

## Effect of Gelatinization and Starch–Emulsifier Interactions on Aroma Release from Starch-Rich Model Systems

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Release of selected volatile aldehyde compounds from starch-rich matrices was studied by headspace extraction, using solid-phase microextraction, and gas chromatography. Changes in the rheological properties of the starch-based matrices, due to starch concentration, gelatinization, and interactions with emulsifiers, were studied by steady shear and dynamic methods. The degree of volatile retention was found to depend on the compound properties, starch concentration, native structure of the granules, and presence of emulsifiers. The nongelatinized starch granules were more effective in lowering the volatile headspace quantities. Loss of the native structural integrity of the granules decreases the retention ability. For the nongelatinized starch dispersions, the more hydrophilic emulsifier showed a more pronounced effect on the matrix rheology and also on the aroma retention. A different behavior was observed for the gelatinized systems. Interpretation of the volatile release profiles was made on the basis of the matrix physical properties and interactions among components.

**KEYWORDS:** Starch; gelatinization; aroma release; starch–emulsifier interactions; headspace gas chromatography; SPME extraction; rheology

### INTRODUCTION

Human perception of flavor is closely related to the nature and concentration of the aroma compounds in the vapor phase. The amount of these compounds that reach the sensory system is influenced by their volatility and by their affinity for particular food matrix constituents. Temperature, pH, ionic strength, and matrix complexity are some of the factors that may influence the rate and extent of aroma release and thus consumer perception. Aroma stability during storage is also related to the interactions of the aroma compounds with other food components present in the food matrix. The subject of flavor interactions with other food components is clearly a relevant research subject with important technological implications. Many studies have addressed this subject and have considered the most important food macromolecules: proteins and polysaccharides.

Changes in the matrix physical properties, for example, increasing viscosity or gelation, may be expected to decrease mass transfer through the matrix and thus increase the retention of aroma compounds. Diffusivities of some volatiles were shown to be inversely related to the viscosity of the matrix (1). For some hydrocolloids, the decrease in headspace volatiles has been related either to a simple viscosity increase or to more specific effects depending on the gum/odorant combination (2–4).

In the case of polysaccharides, the interaction with aroma compounds is characterized by a high variability, depending on the nature of the macromolecule and the volatile compound.

Different interaction modes and retention mechanisms have been described, including adsorption or inclusion with starches, dextrans, galactomannans, and hydroxypropylcelluloses. A salting-out effect prevails with dextrans at high concentrations (5, 6).

The ability of gelatinized starch to interact with several ligands such as iodine, some aroma compounds, and emulsifiers has been reported and related to the formation of inclusion complexes (5, 7–12). It is generally thought that these interactions are mainly due to the amylose fraction. The size and shape of the amylose helix have been shown to be affected by the ligand (10). Amylopectin can form only weak inclusion complexes or none at all (13, 14). Recently, it has been shown that microcellular foams of dried starch, prepared from gelatinized starch granules, are effective in adsorbing and lowering the headspace partial pressure of many volatile compounds, an effect attributed to the significant microporous structure of these systems (15).

Most previous studies on starch–flavor interactions have focused on gelatinized systems and/or used diluted aqueous dispersions of starch, whereas the native starch granules have been considered virtually inert entities in many of these studies. One of the few exceptions includes the work of Hau and co-workers (16), where it was reported the sorption or binding of volatile compounds by starch powder, at room temperature, with the volatile headspace partial pressure reduced to ~50–80%. Also, spherical aggregates of native small starch granules, obtained by spray-drying the starch dispersions in the presence of a binding agent, have been proposed as potential flavor carriers (17).

