Influence of λ-Carrageenan on the Release of Systematic Series of Volatile Flavor Compounds from Viscous Food Model Systems

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The effect of λ-carrageenan addition level (0.1, 0.25, 0.4, and 0.5% w/w) and viscosity on the release of systematic series of aroma compounds (aldehydes, esters, ketones, and alcohols) was studied in thickened viscous solutions containing λ-carrageenan and 10 wt % of sucrose. Air−liquid partition coefficients K (37 °C) of a total of 43 aroma compounds were determined in pure water and in the λ-carrageenan solutions by static headspace gas chromatography. Mass transfer of the aroma compounds in water and in the thickened λ-carrageenan solutions which had a wide viscosity range was assessed by dynamic headspace gas chromatography. K (37 °C) increased as the carbon chain increased within each homologous series. Esters exhibited the highest volatility, followed by aldehydes, ketones, and alcohols. Under equilibrium, no overall effect of λ-carrageenan was found, except with the most hydrophobic compounds. Analysis of flavor release under nonequilibrium conditions revealed a suppressing effect of λ-carrageenan on the release rates of aroma compounds, and the extent of decrease in release rates was dependent on the physicochemical characteristics of the aroma compounds, with the largest effect for the most volatile compounds. However, none of the effects was of a magnitude similar to the obtained changes in the macroscopic viscosity, and the suppressing effects are therefore attributable to the thickener and not the physical properties of the increasingly viscous systems.

KEYWORDS: Aroma; volatiles; λ-carrageenan; partition coefficients; release rate; diffusion; thickeners; hydrocolloids; viscosity

INTRODUCTION

The increased concerns about dietary intake of fat and demand for new, convenience-orientated products in the past decade have prompted an increased usage of hydrocolloids as thickeners, stabilizers, texturizers, and fat replacers in a range of food formulations. However, even when used at low concentrations, hydrocolloids not only can change the structure and texture of the product, but also can lead to modifications of the flavor profile and/or perception (*1−9*). The flavor perception is determined by evaluating the sensory responses to different aroma compounds and levels as a function of time (*10*). To optimize product quality, it is important to understand how flavor compounds are released from such viscous food matrices. The factors that govern flavor release from any food product are phase partitioning and mass transport (*11*). Expressed as the ratio between flavor concentration in the air phase above the product, C_a, and flavor concentration in the product at equilibrium, C_p, the partition coefficient $K_{ap} = C_a/C_p$ defines the maximum potential extent of flavor release. Because the affinity of aroma compounds for the matrix is influenced by the nature of the matrix, the analysis of equilibrium headspace concentration above the product can help to estimate the level of interaction between flavor compounds and matrix. Under nonequilibrium conditions that exist during the food consumption, mass transfer participates in flavor release along with partitioning and defines the rate at which aroma compounds are transferred from one environment to another. Therefore, knowledge of aroma compounds behavior within the food and of their rates of partitioning is of interest in the flavoring of foods during product development, production, and of course consumption.

Carrageenan is a generic name for a family of natural, water-soluble galactans that are isolated from red seaweeds and principally composed of highly sulfated, alternating α(1→3)- and β(1→4)-linked galactose residues. Carrageenans are widely used in the food industry as viscosity, gel, or texture enhancers,

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stabilizers, and fat substitutes, and carrageenans are incorporated into a wide range of products such as yogurt, chocolate milk, jellies, relishes, sauces, frozen desserts, cheese, instant breakfast, and meat products (*12–14*). λ-Carrageenan has three sulfate groups per repeating disaccharide and, in contrast to κ- and ι-forms, does not undergo conformational ordering nor form gels (*15*); therefore, λ-carrageenan is used as nongelling, thickening agent.

The effect of various hydrocolloids on partitioning and release of aroma compounds has been investigated previously (*2–6, 16, 17*). Reported studies showed different impacts of hydrocolloids on flavor release, from no effect (*2, 17*) to large decreases in aroma headspace concentrations (*2–6*). However, the impact and extent of flavor retention by hydrocolloids differed depending on the type of hydrocolloid, aroma compounds, composition of the model system, and methods of analysis employed in the studies. Perception studies showed that taste and aroma were perceived less in carrageenan-thickened systems than in gellan, gelatin, and starch systems with comparable rheological properties (*8, 9*).

To better understand the influence of hydrocolloids on flavor perception versus flavor release, the specific thermodynamic effects must first be distinguished from the viscosity and sensory effects. Second, in food systems, the molecular diffusion must be understood versus convective or Eddy diffusion effects. Despite their widespread use in the food industry, very little is known about the influence of carrageenans and carrageenan-induced thickening on flavor release. This study was undertaken to investigate the effect of λ-carrageenan and macroscopic viscosity changes on the release of a range of aroma compounds under static and dynamic conditions in viscous solutions. In this connection, macroscopic viscosity relates to the viscosity of the system where water mobility remains nearly unchanged. To evaluate differences in release behavior among aroma compounds of different physicochemical properties, the partitioning of 43 aroma compounds of different chemical classes, carbon chain lengths, and functional groups was studied in water and λ-carrageenan-thickened solutions of four different concentrations. To evaluate the impact of hydrocolloid and structure of matrices on the release rates of aroma compounds and thus abolish Eddy diffusion effects, dynamic headspace analyses with only molecular diffusion were carried out in combination with gas chromatography.

