aroma compounds was estimated by dynamic headspace gas chromatography. Notably, limonene and some of the esters and aldehydes exhibited decreased K values in the presence of xanthan, indicating that the release of these volatile aroma compounds was reduced due to interaction with the xanthan matrix. The degree of interaction depended on the physicochemical characteristics of the aroma compounds. A similar tendency was observed at nonequilibrium with the decreases in release rates being most pronounced for limonene, followed by the esters and aldehydes, with no effect for ketones and an apparent “salting out” effect for alcohols. The reduction in flavor release by xanthan was thus dependent on the physicochemical properties of the aroma compounds and was apparently a result of the aroma–xanthan interactions and not influenced by the viscosity of the system itself.

KEYWORDS: Aroma; partition coefficients; release rate constant; diffusion; polysaccharides; thickeners; viscosity; xanthan

INTRODUCTION

The texture or consistency of industrially manufactured liquid foods is often controlled by the use of hydrocolloid thickeners. Hydrocolloids are also increasingly used in reduced-fat products. However, the use of hydrocolloids may induce a significant decrease in aroma perception and/or release as reported in previous studies (1–6). Only compounds released in sufficiently high concentrations can be perceived as flavor, and even small modifications of a food matrix have been documented to generate a great change in perceived flavor intensity (2–5, 7). According to the published sensory and physicochemical studies, the apparent decrease of aroma release induced by hydrocolloids may be the result of two main mechanisms: (a) lowering of the diffusion rate in the media due to the increased solution viscosity (1, 5, 6, 8, 10, 11) and (b) molecular binding interactions between the flavor compounds and the hydrocolloid matrix constituents (6, 7, 9, 10, 12). However, the hindrance of molecular migration attributed as an effect of viscosity and/or three-dimensional structural network cannot account for why changes in viscosity on the order of ~100-fold decrease the diffusion coefficients of the aroma compounds by only ~2–3-fold (5, 6, 8, 10).

The diffusion rate and, thus, the rate of release of aroma compounds from food systems depend on the type of diffusion mechanism in the system (13). When the fluid system is stagnant, mass transport takes place by molecular diffusion, and the rate of release depends on the speed of the random movement of the present molecules and on the resistance at the boundary layers, notably at the air–surface layer in the system (13). In contrast, during mastication or other mechanical treatment of the system, mass transport takes place by eddy diffusion, which results in higher concentrations of aroma compounds at the surface boundary layer and, consequently, higher release rates. The existing literature data on aroma release from hydrocolloid solutions thus clearly show that the type of diffusion implemented in the system governs the release mechanism of volatiles and in turn determines the influence of viscosity and hydrocolloids on the aroma release rates. Several studies have documented (5, 8, 11) that flavor release may be significantly affected by the matrix consistency or viscosity under conditions of molecular diffusion, whereas no significant effects of viscosity have been observed under implementation of eddy diffusion or mastication in the experimental procedure (3–5, 8). Other studies (12, 14, 15) have concluded that increases in the viscosity of hydrocolloid solutions do not influence the release of aroma compounds from the matrices under molecular diffusion.

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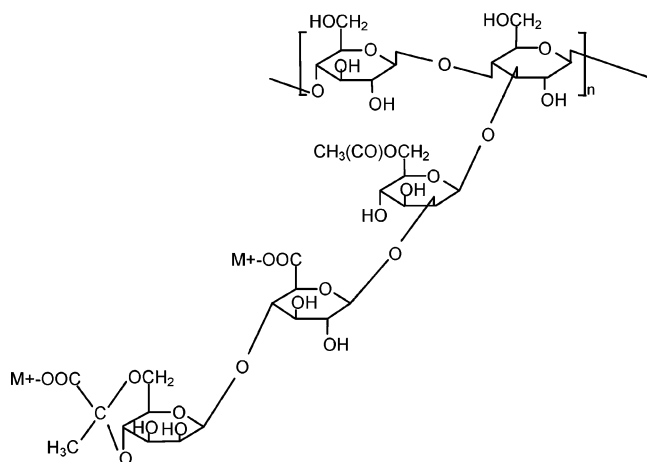


Figure 1. Structure of xanthan gum.

However, particular effects, interpreted as specific aroma binding or retarded diffusion effects of certain hydrocolloids, notably carrageenan, pectin, and xanthan, appear in the literature (7, 9–12, 16, 17).