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**Table 1.** Some Characteristics of the Studied Aroma Compounds

compound/source	$d^{20}_4$ <sup>a</sup>	$M_r$ <sup>b</sup>	boiling point (°C)	odor description	concn <sup>c</sup> (mmol dm <sup>-3</sup> )
hexanal (98%, Aldrich)	0.834	100.16	131	freshly cut grass; horseradish; fatty	96
nonanal (97%, Fluka)	0.827	142.24	191	fruity; flowery; fresh	14
<i>trans</i> -2-nonenal (97%, Aldrich)	0.846	140.23	na <sup>d</sup>	green; cucumber; aldehydic; fatty; citrus	26
decanal (97%, Fluka)	0.832	156.27	208	cooked; waxy; orange peel; floral	8
( <i>E,E</i> )-2,4-decadienal (85–90%, Fluka)	0.868	152.24	280	orange; sweet; fresh; fatty; green	23

<sup>a</sup> Compound density at 20 °C, relative to water at 4 °C. <sup>b</sup> Relative molecular mass. <sup>c</sup> Concentration in the ethanolic standard solution containing all of the compounds. <sup>d</sup> Not available at normal pressure.

Carbonyl compounds are one among several volatiles with important odor activities associated with raw forms of wheat (grain or flour) (18) and bread systems (19). In starches from different sources, aldehydes have also been reported as the most abundant organic volatiles (20). In this work, certain volatile aldehydes have been selected to have a similar chemical functionality but different size chains and, thus, different hydrophobic character. These particular compounds were described as characteristic aroma constituents of bread or baked products (18, 19, 21). Most result from lipid autoxidation and are associated with off-flavors.

The aim of this work was to first compare the retention ability of hydrated and gelatinized starch granules for the selected aroma compounds and, second, to study the effect of certain emulsifiers on these retention properties. Gelatinization of the starch granules was used as a relatively simple way to change the structure of native starch, allowing starch components to reassociate in a different way. Certain emulsifiers are also known to affect the properties of starch during gelatinization and retrogradation (22–24) and might, therefore, lead to changes in volatile retention. The chosen emulsifiers were sodium stearyl-2-lactylate (SSL) and lecithin (LEC). The former forms inclusion complexes with starch, whereas the latter does not (25).

Unlike most past studies on fairly dilute starch dispersions (<10%), the present work deals with a wide range of starch concentrations [5–40% (w/w) starch aqueous dispersions] to approach more realistic food situations. In addition, an attempt was made to relate the macromolecular organization and matrix structure, as assessed by rheological measurements, to the observed aroma release behavior.

Knowledge of the effect of these model matrices on the release of aroma compounds may lead to a better understanding of flavor interactions in more complex food systems, which may in turn lead to optimization of the release of pleasant aromas and reduction of the perception of unpleasant volatiles.

## MATERIALS AND METHODS

**Materials.** Hexanal and *trans*-2-nonenal were obtained from Aldrich (Sigma-Aldrich Co., Milwaukee, WI); nonanal, decanal, and (*E,E*)-2,4-decadienal were obtained from Fluka (Sigma-Aldrich Co., Milwaukee, WI). An initial solution of all aroma compounds was prepared in ethanol. **Table 1** displays characteristics of the studied aldehydes. Two different emulsifiers have been studied: an amphoteric emulsifier, soy lecithin from Sigma (Sigma-Aldrich Co., St. Louis, MO), and an anionic emulsifier, sodium stearyl-2-lactylate, supplied by Credin Palsgaard Industri A/S (Credin Portugal, Loures, Portugal). Unmodified wheat starch was obtained from Sigma (Sigma-Aldrich Co.). The composition of the starch sample is shown in **Table 2**. Distilled water was used in the experiments, using sodium azide as a preservative.

**Methods.** *Starch Composition.* Moisture, ash, protein, and crude fat content were determined using AACC approved methods (26). Total starch and amylose contents were determined by the methods of

**Table 2.** Some Characteristics of the Wheat Starch Sample (Sigma, S5127)

parameter	value <sup>a</sup>
total starch	98.8 ± 0.3
amylose/amylopectin ratio	26:74
protein	0.180 ± 0.001
crude fat	0.408 ± 0.009
total ash	0.339 ± 0.004

<sup>a</sup> % (w/w) on dry weight basis (moisture = 11%); results from triplicate analyses are shown as mean ± standard deviation values.