MATERIALS AND METHODS

Sample Preparation. In total, 43 aroma compounds were used in this study, dissolved as stock solutions in ethanol as four different mixtures: **I**, **saturated aldehydes** (2-methylpropanal, 2-methylbutanal, 3-methylbutanal, 2-methylpentanal, butanal, pentanal, hexanal, heptanal, octanal, and nonanal); **II**, **esters** (2-methylbutyl acetate, 3-methylbutyl acetate, ethyl 2-methylbutanoate, methyl butanoate, ethyl butanoate, ethyl valerate, pentyl acetate, ethyl hexanoate, ethyl heptanoate, and ethyl octanoate); **III**, **ketones** (2,3-butanedione, 2,3-pentanedione, 2,3-hexanedione, 2,3-heptanedione, 2-butanone, 2-pentanone, 3-pentanone, 2-hexanone, 2-heptanone, 3-heptanone, 2-octanone, 2-nonanone, and 3-nonanone); and **IV**, **alcohols** (3-methyl-1-butanol, 2-methyl-1-butanol, 1-pentanol, 1-penten-3-ol, 3-pentanol, 1-hexanol, 1-heptanol, 1-octanol, and 1-octen-3-ol). Supplier, chemical purity, and physicochemical and odor characteristics (molecular weight, boiling point, hydrophobic fragmental constants, saturated vapor pressure, and odor descriptors) of these aroma compounds are presented in **Table 1**. All compounds were dissolved in ethanol at a concentration of 10 mg/g. Aliquots of each stock solution were further diluted in Milli-Q water to give a final concentration of 20 μg/g for every flavor compound. Diluted solutions were transferred into 22.3-mL gas chromatography (GC) vials for determination of air–water partition coefficients by static headspace GC (SHS-GC).

Thickened solutions with different carrageenan concentrations were prepared by using 0.1, 0.25, 0.4, and 0.5% (w/w) λ-carrageenan (FMC Biopolymer, Denmark) and 10% (w/w) sucrose (Sigma-Aldrich Chemie, Steinheim, Germany). The mixture of λ-carrageenan and sucrose was dissolved and gently stirred for 5 min in cold water at room temperature in order to solubilize ingredients. The solution was then heated to 85 °C, stirred for 5 min at this temperature, and cooled to ∼50 °C. For each λ-carrageenan concentration, every stock solution of aroma compounds was then added to a preweighed quantity of the viscous solution, such that the final concentration of aroma compounds was 20 ppm. Flavored solutions were transferred to the GC vials, capped, and stored for 24 h at ambient temperature before SHS-GC analysis.

Methods of Analysis. *Static Headspace Gas Chromatography (SHS-GC).* Liquid–vapor partition coefficients of the aroma compounds in water and thickened solutions were determined using a phase ratio variation (PRV) method that does not require the use of internal or external standards and was described by Kolb and Ettre (*18*). Five independent measurements were carried out for each thickened and aqueous system. Aromatized samples were equilibrated at 37 °C for 2 h and analyzed by static headspace gas chromatography as described previously (*17*).

Dynamic Headspace Gas Chromatography (DHS-GC). The release rates of the different aroma compounds were assessed by DHS-GC principally as described previously (*17*). In brief, samples were flushed with pure nitrogen for set periods of time (15, 30, 60, 90, 120, 240, 360, and 600 s), and then the released volatiles were collected on Tenax TA packed traps, thermally desorbed, and analyzed by GC with a flame ionization detector (FID). 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 determined during the collection of aroma compounds over 600 s on eight Tenax traps. Release rate constants (k) were calculated from the rate of adsorption on the Tenax traps as described by Roberts and Acree (*19*):

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

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

As the amounts of aroma compounds collected on the traps were negligible 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)$_{trap}$, from plotting micrograms of flavor compound collected from the trap vs time, were then determined.

Rheological Measurements. Thickened solutions were characterized by shear viscosity 24 h after preparation and equilibration at 37 °C. The measurements were performed 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. The measurement delay time was 20 s, and the integration time was 30 s.

Statistical Analysis. Analysis of variance (ANOVA) and Tukey's test were used to determine significant differences among the air–liquid partition coefficients and release rate constants (Minitab Statistical Software, Addison-Wesley, Reading, MA). Significance was established at $p < 0.05$.

RESULTS AND DISCUSSION

Viscosity. The influence of viscosity and matrix structure on the release of aroma compounds from thickened solutions was evaluated at different λ-carrageenan addition levels in a food model system containing 10% sucrose. The apparent viscosity of the model systems varied ∼50 000-fold in response to changes in λ-carrageenan concentrations (**Figure 1**). Solutions thickened by 0.1 and 0.2% λ-carrageenan showed slight shear

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Table 1. Chemical Characteristics of Volatile Compounds: Supplier, Purity, Molecular Weights (M_w), Boiling Points (bp), Hydrophobic Fragmental Constants (log P), Saturated Vapor Pressure (P_s), and Odor Descriptors at 25 °C