Xanthan gum is an exocellular biopolymer secreted by *Xanthomonas* sp. with a main chain consisting of a linear backbone of 1,4-linked β-D-glucose and side chains of two mannose and one glucuronic acid (Figure 1) (18). In aqueous solutions xanthan undergoes a conformational transition from an ordered double helix to a random coil under the influence of temperature and ionic strength (19). Because of its unique properties such as solubility in both cold and hot water, high viscosity at low concentrations, little variation in the viscosity with changes in temperature, and stability in acid systems, xanthan is used as a thickener, stabilizer, and emulsifier in numerous food applications such as salad dressings, sauces, gravies, relishes, dairy products, whipped cream and mousses, instant mixes of drinks and soups, bakery products, and syrups (18, 19).

To control flavor perception in xanthan-thickened foods, a better understanding of the influence of xanthan on the aroma release from viscous xanthan matrices is needed. Despite the large number of studies carried out to understand the impact of hydrocolloids on the release and perception of aroma compounds, there is still a need for a more general approach that takes into account the matrix structure and the behavior of systematic chemical series of aroma compounds rather than of a single aroma compound.

The aim of this study was to better understand the release of aroma compounds from xanthan-thickened food model systems. The viscous food model was developed by increasing xanthan concentration to vary the “macroscopic viscosity” of the food model. The aroma release was evaluated in the xanthan-thickened solutions by assessing the partitioning and mass transfer behavior of 20 selected aroma compounds (aldehydes, esters, ketones, alcohols, and terpenes) having a wide range of physicochemical properties. To specifically understand the influence of viscosity on molecular diffusion of aroma compounds and thus abolish the effects of eddy diffusion, the dynamic headspace analyses were carried out with solutions under stagnant conditions.

MATERIALS AND METHODS

Sample Preparation. Model Flavor Mix. Twenty aroma compounds of different chemical classes were chosen for their broad physicochemical properties: *aldehydes* [3-methylbutanal, hexanal, (*E*)-2-hexenal, heptanal]; *esters* (methyl butanoate, 3-methylbutyl acetate, ethyl

butanoate, ethyl heptanoate); *ketones* (2,3-butanedione, 2,3-hexanedione, 2-butanone, 2-heptanone, 2-octanone); *alcohols* (3-methyl-1-butanol, 1-pentanol, 1-heptanol); and *terpenes* (limonene, linalool, menthone). The aroma compounds were prepared as a stock solution in ethanol at different concentration levels to give a 0.03% (w/w) flavor mix/matrix solution for flavor release experiments. Supplier, chemical purity, physicochemical characteristics, and the concentrations of aroma compounds in the stock flavor mixture and in the diluted solutions are presented in Table 1.

Aqueous Aroma Solution. Aliquots of the stock flavor solution were diluted in Milli-Q water. The diluted aqueous solutions were gently stirred in closed containers for 30 min to ensure equal distribution of the aroma compounds and then heated to 80 °C. The aromatized diluted solutions were then transferred into 22.3 mL gas chromatography (GC) vials for the determination of air–water partition coefficients, K_{aw} , by static headspace gas chromatography (SHS-GC).

Thickened Solutions. Xanthan-thickened viscous solutions were prepared by using 0.02, 0.1, 0.4, and 0.8% (w/w) xanthan (xanthan gum, Grindsted X, Danisco, Denmark) and 10% (w/w) sucrose (Sigma-Aldrich Chemie, Steinheim, Germany). The mixture of xanthan and sucrose was added to the aqueous aroma solution under agitation. The jar was then immediately sealed, and the solution was heated to 80 °C with a gentle stirring for 20 min to complete solvation of the xanthan molecules. Flavored viscous solutions were then cooled to ~45 °C, transferred to the GC vials, capped, and equilibrated, as described below for methods of analysis, prior to SHS-GC analysis. The influence on aroma release of adding aroma compounds before and after heating of the model systems, respectively, was compared in preliminary tests. No significant differences in headspace concentrations were found between the two procedures, proving no losses by thermal degradation at the experimental conditions.

Methods of Analysis. SHS-GC. Liquid–vapor partition coefficients of the aroma compounds in water and xanthan solutions were determined using a phase ratio variation (PRV) method that does not require the use of internal or external standards (20). Five independent measurements were carried out for each thickened and aqueous system. Sealed vials with aqueous and thickened aroma solutions were pre-equilibrated for 24 h at ambient temperature and then for 2 h at 37 °C to ensure that the equilibrium gas/matrix in the vial was reached. This experimental procedure was based on preliminary timed experiments verifying that equilibrium was reached after 100 min. After equilibration was completed, the headspace sample was automatically withdrawn using a Perkin-Elmer HS 40 XL autosampler and injected into a Perkin-Elmer XL gas chromatograph and analyzed as described previously (15).

Dynamic Headspace Gas Chromatography (DHS-GC). The release rates of the different aroma compounds in aqueous and xanthan-thickened solutions were assessed by DHS-GC. Samples were flushed with pure nitrogen (70 mL/min), and released volatiles were collected on eight Tenax TA traps over 600 s as described previously (15). For the quantification of aroma compounds, six standard solutions of aroma compounds of known concentrations were injected and analyzed ($n = 3$).