McCleary and co-workers (27, 28), using enzymatic kits (Megazyme total starch kit, Megazyme, Wicklow, Ireland).

*Preparation of Starch Dispersions and Gels.* Starch dispersions (2–40%, w/w) were prepared in 120 mL flasks, fitted with poly-(tetrafluoroethylene) (PTFE) lined silicone septa and aluminum caps. For the gelatinized systems, an initial pregelatinized starch dispersion was prepared at 2% (w/w) in distilled water (0.02% Na<sub>3</sub>N<sub>3</sub>), by mixing for 10 min at room temperature and then heating in a bath at 95 °C for 30 min. After cooling, aliquots of this dispersion were transferred into the 120 mL flasks, and then native starch was added to prepare dispersions at different concentrations (5, 10, 20, and 40%, w/w). This procedure was used to minimize sedimentation of starch granules during the measurements. For the preparation of starch–emulsifier systems, the emulsifier, predispersed in water, was added to the starch dispersion (1 g/100 g of dry starch). The flasks were then left under orbital shaking for 16 h at 25 °C. Addition of the aroma compounds was done after this step (see below). Preparation of the gelatinized samples was achieved by heating dispersions prepared as described above, with or without the aroma compounds, in a bath at 95 °C for 10 min, under gentle stirring, and then cooling to 20 °C.

*Headspace Analysis.* For the solid-phase microextraction (SPME) and gas chromatography (GC) analysis, 20 µL of the volatiles stock solution was added to the flasks containing 50 mL of distilled water or to the same volume of the starch dispersion, using a syringe. All samples (water, gelatinized or nongelatinized starch dispersions) were equilibrated in the sealed flasks for 45 min at 25 °C, prior to headspace analysis. For SPME, a fused silica fiber, coated with an 85 µm layer of polyacrylate (Supelco Inc., Bellefonte, PA), was used, with an adsorption time of 15 min. Triplicate SPME extractions in static headspace were performed for each sample and then analyzed by GC. For thermal desorption the fiber remained in the injection port at 250 °C for 5 min.

*Gas Chromatography.* Analysis has been performed on a Hewlett-Packard 5890 II gas chromatograph equipped with a conventional split/splitless injector and a flame ionization detector (FID). Conditions of chromatography were as follows: fused silica capillary column (30 m length × 0.32 mm i.d.) coated with DB-FFAP (J&W Scientific); temperature program, 35–135 °C at 2 °C/min and then 135 °C for 1 min; nitrogen as carrier gas; injection port temperature, 250 °C; detector temperature, 255 °C; splitless injection mode. From the gas chromatograms obtained, relative peak areas (RPA) have been calculated as the ratio of area for aroma compound in the headspace above the starch-rich system compared to the same compound in the headspace above water. Both measurements were performed under the same experimental conditions (time/temperature history). A value of 1 for this ratio was

considered to indicate no net effect of the presence of starch on the aroma release. A value  $<1$  indicates retention, whereas a value  $>1$  indicates a lower retention as compared with water. A similar approach was followed to analyze the effect of the emulsifiers. In this case, RPA were calculated relative to starch without emulsifier, dividing the peak area of the aroma compound released from the starch/emulsifier sample by the peak area of the same compound released from the starch sample, also under the same experimental conditions.