volatile compound	supplier	purity (%)	M_w, (g/mol)	bp, (°C)	log P^a	P_s (mmHg)^b	odor descriptors^{c,d}
			Aldehydes				
2-methylpropanal	Aldrich	99	72	65	0.82	147.40	green, pungent
3-methylbutanal	Fluka	98	86	93	1.34	49.32	herbaceous, green, malty
2-methylbutanal	Acros	95	86	93	1.34	49.32	green, cocoa and coffee
2-methylpentanal	Aldrich	97	100	117	1.86	16.92	−
butanal	Fluka	98	72	75	0.81	95.97	green, pungent
pentanal	Aldrich	99	86	103	1.29	31.79	pungent, nutty
hexanal	Aldrich	98	100	128	1.80	10.89	grassy, leafy, tallowy
heptanal	Aldrich	95	114	153	2.32	3.85	fatty, pungent
octanal	Aldrich	99	128	171	2.86	2.07	fatty
nonanal	Aldrich	99	142	191	3.36	0.53	fatty, fruity, citrus
			Esters				
methyl butanoate	Fluka	99	102	103	1.28	31.13	sweet, apple
ethyl 2-methylbutanoate	Acros	99	130	133	2.31	9.86	fruity
3-methylbutyl acetate	Merck	98	130	143	2.3	5.68	banana
2-methylbutyl acetate	Aldrich	94	130	140	2.3	7.85	apple, banana
pentyl acetate	Aldrich	99	130	149	2.31	3.93	−
ethyl butanoate	Aldrich	98	116	122	1.80	13.94	fruity, pineapple
ethyl pentanoate	Aldrich	99	130	146	2.32	4.75	fruity, apple
ethyl hexanoate	Aldrich	98	144	167	2.80	1.66	fruity, pineapple, banana
ethyl heptanoate	Aldrich	99	158	187	3.31	0.60	fruity, cognac
ethyl octanoate	Aldrich	98	172	208	3.83	0.22	fatty, fruity, floral
			Ketones				
2,3-butanedione	Aldrich	98	86	88	−1.80	62.28	buttery
2,3-pentanedione	Aldrich	97	100	108	−0.85	26.41	sweet, buttery
2,3-hexanedione	Aldrich	90	114	128	−0.78	12.44	sweet, creamy
2,3-heptanedione	Aldrich	98	128	150	−0.25	3.98	sweet, cheesy, oily
2-butanone	Aldrich	99	72	80	0.33	114.52	etheric
2-pentanone	Aldrich	97	86	102	0.85	38.58	wine, acetone
3-pentanone	Aldrich	99	86	102	0.85	35.77	−
2-hexanone	Aldrich	98	100	128	1.37	13.33	−
3-heptanone	Fluka	97	114	147	1.90	3.05	green, fruity
2-heptanone	Aldrich	98	114	151	1.90	4.73	soapy, banana
2-octanone	Aldrich	98	128	172	2.42	1.72	floral, green, fruity
3-nonanone	Aldrich	99	142	190	2.94	0.55	leafy, herbaceous, fruity
2-nonanone	Aldrich	99	142	195	2.94	0.64	rose, tea, soapy
			Alcohols				
3-methyl-1-butanol	Fluka	98	88	131	1.35	4.16	malty, fruity-winey
2-methyl-1-butanol	Merck	99	88	128	1.35	4.76	malty
1-pentanol	Aldrich	99	88	138	1.35	2.81	fusel
1-penten-3-ol	Aldrich	99	86	115	0.94	11.18	butter, green
3-pentanol	Fluka	99	88	116	1.35	9.66	−
1-hexanol	Aldrich	98	102	158	1.87	0.95	green, flowery
3-hexanol	Aldrich	97	102	136	1.87	3.39	ethereal, medicinal
1-heptanol	Aldrich	98	116	176	2.39	0.32	fatty, pungent
1-octanol	Aldrich	99	130	195	2.90	0.11	fresh, orange
1-octen-3-ol	Aldrich	98	128	175	2.50	0.53	metallic, mushroom

^{a} Calculated by the method of Rekker (*28*). ^{b} Calculated with ACD demosoftware. ^{c} Reference *29*. ^{d} Reference *30*.
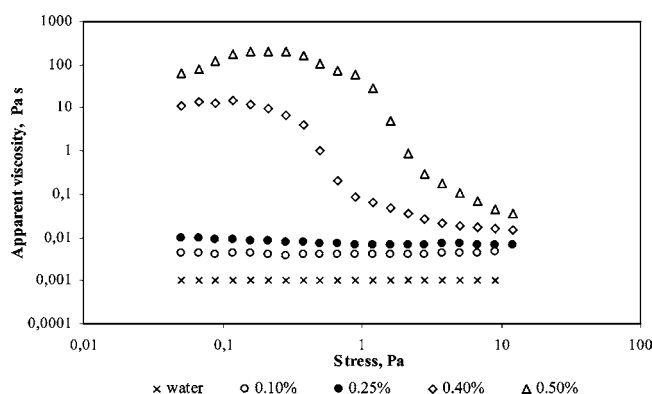
Figure 1. Viscosities curves of λ-carrageenan solutions of different concentrations (% w/w).

thinning behavior within the range of applied stress, whereas systems with 0.4 and 0.5% λ-carrageenan exhibited formation

of structured zones, as evidenced by their high apparent viscosities at low applied stress levels (**Figure 1**). Though λ-carrageenan is described as a nongelling, thickening, and viscosity-increasing agent (*12*, *15*), the formation of incipient gel could thus be observed in the test systems having the highest levels of carrageenan.