Determination of Release Rate Constants. Release rate constants (k) were calculated from the rate of adsorption on the Tenax traps as described by Roberts and Acree (21)

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

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).

The release rate constant (k) is defined as the linear release rate over time divided by the initial concentration (21).

Rheological Characterization. Shear viscosity measurements of viscous solutions were performed 24 h after preparation. Before analysis, the viscous solutions were equilibrated at 37 °C to describe the structural matrix properties at the headspace measurement temperature. The measurements were performed after the equilibration of solutions using a Stress Tech (Reologica, Lund, Sweden), a controlled stress rheometer with cone and plate geometry C40 4. Flow curves

Table 1. Composition of the Flavor Mix, Final Concentrations, and Chemical Characteristics of Volatile Compounds: Supplier, Purity, Molecular Weights (M_w), Boiling Points (B_p), Hydrophobic Fragmental Constants ($\log P$), and Saturated Vapor Pressure (P_s) at 25 °C

volatile compound	supplier	purity (%)	% in flavor mix	final concn ($\mu\text{g/g}$)	M_w	B_p (°C)	$\log P^a$	P_s^b (mmHg)
aldehydes								
(E)-2-hexenal	Aldrich	98	6.41	19.44	98	147	1.50	6.60
3-methylbutanal	Fluka	98	3.26	10.00	86	93	1.34	49.32
hexanal	Aldrich	98	3.35	10.28	100	128	1.80	10.89
heptanal	Aldrich	95	3.15	9.35	114	153	2.32	3.85
octanal	Aldrich	99	4.60	14.25	128	171	2.86	2.07
esters								
methyl butanoate	Fluka	99	3.44	10.64	102	103	1.28	31.13
ethyl butanoate	Aldrich	98	3.60	11.02	116	122	1.80	13.94
3-methylbutyl acetate	Merck	98	2.97	9.10	130	143	2.3	5.68
ethyl heptanoate	Aldrich	99	3.33	10.29	158	187	3.31	0.60
ketones								
2,3-butanedione	Aldrich	98	4.91	15.05	86	88	-1.80	62.28
2,3-hexanedione	Aldrich	90	5.92	16.65	114	128	-0.78	12.44
2-butanone	Aldrich	99	3.30	10.27	72	80	0.33	114.52
2-heptanone	Aldrich	98	3.19	9.77	114	151	1.90	4.73
2-octanone	Aldrich	98	3.12	9.56	128	172	2.42	1.72
alcohols								
3-methyl-1-butanol	Fluka	98	5.09	15.60	88	131	1.35	4.16
1-pentanol	Aldrich	99	9.92	30.71	88	138	1.35	2.81
1-heptanol	Aldrich	98	9.37	28.70	116	176	2.39	0.32
terpenes								
linalool	Aldrich	98	9.72	29.78	154	198	2.97	0.16
menthone	Aldrich	96	9.60	28.80	154	210	3.05	
limonene	Aldrich	97	1.67	5.08	136	177	4.57	1.98
			100	304.4				

^a Calculated by using the method of Rekker (31). ^b Calculated with ACD demosoftware.

were recorded by increasing the stress from 0.05 to 12 Pa in 20 logarithmic steps.

For an estimation of the c^* value, four additional xanthan concentration solutions (0.01, 0.05, 0.5, 0.1%) were prepared and analyzed as described above. Generally, c^* is defined as the concentration at which individual polymer molecules begin to physically interact, that is, the point at which a small increase in the hydrocolloid concentration induces a rapid increase in viscosity (1, 4, 19). To extrapolate an estimation of zero-shear viscosity of each solution, flow curves were fitted to the Cross equation (22). The value of c^* was then estimated from a double-logarithmic plot of zero-shear viscosity versus concentration, as described by Rodd et al. (19).

Statistical Analysis. The effect of xanthan on the vapor-liquid partition coefficients and release rate constants was assessed by analysis of variance (ANOVA) and Tukey's test (Minitab Statistical Software, Addison-Wesley, Reading, MA). Significance was established at $p < 0.05$.