**Rheological Measurements.** Steady-state flow and viscoelastic measurements were performed using a rheometer operating in controlled stress mode (AR1000, TA Instruments). For the nongelatinized starch dispersions the experiments were conducted with cone-and-plate geometry, using a 60 mm diameter acrylic cone,  $2^\circ$  angle. Dynamic experiments were conducted at strain amplitudes between 0.03 and 0.2 depending on the sample, in the frequency range of 0.05–5 Hz and at  $20^\circ\text{C}$ . For the gelatinized systems, the starch dispersions were allowed to gelatinize in situ, and the temperature-dependent measurements of the dynamic shear moduli  $G'$  and  $G''$  (temperature sweeps) were performed at heating and cooling rates of  $5^\circ\text{C}/\text{min}$ , a constant frequency of 0.5 Hz, and 0.01 strain amplitude. The starch dispersions were heated from 30 to  $90^\circ\text{C}$ , held at this temperature during 5 min, and then cooled to  $20^\circ\text{C}$ . This thermal history was similar to that used for the preparation of samples for the SPME-GC-FID analysis. Frequency-dependent measurements were performed at the same small strain amplitude in the frequency range of 0.05–50 Hz,  $20^\circ\text{C}$ .

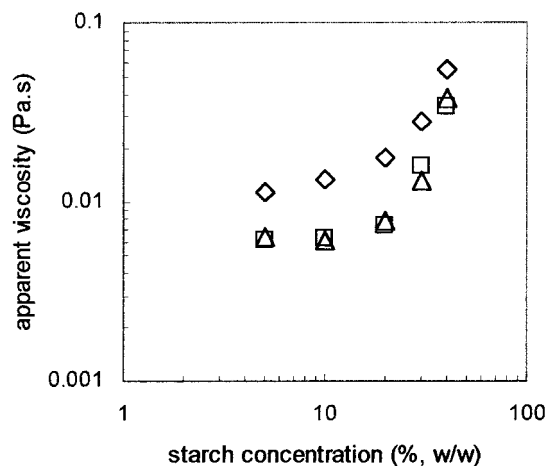
**Statistical Analysis.** Analysis of variance and comparisons among matrices were conducted on the SPME-GC-FID data and were computed using the SPSS software (v. 10.1.0, SPSS Inc., Chicago, IL). The statistical significance of the differences among the matrices was determined by pairwise comparisons of the mean responses among the different treatment groups using the Tukey test, after a preliminary  $F$  test at the 5% probability level. Pearson's correlation analysis was also computed using the SPSS software.

## RESULTS AND DISCUSSION

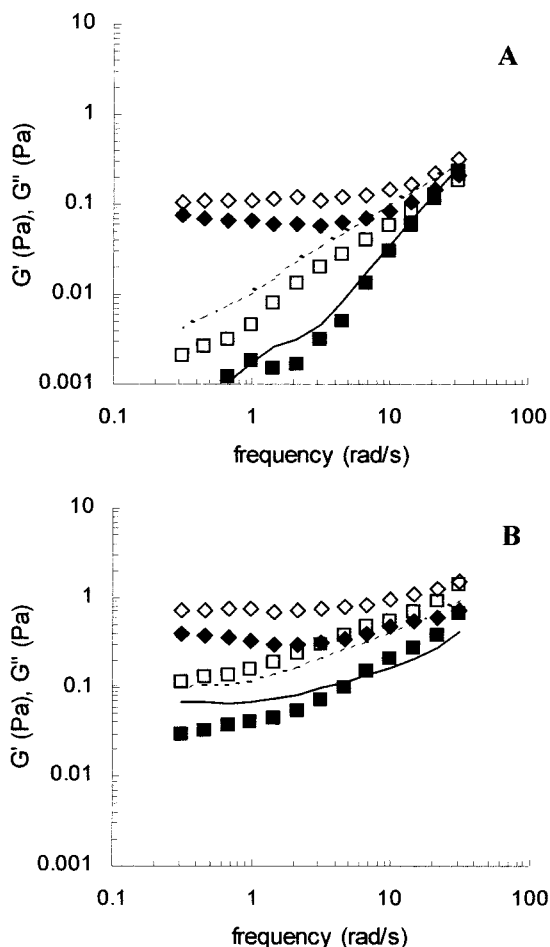
**Rheological Characterization of Nongelatinized Starch-Rich Matrices.** Under steady shear flow, the starch dispersions have shown the typical flow behavior reported in previous studies (29–31): shear-thinning behavior, but absence of the Newtonian plateau at low shear rates (yield stress), the apparent steady viscosity increasing with starch concentration, and an increase in viscosity at higher shear rates, especially for the more concentrated starch dispersions. These relevant rheological properties are indicative of important structural characteristics, namely, granule deformability and strong granule-to-granule interactions, especially for high starch concentrations, which may be anticipated to play an important role on aroma retention.