Partitioning of Aroma Compounds. *Pure Water.* To evaluate the influence of the presence of λ-carrageenan on the thermodynamic properties of the thickened model systems, air–water partition coefficients (K_{aw}) of the 43 aroma compounds were first measured in pure water at 37 °C. The results revealed that K_{aw} differed significantly depending on the class of compound, chain length, the functional group, and the position of the functional group. As expected, K_{aw} increased with increasing C number in the molecule within each homologous series (**Figure 2**). Among homologous series, esters showed the highest volatility, followed by aldehydes, ketones, and diketones, with alcohols as the least volatile series. These findings are in
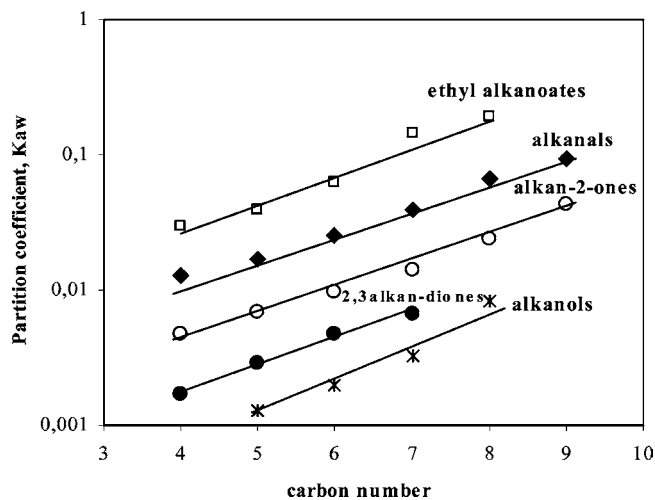
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Figure 2. Average air—water partition coefficients, K_{aw}, of aldehydes, esters, ketones, diketones, and alcohols at 37 °C ($n = 5$).

agreement with the classical studies by Buttery et al. (*20*, *21*), who also reported esters and aliphatic aldehydes to be the most volatile substance class, with methyl ketones intermediate, and alcohols the least volatile. Air—water partitioning values of K_{aw} for C_4—C_8 alkanals, experimentally determined in the study by Hall and Andersson (*22*), are also in a good agreement with those obtained in our study.

It is worth mentioning that K_{aw} depends on the presence of functional groups as such, but it is also influenced by the position of this functional group in the molecule. Aldehydes with a —CH_3 group (methylalkanals) were more volatile than those with a straight chain (alkanals) (**Table 2**). Ketones with functional "keto" group at the third position within the molecule (3-pentanone, 3-heptanone, 3-nonanone) had higher K_{aw} than those having the keto group at the second carbon atom (2-pentanone, 2-heptanone, 2-nonanone). The volatility of ketones was significantly suppressed when two "keto" groups were present in the molecule, thus making the series of 2,3-alkanediones less volatile than the 2-alkanones (**Table 2**). Among the alcohol series, the consistency between partitioning of 1-, 2-, and 3-alkanols could hardly be observed, most probably because of their low vapor pressure, which gives higher experimental uncertainty.

Viscous Carrageenan Solutions. To estimate the influence of λ-carrageenan on thermodynamic properties of aromatized aqueous systems, air—liquid partition coefficients K were measured in systems containing different amounts of λ-carrageenan (**Table 2**). Overall, there was no observed retention effect by λ-carrageenan for most of the compounds employed in this study. However, some effect of the presence of the hydrocolloid on headspace concentrations for aroma compounds with high partition coefficients, and thus higher C number and log P values, was observed. This tendency was noted within each homologous series. Release of C_9 ketones at equilibrium was reduced by ~40 and 60% for 3- and 2-nonanone, respectively, in the presence of λ-carrageenan (independent of dose); meanwhile, a significant reduction of aldehydes' headspace concentrations was observed for C_6—C_9 alkanals, which corresponded to a reduction of ~15—44% compared to release from water. As for the esters, only the release of ethyl octanoate (K_{aw} = 190 × 10^{-3}, log P = 3.83) was significantly reduced after addition of λ-carrageenan to the model system. Alcohols partitioning showed a tendency toward increased headspace concentration at equilibrium in the presence of λ-carrageenan. This could be a "salting out" effect. However, the increase was

Table 2. Air—Liquid Partition Coefficients of Aroma Compounds ($K \times 10^{-3}$)[a] in Water and in λ-Carrageenan Solutions of Different Concentrations (%)