RESULTS AND DISCUSSION

Rheological Characterization of the Xanthan Models. The xanthan solutions exhibited non-Newtonian, pseudoplastic, and shear-thinning behavior and became highly viscous even at low polymer concentrations (Figure 2). As a thickener, xanthan exhibits much more pronounced thickening properties than other hydrocolloids. The model solution with the lowest xanthan concentration employed in this study 0.02% (w/w) was nearly as viscous as 0.4 and 0.25% (w/w) solutions thickened with HM pectin and λ -carrageenan, respectively, in our previous studies (12, 15) at the same applied shear stress. According to Morris (23), xanthan molecules exist in solution in a rigid, ordered conformation and form a tenuous three-dimensional network; therefore, a finite shear stress is required to rupture the network, above which the viscosity decreases with increasing shear rate. This behavior was also observed in the present study. The apparent viscosity of xanthan solutions decreased significantly with increasing shear stress, and shear-thinning character of solutions increased with increasing xanthan concentration

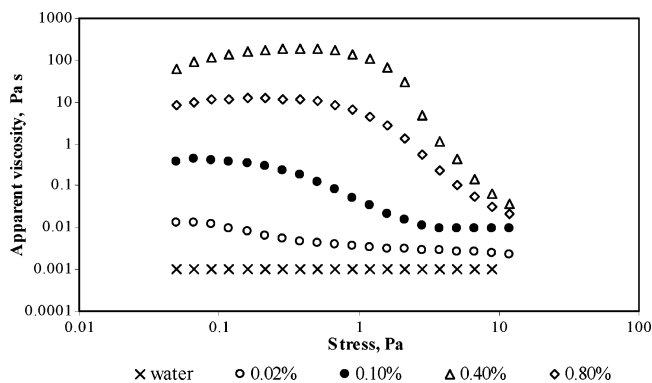


Figure 2. Viscosity curves of xanthan solutions of different concentrations (% w/w).

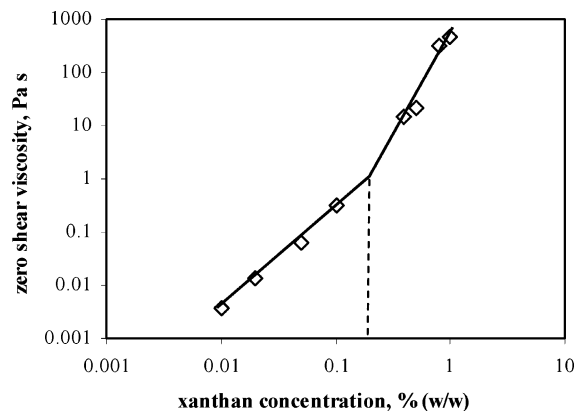


Figure 3. Variation of zero shear viscosity versus xanthan concentration (% w/w) in model solutions.

(Figure 2). Plotting zero-shear viscosity of model solutions against concentration resulted in a c^* value of 0.24% (w/w) (Figure 3). In the study of Milas et al. (24), two concentration transitions in xanthan solutions were observed and assigned c^*

Table 2. Air–Liquid Partition Coefficients, K , of Aroma Compounds ($K \times 10^{-3}$)^a in Water and in Xanthan Solutions of Different Concentrations

compound	water	xanthan concn in solutions			
		0.02%	0.10%	0.40%	0.80%
aldehydes					
(E)-2-hexenal	5.5a	5.6a	5.7a	5.0ab	4.6b
3-methylbutanal	23.2a	22.5ab	21.7ab	21.3ab	20.6b
hexanal	21.6a	20.2ab	19.9ab	19.0b	18.4b
heptanal	30.8a	26.9b	26.8b	26.1b	24.5b
octanal	47.7a	41.9b	35.2bc	33.7bc	31.7c
esters					
methyl butanoate	18.8a	19.2a	19.3a	18.5a	17.1a
ethyl butanoate	26.8a	26.9ab	25.7ab	25.2ab	24.1b
3-methylbutyl acetate	35.2a	34.2ab	32.2abc	31.1bc	27.8c
ethyl heptanoate	93.3a	79.4a	78.9ab	64.2b	51.5b
ketones					
2,3-butanedione	2.3a	2.1a	2.2a	2.1a	2.3a
2,3-hexanedione	5.1a	4.7a	4.8a	4.3a	4.7a
2-butanone	4.5a	4.6a	4.6a	4.3a	4.6a
2-heptanone	13.1ab	13.6a	13.0ab	11.9ab	11.1b
2-octanone	20.4a	19.8ab	18.3ab	18.0ab	16.6b
alcohols					
3-methyl-1-butanol	1.8a	1.9a	2.0a	1.9a	2.5b
1-pentanol	1.8a	1.6a	1.6a	1.9a	1.7a
1-heptanol	4.2a	5.7b	3.9a	4.2a	5.6b
terpenes					
linalool	11.8a	11.3a	10.8a	10.6a	10.2a
menthone	14.6a	13.2a	13.8a	13.2a	15.6a
limonene	457.0a	320.8b	243.2b	213.9bc	156.5c
CV (%)	7.8	9.6	10.8	11.2	11.4

^a Mean value of five measurements. Different letters in a row indicate significance at $p < 0.05$.

and c^{**} corresponding to 0.126 and 0.60–0.78 wt %, respectively. Their work proved that c^* and c^{**} are highly dependent on the nature of xanthan sample, whereas Coviello et al. (25) showed that the value obtained in determining c^* for semi-flexible objects as xanthan is often dependent on experimental technique and interpretation of data. Our study employed a food model system with 10% (w/w) sucrose content, and the presence of sucrose may lead to a relatively higher value of the critical concentrations c^* of xanthan solutions (26).