**Figure 1** shows the apparent viscosity [shear rate ( $\dot{\gamma}$ ) =  $31\text{ s}^{-1}$ ] as a function of the starch concentration, for starch alone or starch–emulsifier mixtures. In the presence of the emulsifiers, SSL and lecithin LEC, the flow behavior is qualitatively similar. However, SSL clearly increases the viscosity of the starch dispersions, whereas LEC has no significant quantitative effect. The increase in viscosity may be related to the increase in granule-to-granule interactions, mediated by the SSL, complexed or freely adsorbed at the granule surface.

Oscillatory tests have provided additional insights into the structural organization of the starch suspensions. **Figure 2** shows plots of  $G'$  and  $G''$  as a function of oscillatory frequency ( $\omega$ ), for 20 and 40% starch dispersions as examples. Both viscoelastic moduli increase with starch concentration, but the difference between them and their dependence on frequency decrease, meaning that the elastic character increases with starch concentration. At low starch concentration the presence of emulsifiers had no significant effect on the viscoelastic behavior. However, for starch concentrations  $>10\%$  (w/w), the viscoelastic behavior is clearly influenced by the presence of SSL, whereas



**Figure 1.** Apparent viscosity as a function of starch concentration, measured at a shear rate of  $31\text{ s}^{-1}$ : ( $\Delta$ ) without adding emulsifier; ( $\square$ ) in the presence of LEC; ( $\diamond$ ) in the presence of SSL (emulsifiers at 1% w/w, based on dry starch).



**Figure 2.** Storage ( $G'$ , solid symbols) and loss ( $G''$ , open symbols) moduli as a function of oscillatory frequency for nongelatinized starch dispersions, without adding emulsifier (—, ---), in the presence of LEC ( $\blacksquare$ ,  $\square$ ), and in the presence of SSL ( $\blacklozenge$ ,  $\diamond$ ) (1% w/w, based on dry starch): (A) 20% (w/w); (B) 40% (w/w) starch.

LEC had only a slight effect. At high starch concentrations and in the presence of SSL, the starch dispersions behave like viscoelastic structured materials (**Figure 2**)—both viscoelastic moduli increase their values and decrease their dependence upon oscillatory frequency, although  $G''$  remains higher than  $G'$ . SSL

promotes granule-to-granule interactions, giving systems with fragile gellike behavior.