compound	water	λ-carrageenan concentration			
		0.10%	0.25%	0.40%	0.50%
Aldehydes					
2-methylpropanal	22.3[a]	22.0[a]	19.9[a]	23.0[a]	21.2[a]
2-methylbutanal	31.6[a]	30.5[a]	29.9[a]	32.7[a]	33.7[a]
3-methylbutanal	25.7[a]	26.3[a]	24.7[a]	26.4[a]	26.7[a]
2-methylpentanal	43.9[a]	39.6[a]	40.9[a]	44.1[a]	42.7[a]
butanal	12.7[a]	10.9[ab]	7.6[b]	10.2[ab]	10.5[ab]
pentanal	16.9[a]	15.7[ab]	15.8[ab]	12.9[b]	16.2[ab]
hexanal	25.7[a]	21.9[b]	22.0[b]	23.6[ab]	23.8[ab]
heptanal	39.4[a]	30.1[b]	31.5[b]	27.6[b]	32.8[b]
octanal	67.5[a]	51.5[b]	47.5[b]	52.2[b]	51.3[b]
nonanal	95.0[a]	67.3[b]	64.4[b]	60.0[b]	53.4[b]
Esters					
methyl butanoate	21.3[a]	25.3[a]	22.7[a]	23.6[a]	23.9[a]
ethyl 2-methylbutanoate	66.6[a]	66.2[a]	61.2[a]	63.6[a]	62.3[a]
3-methylbutyl acetate	40.3[a]	47.0[a]	48.4[a]	42.6[a]	42.7[a]
2-methylbutyl acetate	39.2[a]	36.3[a]	39.3[a]	34.0[a]	38.4[a]
pentyl acetate	42.2[a]	41.9[a]	37.8[a]	38.9[a]	39.2[a]
ethyl butanoate	29.9[a]	33.1[a]	31.1[a]	32.9[a]	33.0[a]
ethyl pentanoate	39.0[a]	47.4[a]	44.7[a]	44.8[a]	44.4[a]
ethyl hexanoate	62.0[a]	67.5[a]	67.9[a]	70.9[a]	73.1[a]
ethyl heptanoate	146.7[a]	128.5[a]	125.0[a]	121.5[a,b]	89.6[b]
ethyl octanoate	190.6[a]	132.6[ab]	102.4[b]	89.5[b]	105.6[b]
Ketones					
2,3-butanedione	1.7[a]	2.3[ab]	2.3[ab]	2.8[bc]	3.3[c]
2,3-pentanedione	2.9[a]	2.5[ab]	1.9[b]	2.9[a]	3.3[a]
2,3-hexanedione	4.7[ab]	4.0[a]	4.3[b]	5.5[b]	5.5[b]
2,3-heptanedione	6.7[ab]	5.6[a]	7.0[ab]	8.0[b]	8.2[b]
2-butanone	4.8[a]	5.0[a]	5.0[a]	4.7[a]	5.2[a]
2-pentanone	6.9[a]	7.7[a]	6.6[a]	6.3[a]	6.8[a]
3-pentanone	8.2[a]	8.8[a]	7.9[a]	8.3[a]	9.0[a]
2-hexanone	9.6[a]	8.7[a]	8.6[a]	9.1[a]	10.0[a]
3-heptanone	17.2[a]	16.2[a]	17.1[a]	16.6[a]	17.6[a]
2-heptanone	14.1[a]	14.3[a]	14.7[a]	14.8[a]	14.4[a]
2-octanone	23.9[a]	21.6[a]	22.9[a]	19.5[a]	22.8[a]
3-nonanone	48.9[a]	31.9[b]	36.1[b]	31.2[b]	30.4[b]
2-nonanone	43.4[a]	25.6[b]	25.0[b]	18.6[b]	17.8[b]
Alcohols					
3-methyl-1-butanol	1.3[a]	1.5[a]	1.3[a]	1.3[a]	1.3[a]
2-methyl-1-butanol	1.5[a]	1.6[a]	1.6[a]	1.3[a]	1.6[a]
1-pentanol	1.1[a]	1.8[b]	1.4[ab]	1.3[a]	1.6[b]
1-penten-3-ol	1.4[a]	1.4[a]	1.3[a]	1.4[a]	1.2[a]
3-pentanol	1.7[a]	1.8[a]	2.0[a]	1.9[a]	1.9[a]
1-hexanol	2.0[a]	2.0[a]	1.7[ab]	1.4[b]	2.1[a]
3-hexanol	2.5[a]	2.5[a]	2.4[a]	2.2[a]	2.4[a]
1-heptanol	3.3[a]	3.7[a]	2.5[b]	1.3[b]	1.5[b]
1-octanol	8.2[a]	4.1[b]	3.2[b]	3.0[b]	2.9[b]
1-octen-3-ol	4.4[a]	5.1[a]	2.8[b]	3.0[b]	2.8[b]
CV (%)	9.8	11.0	12.3	14.2	12.5

[a] Mean value of five measurements. Different superscript letters row-wise indicate significance at $p < 0.05$.

not found to reach statistical significance ($p > 0.05$), as can be seen from the K values obtained for 2- and 3-methyl-1-butanol, 3-pentanol, 1-hexanol, and 1-heptanol (**Table 2**). For higher C alcohols, which possess high log P, such as 1-heptanol, 1-octanol, and 1-octen-3-ol, the suppressed partitioning was observed in the systems with λ-carrageenan.

Overall, the headspace results obtained under equilibrium conditions indicate that addition of λ-carrageenan and increasing concentration does not affect flavor release under equilibrium conditions, showing an absence of global flavor—matrix interactions. However, some exceptional flavor—matrix interactions are occurring in the presence of λ-carrageenan. These interactions are most pronounced for highly volatile and hydrophobic compounds but are not significant for compounds having low

K_{aw} and log P values. No particular trend was observed between retention and chemical class of aroma compounds. These observations parallel the findings of Yven et al. (*4*), who reported that aroma compounds with high K_{aw} were most affected by the presence of hydrocolloids in the system. This indicates that the observations may be due to weak interactions between highly hydrophobic compounds and the carrageenan chains. However, the differences in partitioning among all thickened solutions of different λ-carrageenan concentrations (0.1, 0.25, 0.4, and 0.5%) that comprises a structural range from thin liquid to incipient gel (**Figure 1**) were not significantly different. That implies that neither increasing concentration of λ-carrageenan nor any formed network has a suppressing influence on the equilibrium headspace concentrations. If that were the case, the retention should be dropping progressively.

In the recent study by Juteau et al. (*5*), the equilibrium concentrations of ethyl butanoate and ethyl hexanoate above aqueous NaCl solutions (0.1, 0.3, and 0.5%) were found to be significantly reduced after addition of 1% of ι-carrageenan. However, no differences in aroma release were observed between water and polysaccharide solutions (0.5 and 1%) after ι-carrageenan was dispersed into water without NaCl addition. In analogy, the release of both ethyl butanoate and ethyl hexanoate at equilibrium was not influenced by the presence of λ-carrageenan in our study. This is not surprising, taking into account that binding constants for carrageenan are very low (*23*). However, one should be aware of this when comparing results obtained from experiments with different model or food systems. Depending on the model system which is targeted to simulate particular food systems, different components and their quantities (for example, hydrocolloids, salts, sugars, proteins) are involved in each particular study, which may have an essential influence on the results. Being a method that measures interactions of aroma compounds with solutes present in the system, static headspace analysis takes into account global interactions and retention occurring between aroma compounds and matrices. Therefore, the presence of other ingredients or factors such as ionic strength, salt, sugar, or protein in the matrix should be carefully considered when comparing data from different studies.