SHS-GC Measurements. To estimate the effect of xanthan gum on the thermodynamic properties of the aroma compounds in the thickened solutions, SHS-GC measurements were carried out at 37 °C at equilibrium. At equilibrium, the viscosity effects are nullified; therefore, any differences in static equilibrium headspace concentrations between water and xanthan solutions would be due to interactions between the aroma compounds and the matrix (13). Expressed as the ratio between the flavor concentration in the air phase above the product (C_a) and the flavor concentration in the product phase (C_p) at equilibrium, the partition coefficient $K = C_a/C_p$ defines the maximum potential extent of flavor release (13).

Pure Water. For the homologous series of aldehydes (C_6 , hexanal; C_7 , heptanal; C_8 , octanal), esters (C_4 , ethyl butanoate; C_7 , ethyl heptanoate), 2-ketones (C_4 , butanone, C_7 , heptanone; C_8 , octanone), 2,3-diketones (C_4 , butanedione; C_6 , hexanedione), and 1-alcohols (C_5 , pentanol; C_7 , heptanol) the more hydrophobic compounds were more volatile (Table 2). Among all of the volatiles studied, the partitioning of limonene was the highest. Being a pure hydrocarbon without functional groups ($C_{10}H_{16}$) and possessing high hydrophobic properties and high vapor pressure in the pure state (Table 1), limonene is thus hardly retained in the aqueous phase. The oxygenated terpenes menthone and linalool are more polar (Table 1);

therefore, their partitioning from water was lower than limonene's (Table 2).

The observed tendencies in the partitioning of the aroma compounds are in good agreement with the data available in the literature including our own previous studies (7, 10, 12). However, some differences in the values of air–water partition coefficients, K_{aw} , of the aroma compounds could be observed when the values obtained in the current study were compared with those we had obtained previously. The values of K_{aw} for the saturated aldehydes, esters, and 2-ketones from aqueous solutions were lower in the present study than those recorded in earlier (12, 15). In the present study each of the aroma compounds was added as a flavor mixture composed of 20 aroma compounds of different chemical classes with higher proportions (percent) of less volatile aroma compounds such as alcohols, 2,3-diketones, and oxygenated terpenes (Table 1). On the other hand, our previous studies were conducted with four different mixtures (saturated aldehydes, esters, ketones, and alcohols, respectively) composed of 10 aroma compounds of the same chemical class with an equal portion of each compound (12, 15). It is possible that interactions among aroma compounds are occurring in the 20-compound flavor mixture. The aqueous solubility of more hydrophobic compounds (esters, aldehydes, terpene limonene) could be enhanced by the presence of more hydrophilic compounds such as alcohols, 2,3-diketones, and oxygenated terpenes in the mixture. Compounds possessing hydrophobic properties, thereby, become better retained in aqueous phase, resulting in lower partition coefficients. This type of flavor compound–compound interaction was recently well described by Schober and Peterson (27), who demonstrated that the release of L-menthol and cineol from a candy model system was lower when the aroma compounds were added as a mixture compared to when these compounds were added separately. The obtained results indicate that flavor compound–compound interactions should also be taken into account when aroma mixtures are formulated and flavor release is to be controlled.

Release from the Xanthan Solutions. The influence of xanthan on the release of aroma compounds was assessed by measuring the partitioning of the aroma compounds from the xanthan solutions containing 0.02–0.8% (w/w) xanthan. A systematic effect of xanthan on the equilibrium headspace concentrations of aroma compounds could be observed (Table 2). The extent of retention varied for different compounds depending on their physicochemical properties and varied systematically with the xanthan concentration in the solutions. The highest retention was observed for limonene followed by the esters and saturated aldehydes. Some suppression was also recorded for the 2-ketones, but mainly at the higher xanthan addition levels (Table 2). The partition coefficients of the 2,3-diketones also tended to be lower in the xanthan solutions than in water, but this effect was not statistically significant ($p > 0.05$) (Table 2).

Among all of the volatile aroma compounds studied, the release of limonene was most suppressed. We propose that this retention is due to limonene's highly hydrophobic nature. The two oxygenated terpenes, linalool and menthone, which are less hydrophobic than limonene, did not show significant changes in equilibrium concentrations in the presence of xanthan. These results thus confirm that differences in the aroma compound structures, and in turn in the physicochemical characteristics of the aroma compounds, significantly affect the release behavior of the compounds.