Dynamic Headspace Measurements of Flavor Release. To develop a full understanding how the release of aroma compounds is (or is not) influenced by the presence of hydrocolloid λ-carrageenan and matrix structure, the evaluation of aroma release kinetics was carried out under nonequilibrium conditions in water and λ-carrageenan solutions of different viscosities. Nonequilibrium is the driving force for mass transport, which together with phase partitioning are the main factors that control flavor release from foods (*11*).

Release from Water. To estimate the influence of λ-carrageenan on the mass transfer and thus release rates of aroma compounds, the release rate constants of series of aroma compounds were determined, primarily in aqueous solutions and later in λ-carrageenan-thickened viscous solutions (0.1, 0.25, 0.4, and 0.5%). The release of aroma compounds from aqueous solutions under nonequilibrium showed tendencies similar to those observed under equilibrium conditions among the tested series of homologues: esters were most volatile and had the highest release rates, followed by aldehydes, ketones, diketones, and alcohols as the least volatile series (**Figure 3**). The release rate constant found for 1-octanol (C_8) seems to be too low. This may be a result of retarded volatilization due to very low vapor pressure ($P = 0.11$ mmHg) of this compound.

The results indicate that, even under nonequilibrium conditions, phase partitioning plays a main role in the release. Because
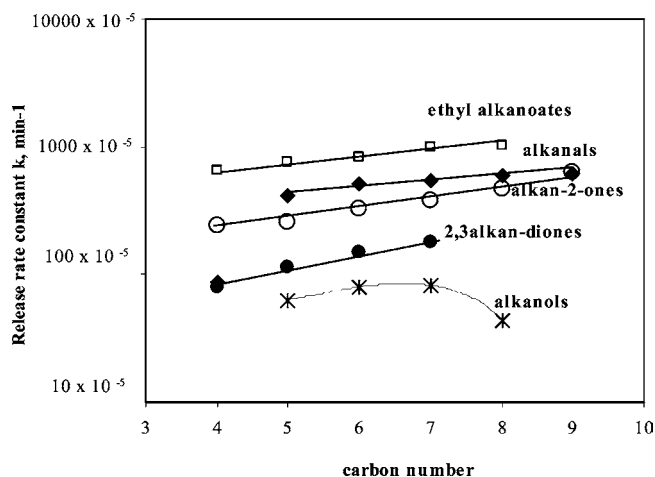

Figure 3. Average release rate constants k (min^{-1}) of aldehydes, esters, ketones, diketones, and alcohols at 37 °C ($n = 5$).

one of the goals of the present study was to elucidate the impact of matrix structure on the release of aroma compounds, it was decided to consider only molecular diffusion and not to implement any mechanical treatment of the system which leads to the breakage of matrix structure, thus abolishing its effect on release. In such a system, the boundary layers at the interface are stagnant, and mass transport through these layers is determined by molecular diffusion, which is a result of random movements of molecules. Thus, the "stagnant film" model can be applied to describe mass transport, which varies with diffusion coefficient and thickness of the stagnant layer (*11*). Because the rate of molecular diffusion varied only slightly with flavor type, the phase partitioning remained the governing factor for flavor release under nonequilibrium conditions with molecular diffusion employed in static liquid phase.

Release from λ-Carrageenan Solutions. After the release rate constants of aroma compounds from water were measured under nonequilibrium conditions, the same experiments were carried out in λ-carrageenan-thickened solutions of four different concentrations and structures. Analysis of release rate constants, which can be directly related to interfacial mass transfer, and thus diffusion, showed that, overall, there was a global effect of λ-carrageenan on release rates of aroma compounds from the λ-carrageenan-thickened solutions (**Table 3**). The release rates decreased for almost all of the compounds after addition of λ-carrageenan into the system. However, the extent of the decrease varied with chemical class, chain length, and hydrophobicity of aroma compounds. The reduction in release rate constants was highest for esters; their decrease in release rates constants was observed in a range of 8−75% of that measured in aqueous solution. Esters were followed by aldehydes with decreases up to 67%, and ketones with ∼30% decrease. The release rates of alcohols were affected least, with a maximum decrease of ∼20%, which in many cases was found to be statistically insignificant ($p > 0.05$). Furthermore, within the same homologous series, the reduction in release rates was increasing with increasing K_{aw} of the flavor compound (**Table 3**). The data obtained for release under nonequilibrium conditions thus clearly indicate that release rates, and thus diffusion of aroma compounds, are affected by the presence of λ-carrageenan rather than by its level, and hence its effect on matrix structure, in the solutions. However, the character and extent of this effect varied among different flavor compounds.

Aldehydes. Release of aldehydes was suppressed significantly at 0.25, 0.4, and 0.5% concentrations of carrageenan; meanwhile, the release rates at 0.1% were not significantly different from

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

compound	water	carrageenan solutions (%)			
		0.10	0.25	0.40	0.50
Aldehydes					
2-methylpropanal	120[a]	113[a]	68[b]	61[b]	74[b]
2-methylbutanal	529[a]	504[a]	300[b]	294[b]	292[b]
3-methylbutanal	863[a]	807[a]	447[b]	404[b]	396[b]
2-methylpentanal	749[a]	694[a]	339[b]	312[b]	299[b]
butanal	86[a]	94[a]	86[a]	87[a]	90[a]
pentanal	417[a]	402[a]	248[b]	247[b]	259[b]
hexanal	513[a]	486[a]	270[b]	269[b]	268[b]
heptanal	546[a]	514[a]	257[b]	236[b]	230[b]
octanal	602[a]	565[a]	247[b]	226[b]	228[b]
nonanal	620[a]	552[a]	211[b]	220[b]	206[b]
Esters					
methyl butanoate	602[a]	556[ab]	506[b]	468[bc]	395[c]
ethyl 2-methylbutanoate	986[a]	764[b]	741[b]	685[b]	471[c]
3-methylbutyl acetate	814[a]	625[b]	632[b]	528[bc]	417[c]
2-methylbutyl acetate	812[a]	625[b]	583[b]	527[bc]	417[c]
pentyl acetate	707[a]	563[b]	538[b]	480[bc]	387[c]
ethyl butanoate	647[a]	570[ab]	517[b]	422[bc]	382[c]
ethyl pentanoate	760[a]	587[b]	563[b]	499[bc]	396[c]
ethyl hexanoate	834[a]	575[b]	568[b]	533[bc]	387[c]
ethyl heptanoate	983[a]	506[b]	478[b]	460[b]	345[c]
ethyl octanoate	1034[a]	362[b]	338[b]	335[b]	256[c]
Ketones					
2,3-butanedione	79[a]	67[b]	62[b]	62[b]	59[b]
2,3-pentanedione	115[a]	101[ab]	98[b]	96[b]	97[b]
2,3-hexanedione	150[a]	122[ab]	114[b]	113[b]	113[b]
2,3-heptanedione	180[a]	151[ab]	140[b]	142[b]	136[b]
2-butanone	244[a]	215[ab]	211[b]	210[b]	203[b]
2-pentanone	260[a]	228[ab]	222[b]	216[b]	222[b]
3-pentanone	331[a]	293[ab]	293[ab]	283[b]	285[b]
2-hexanone	324[a]	280[ab]	280[ab]	272[b]	274[b]
3-heptanone	398[a]	373[a]	341[a]	345[a]	354[a]
2-heptanone	379[a]	322[ab]	318[a]	316[b]	320[b]
2-octanone	462[a]	390[ab]	366[b]	366[b]	367[b]
3-nonanone	679[a]	536[b]	528[b]	480[b]	480[b]
2-nonanone	623[a]	504[b]	499[b]	478[b]	453[b]
Alcohols					
3-methyl-1-butanol	71[a]	65[a]	61[a]	64[a]	60[a]
2-methyl-1-butanol	71[a]	60[a]	58[a]	63[a]	60[a]
1-pentanol	63[a]	53[a]	53[a]	54[a]	51[a]
1-penten-3-ol	66[a]	55[a]	53[a]	58[a]	55[a]
3-pentanol	88[a]	72[a]	72[a]	74[a]	70[a]
1-hexanol	80[a]	67[a]	67[a]	73[a]	65[a]
3-hexanol	123[a]	99[ab]	98[ab]	101[a,b]	92[b]
1-heptanol	80[a]	69[a]	69[a]	73[a]	70[a]
1-octanol	43[a]	53[a]	45[a]	67[b]	50[a]
1-octen-3-ol	115[a]	108[a]	107[a]	121[a]	106[a]
CV (%)	9.0	11.5	10.4	12.0	14.2

[a] Mean value of five independent measurements. Different superscript letters row-wise indicate significance at $p < 0.05$.

those obtained in pure water. The suppression of aldehydes release rates observed at 0.25% λ-carrageenan concentration remained nearly constant for increased carrageenan concentrations of 0.4 and 0.5% (w/w), while the matrix structure dramatically changed from liquid (0.25%) to high-viscosity, structured state (0.4 and 0.5%) (**Figure 1**). It follows that changing the viscosity from 0.01 Pa s (0.25% solution) to 200 Pa s (0.5% solution), and thus the matrix structure, did not affect the release of aldehydes from thickened solutions. One can note that decreased release rates relate to K_{aw} and log P within homologous series: i.e., the higher K_{aw} (volatility) and log P (hydrophobicity) of a compound, the larger the decrease in release rates. When comparing the results of release rates of aldehydes obtained in this study with those reported in pectin-

thickened systems (*17*), an obstruction, i.e., a retarding effect on flavor release of λ-carrageenan, could thus be discerned in thickened solutions. Release rates of aldehydes remained unchanged in the systems thickened by high methoxylated pectin of a range of viscosities and concentrations similar to those of λ-carrageenan used in this study. As in the previous study with pectin (*17*), butanal exhibited exceptional behavior: among all aldehydes it was the only compound for which the release rate was not suppressed by carrageenan at all concentrations and matrix structures. The release of butanal was even higher after hydrocolloid was added; however, this increase was statistically insignificant (**Table 3**). The results on aldehydes release imply that λ-carrageenan, despite being a hydrophilic compound, might have more hydrophobic character than pectin.

Esters. The release of esters from λ-carrageenan showed slightly different character than that of aldehydes. Their release was suppressed to a higher degree than that of aldehydes. The significant changes in release rates were recorded at λ-carrageenan concentrations as low as 0.1%, and these changes decreased progressively with increasing λ-carrageenan content in the system (**Table 3**). The decrease in release rates was dependent on compound characteristics: the higher log P and K_{aw} of the esters, the larger the retention. The least reduction in release rate was found for methyl butanoate, whose release was reduced in the range of only 8−34% in λ-carrageenan solutions. Methyl butanoate has a log $P = 1.28$ and a $K_{aw} = 21.3 \times 10^{-3}$, which are the smallest among the esters. The highest suppression (65−75%) in release rates was for ethyl octanoate, which possesses the highest log $P = 3.83$ and $K_{aw} = 190.63 \times 10^{-3}$ values among the homologous esters examined in this study. Esters are the most volatile series among all compounds, with the highest partitioning and release rates in water. So, it is very likely that, during the polymer network formation, their release is affected the most.