The relative retention of esters ranged from 0 to 45% and also depended on the physicochemical properties of the com-

pounds (**Table 2**). The least hydrophobic and least volatile compound among the esters, namely, methyl butanoate ($\log P = 1.28$, $K_{aw} = 18.8 \times 10^{-3}$) was not significantly affected by the xanthan at any of the studied xanthan concentrations. Ester retention increased with increasing aroma compound volatility and xanthan concentration. The largest effect was seen with ethyl heptanoate ($\log P = 3.31$, $K_{aw} = 93.38 \times 10^{-3}$), where release was reduced by 15–45%, depending on the xanthan concentration in the solution (**Table 2**).

The same tendency was observed for the aldehydes. The more hydrophobic and volatile compounds, that is, heptanal and octanal, were retained by xanthan at all concentrations, with the highest retentions being 20 and 34%, respectively. The release of the more hydrophilic compounds with low $\log P$, (*E*)-2-hexenal and 3-methylbutanal, was significantly affected only at the highest xanthan concentration.

Among the ketones, only the partitioning of compounds having the highest carbon numbers, that is, 2-heptanone and 2-octanone, was (slightly) affected by xanthan at equilibrium. The suppression of both 2-heptanone and 2-octanone was statistically significant only at the highest xanthan concentration, resulting in headspace concentration decreases of 15 and 19%, respectively.

The release of alcohols at equilibrium was not suppressed by xanthan. Rather, some of the alcohols showed a tendency to exhibit increased partitioning in the presence of xanthan (**Table 2**). The release of 3-methyl-1-butanol and 1-heptanol was higher by 39 and 33%, respectively, in the 0.8% xanthan solutions. This can be described as a “salting out” effect of the most hydrophilic aroma compounds.

Altogether the results show that xanthan tends to suppress aroma release, especially for highly hydrophobic aroma compounds. The changes in the thermodynamic properties of aroma compounds thus indicate the existence of certain xanthan–flavor compound interactions. Because these hydrocolloid–aroma interactions are most pronounced for the more hydrophobic compounds, we believe the interactions are a result of hydrophobic binding. Contrary to proteins that possess hydrophobic regions (hydrophobic side chains of the amino acids), hydrocolloids have minimal opportunity for the equivalent interaction due to their rather hydrophilic nature (12, 28). Nevertheless, the results of this study together with the available literature data indicate that xanthan has a more distinctive hydrophobic character compared to other hydrocolloids, and this may influence flavor release (7, 9, 10). Xanthan consists of a cellulose backbone with ionized trisaccharide branches on every second residue (**Figure 1**). In the ordered conformation, the side chains fold back around the main chain to give a structure analogous to a double helix (18). In this conformation the ordered molecule is stabilized through hydrogen bonds by non-covalent side chain–main chain interactions involving hydrogen bonding (29). In this way, the configuration of xanthan may create a hydrophobic interior in the carbohydrate molecule, which can “include” flavor compounds.

Previously, the assessment of interactions between xanthan and flavor compounds by headspace and binding methodologies such as exclusion size chromatography resulted in direct evidence of binding some aroma compounds (7, 9), which was interpreted as hydrogen binding. In the study of Yven et al. (7) only diallyl sulfide showed significant binding at a xanthan concentration of 0.01%, whereas at 0.1% xanthan, significant binding was recorded for all tested compounds (diacetyl, 1-octen-3-ol, diallyl sulfide, diallyl disulfide). The extent of interactions and decrease of aroma headspace concentration at

equilibrium followed the same tendency as in our study; the compound with highest volatility and highest K_{aw} was affected most by the xanthan, followed by the compound with second highest K_{aw} . The compound with lowest K_{aw} , 1-octen-3-ol, was affected the least (7). We did not observe any significant binding for diacetyl (2,3-butanedione) in our study, which may be due to differences in binding levels resulting from dissimilarity of the composition of the flavor mixture. Our study was performed with a flavor mixture of 20 aroma compounds, whereas the binding of diacetyl was recorded by adding it as single aroma compound to a xanthan solution (7). The recent study of Secouard et al. (10) on limonene release from polysaccharide matrices corroborates the proposition that the influence of xanthan on the flavor release depends on the chemical structure and hence physicochemical characteristics of the flavor compound. In full agreement with our data (**Table 2**), Secouard et al. showed that release of limonene was suppressed in the presence of xanthan in solution, whereas no significant differences on retention of menthol were detected (10). However, Secouard et al. (10) speculated that viscosity of the media was a potential cause of the reduced headspace concentration of limonene. From our observations this seems to be a rather questionable consideration, taking into account that their experiment measurements were carried out at equilibrium conditions where the effect of the resistance to mass transfer, and thus viscosity, is not apparent.