Ketones. The decrease in release rates of ketones was less than those obtained with esters and aldehydes, but the suppression was nevertheless nearly ∼30%. The tendencies in the release rates was similar to the case of aldehydes: at 0.1% λ-carrageenan concentration, the release rates of most of the ketones were not suppressed significantly, except for most hydrophobic and volatile ketones, such as 3- and 2-nonanone (**Table 3**). The release rates of ketones in λ-carrageenan solutions of 0.25, 0.4, and 0.5% concentration differed significantly from those obtained in water; however, as in the case of aldehydes, no differences were observed among release rates in these solutions containing different amounts of λ-carrageenan and formed structures. Thus, there was no influence of increased λ-carrageenan concentration and matrix structure on the release.

Alcohols. Alcohols turned out to be affected the least of all the compounds employed in this study. Their release rates were reduced a maximum of ∼25% and in most cases did not differ significantly from release rates obtained in pure water. Most probably the reason for this behavior of alcohols is also related to their volatility: being the least volatile series among all the compounds studied, they are the least affected by changes in the water phase after λ-carrageenan is introduced to the solutions.

Altogether, the results obtained in this study show that there is a specific effect of λ-carrageenan on the release of flavor compounds from thickened viscous solutions. However, none of the effects obtained were similar in magnitude to the changes in the viscosity. If the increased viscosity, i.e., the polymer network formation, per se were the limiting parameter on the release, the drop in release rates would be of a much larger

magnitude than observed in this study. Furthermore, the changes in viscosity in the ∼20 000-folds range (0.25−0.5% λ-carrageenan) did not exert a significant effect on the release rates of aldehydes, ketones, and alcohols at all.

Because static headspace analysis under equilibrium conditions showed that weak interactions are occurring only for highly volatile and hydrophobic compounds, it is very likely that λ-carrageenan affects only the kinetics of flavor release by restricting diffusion of flavor compounds. This phenomenon parallels findings obtained with carboxymethylcellulose (CMC) (*11*), where no particular changes in aroma headspace concentrations under equilibrium conditions in the presence of CMC were observed. On the other hand, significant changes were reported under nonequilibrium or dynamic headspace analysis, where the highest decreases in flavor release rates were observed for the most volatile flavor compounds. The reduced release rates of aroma compounds under dynamic conditions were interpreted as an effect of viscosity (*11*). The significant decrease in the release of highly volatile compounds was also demonstrated in solutions of guar gum and CMC by Roberts et al. (*3*), who attributed the decrease to both viscosity and binding.

Except for some studies on the release of single flavor compounds (*5, 24*), no comprehensive data are available on the release of aroma compounds from carrageenan-thickened systems. The release of ethyl butanoate, ethyl hexanoate, and linalool from ι-carrageenan solutions and gels was studied by Juteau et al. (*5*). Their work showed suppressed release of both esters after addition of ι-carrageenan to the model system. The same tendency as seen in our present study was observed: above the certain limit where the formation of the network took place, and which was achieved by dispersing 1% ι-carrageenan in 0.3% NaCl aqueous solution, no further effect of higher structuration (0.5% NaCl) on release slopes of ethyl butanoate and ethyl hexanoate was observed. Furthermore, no effect of either polysaccharide addition or network formation was found for linalool. That is in good agreement with our study, where the release rates of alcohols were not affected by the presence of λ-carrageenan, whereas the decrease in release rates was most pronounced for esters among all the chemical classes studied. The explanation for the decreased release rate of esters in the study of Juteau et al. (*5*) was decreased aroma diffusion rate through macromolecule entanglement induced by weak interactions between the polymer chains and esters. However, by measuring concentrations of ethyl butanoate and ethyl hexanoate at equilibrium, the authors observed significant reductions in headspace concentrations, which implies the existence of molecular interactions between both esters and ι-carrageenan in the presence of NaCl (*5*). So, it is questionable which of the two control parameters—thermodynamic with observed molecular interactions after addition of NaCl to the system or kinetic with recorded reduced mobility due to network formation—affected the release of the esters under nonequilibrium conditions. Our present study showed that the thermodynamic properties of the λ-carrageenan−aroma system remained unchanged in the presence of λ-carrageenan for most of the compounds, so the decrease in flavor release rates might be attributed to high resistance to mass transfer in λ-carrageenan solutions. Unlike κ- and ι-carrageenans, λ-carrageenan does not possess anhydro bridges; thus, helix formation is not occurring at relevant temperatures and molecules remain distributed randomly in the solutions (*15*). Nevertheless, despite their different chemical and functional properties, carrageenans have been reported to lower diffusion of small molecules such as glucose and sucrose (*25, 26*). κ-Carrageenan affects glucose

diffusion because of an obstruction effect which is mainly caused by the hydration water of the gels (*25*). Furthermore, recent work reported by Götz et al. (*27*) on characterization of the structure and transport mechanism of serum in dispersed hydrocolloid systems by NMR diffusion experiments demonstrated that λ-carrageenan, considered as a viscosity increaser, shows restricted diffusion and gel behavior for all studied temperatures between 5 and 50 °C. It is likely that λ-carrageenan molecules are themselves dissolved in the polymer network system, and thus diffusion is reduced (*27*). Altogether, these observations may explain why the diffusion of flavor molecules, i.e., the release rates, was restricted in the λ-carrageenan system.

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