DHS-GC Measurements. Whereas partitioning reflects the maximum potential flavor release, mass transfer plays the main role in determining the rate of flavor release during food consumption and determines the rate at which equilibrium is achieved. The mass transfer coefficient is a measure of the rate of release considering nonequilibrium as a main driving force and may be influenced by both the texture and microstructure of a product (30). Therefore, both thermodynamic and kinetic parameters participate in generating the chemical signal that is perceived as flavor.

To evaluate the influence of matrix structure on flavor release and avoid any eventual confoundings from convective diffusion or eddy diffusion, a stagnant layer model was adopted for kinetic experiments. In accordance with the theory of random movement of molecules in a stagnant fluid, the stagnant layer model assumes that the boundary layers at (or near) the air–liquid interface are stagnant and that the mass is transported through these layers as a result of molecular diffusion (13).

Release from Aqueous Solutions. To evaluate the impact of xanthan and viscosity on the release rates of aroma compounds from xanthan viscous model systems, the aroma compound release rates were primarily established in aqueous solutions (**Table 3**). Among the aroma compound series, the release rates of esters were the highest, indicating that esters were the most volatile, followed by aldehydes, ketones, and alcohols. In comparison to our previous study (12) in which the release of aroma compounds from water was measured after the aroma compounds were added as separate mixtures (aldehydes, esters, ketones, alcohols) at equal proportions, slower rates were observed in the current study. Again, the explanation could be that the flavors were retained in the solution as a result of flavor compound–compound interactions as already discussed above. Considering the chemical structure and volatility of limonene ($C_{10}H_{16}$, $\log P = 4.57$, $K_{aw} = 457 \times 10^{-3}$), it was expected that limonene would exhibit the highest release rate among the other volatile compounds. However, the limonene concentration in the initial flavor mix and in the diluted final solutions was low (~5 ppm) in comparison with the more hydrophilic

Table 3. Release Rate Constants ($k \times 10^{-5}$, min^{-1}) of Aroma Compounds Released in Water and Xanthan Solutions of Different Concentrations

compound	water	xanthan solutions			
		0.02%	0.10%	0.40%	0.80%
aldehydes					
(<i>E</i>)-2-hexenal	228a	225a	210a	224a	203a
3-methylbutanal	555a	478ab	458b	454b	405b
hexanal	435a	377ab	373ab	340ab	329b
heptanal	404a	340ab	338ab	331b	300b
octanal	408a	363ab	371ab	350b	331b
esters					
methyl butanoate	523a	490ab	486ab	487ab	424b
ethyl butanoate	592a	541ab	520ab	531ab	448b
3-methylbutyl acetate	654a	526b	498bc	521bc	448c
ethyl heptanoate	649a	444b	397bc	398bc	341c
ketones					
2,3-butanedione	81a	77a	74a	81a	77a
2,3-hexanedione	142a	141a	126a	149a	137a
2-butanone	213a	216a	208a	215a	200a
2-heptanone	336a	327a	300a	322a	287a
2-octanone	401a	388a	384a	383a	335a
alcohols					
3-methyl-1-butanol	53a	55a	55a	55a	53a
1-pentanol	47a	48a	47a	66b	64b
1-heptanol	61a	62a	59a	62a	58a
terpenes					
linalool	45a	44a	41a	40a	36a
menthone	316a	298ab	257ab	270ab	253b
limonene	128a	57b	44b	46b	42b
CV (%)	6.5	8.4	9.2	8.9	12.1

^a Mean value of five independent measurements. Different letters in a row indicate significance at $p < 0.05$.

compounds. Therefore, it is reasonable to assume that the relatively low release rate observed for limonene in water (Table 3) was a result of flavor compound-compound interactions, which seem to have a particularly pronounced effect on the flavor release of hydrophobic compounds (27).

Release from Viscous Xanthan Solutions. Release rates of 20 aroma compounds in the xanthan solutions of different concentrations and viscosities were calculated after the collection of volatiles on Tenax traps at timed intervals (Table 3). The results clearly indicate that the different aroma compounds are affected differently by the thickener with respect to their release rates from the thickened, viscous solutions. No reduction in release rates was observed for alcohols. Moreover, in many cases the release rate of alcohols was even increased after xanthan was added to the media. However, this increase in release rates (the "salting out" effect) was statistically significant ($p < 0.05$) only for 1-pentanol. Nonsignificant decreases in release rates of ketones were also observed. The highest effect of the thickener on release kinetics was observed for the esters, aldehydes, and limonene. The release rate constants for limonene decreased by up to 67% in xanthan solutions compared to the release from the unthickened aqueous solution (Table 3). This decrease was the largest among all volatiles of this study. However, as can be seen from the data, the release rate values for limonene did not decrease as a result of increasing viscosity. The release rate constants remained nearly the same at all xanthan concentration levels from 0.02 to 0.80%, which corresponds to increases of viscosity from 0.0135 to 190 Pa s. This implies that some other factor rather than viscosity plays a role in the decrease of release rates. One explanation could be interactions between limonene and xanthan as evidenced in SHS-GC measurements. However, the other two terpenes, linalool and menthone, did not exhibit suppressed release.

Linalool release remained constant and independent of increasing viscosity and xanthan concentration as observed in SHS-GC measurements. For the menthone, only release from the solution with highest xanthan concentration (0.8%) was reduced at statistically significant level ($p < 0.05$). This observation is in accordance with findings of Secouard et al. (10) and Juteau et al. (11), who reported that, in contrast to limonene and ethyl butanoate, the release of oxygenated terpenes (linalool and menthol) was not affected by polysaccharide.

In terms of the extent of retention, limonene was followed by esters. Esters showed decreases of up to 47% in release rate constants. Once again, the data confirmed that the extent of decrease is related to the characteristics of the individual compound; more volatile and hydrophobic esters such as 3-methylbutyl acetate ($K_{aw} = 35.2 \times 10^{-3}$, $\log P = 2.30$) and ethyl heptanoate ($K_{aw} = 93.3 \times 10^{-3}$, $\log P = 3.31$) were suppressed to a higher degree and at the lower xanthan concentrations than the less volatile compounds methyl butanoate ($K_{aw} = 18.8 \times 10^{-3}$, $\log P = 1.28$) and ethyl butanoate ($K_{aw} = 26.8 \times 10^{-3}$, $\log P = 1.8$).

The release rate constants of aldehydes decreased by up to ~25%. The changes were mostly pronounced for 3-methylbutanal, hexanal, heptanal, and octanal. Release rates for the mono-unsaturated aldehyde (*E*)-2-hexenal also decreased; however, the decrease was not statistically significant ($p > 0.05$). Hexanal, on the other hand, showed a reduction in release rate of 24%, which was statistically significant. The difference in release behavior of these two aldehydes may be ascribed to the double bond in (*E*)-2-hexenal, which increases polarity.

In general, the trends observed in our study for aroma compounds in the kinetic release experiments correspond well with data obtained in thermodynamic measurements under equilibrium, where the most pronounced changes in thermodynamic characteristics were recorded for esters, aldehydes, and limonene after xanthan was added to the model system. In the case of alcohols, both thermodynamic and kinetic measurements showed a trend of increased release in the presence of xanthan. The release properties of ketones remained constant in both equilibrium and nonequilibrium measurements.

The release results from both thermodynamic and kinetic measurements for all aroma compounds are consistent with the proposition that the reduction in release is due to weak xanthan–aroma interactions occurring for the more hydrophobic aroma compounds, whereas viscosity itself does not influence the release significantly. If the viscosity itself was the cause of the decrease of release rates constants, then the gradually decreasing release rates should be obtained with no effect on equilibrium headspace concentrations. The conclusion that the bulk viscosity does not play a major role in the aroma release of xanthan-thickened solutions is in agreement with our previous findings for other hydrocolloid solutions (12, 15). Another indication that viscosity plays a subordinate role is that we could not relate suppression of aroma release to the c^* value, that is, to the concentration where the polymer chains start to overlap and entangle with one another (1, 19).

Due to its ordered conformation and tenuous network by association of the ordered chains, xanthan has properties between those of solutions and gels. The c^* value in our study was found to be 0.24%, which means that the release of aroma compounds from xanthan solutions should be reduced above this concentration as reported by Secouard et al. (10). However, this was not the case in our study. Depending on aroma class, the suppression appeared at different xanthan concentrations; the release rates of limonene and esters (ethyl heptanoate, 3-methylbutyl acetate)

significantly decreased already at only 0.02% xanthan concentration. Reduction of release rates constants for less hydrophobic and volatile esters, such as methyl butanoate and ethyl butanoate, was found at the highest viscosity, corresponding to a xanthan concentration of 0.8% (w/w). We could relate the suppression of release rate constants to c^* only for the three aldehydes (hexanal, heptanal, octanal). The statistically significant decrease in release rates was recorded above c^* for these compounds. Ketones, alcohols, and the oxygenated terpenes menthone and linalool were not affected by the increase of viscosity. Thus, xanthan concentration as well as the nature and physicochemical characteristics of aroma compounds, and not viscosity, plays the major role in determining the effect of the thickener on aroma release.

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