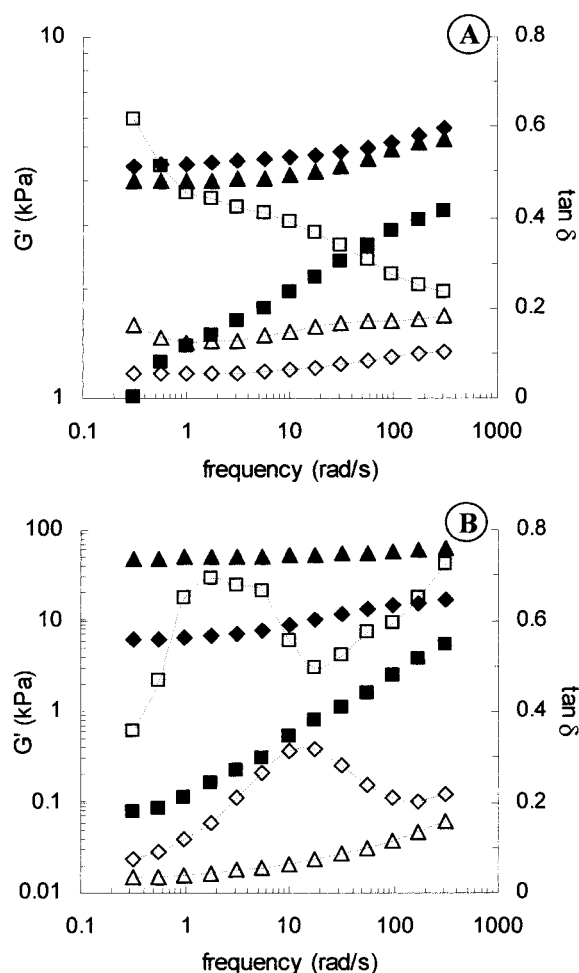
The formation of soft gels induced by the presence of emulsifiers (32, 33) or flavor compounds (34) has been reported for gelatinized dilute starch dispersions, an effect attributed to complex formation with amylose chains and/or amylopectin. In the absence of heating, in the case of the nongelatinized dispersions, not enough intergranular material was leached out to form any significant extragranular amylose-emulsifier complexes (35, 36). In addition, amylose-emulsifier complexes form only at temperatures close to or above the gelatinization temperature (22, 23). Therefore, the complexation with amylose is unlikely to contribute to the increased viscoelasticity. Early work has shown that certain surfactants may penetrate the starch granule and then complex with amylose, forming helical structures (22, 37, 38), but the possibility of surface adsorption has also been postulated (39). Although penetration of the emulsifier into the granule cannot be totally discounted, we suggest that the occurrence of adsorption at the granule surface of the more hydrophilic emulsifier is the most likely explanation for the observed peculiar rheological behavior. Physical entanglements between surface molecules of adjacent granules, or intergranular aggregation induced by the SSL molecules acting as bridging between granules, may be responsible for the structure and gellike behavior of these systems. Steric configuration and hydrophobic character may be responsible for the observed differences between the behaviors of the two emulsifiers.

At the levels used in this work, the volatile compounds had no significant and clear-cut effects on the viscosity and viscoelastic properties of the starch dispersions (results not shown).

**Rheological Characterization of Gelatinized Starch-Rich Matrices.** Gelatinization of dispersions with different starch contents [5–40% (m/m, dwb)], with or without emulsifiers, was followed in situ on the rheometer measuring system, using dynamical rheological measurements at low strain amplitude. Starch dispersions were heated from 30 to 90 °C, held at this temperature during 5 min, and then cooled to 20 °C, allowing gelation to occur.

To relate the physical properties of the starch gels to the aroma release profiles, interest was focused on the rheological behavior of the starch and starch-emulsifier matrices after gelation has occurred. It is at this stage that structural changes and network organization inside the starch matrix would play the most significant influence upon aroma retention. After the matrix has cooled to 20 °C, the storage modulus ( $G'$ ) considerably exceeds the loss modulus ( $G''$ ), and both show only weak dependence on frequency over the range of 0.05–50 Hz. In **Figure 3**, plots of  $G'$  and loss tangent ( $\tan \delta = G''/G'$ ) are shown for 10 and 40% starch gels, as examples. In the absence of emulsifier, the gelatinized starch systems show solidlike behavior, the deformations being essentially recoverable, so that no major relaxation processes are occurring in this frequency range. Both moduli showed a power concentration dependence with similar exponents (2.1–2.2) (results not shown), whereas  $\tan \delta$  decreases with starch concentration, meaning that the elastic character of the system increases as the starch concentration increases.

The presence of the emulsifiers also influences the viscoelastic behavior of the starch gels. LEC decreases both viscoelastic moduli, the moduli show higher frequency dependence, and the viscous character clearly increases (**Figure 3**). For low starch concentrations ( $\leq 10\%$ ), SSL slightly increases the rigidity and



**Figure 3.** Storage modulus ( $G'$ , solid symbols) and  $\tan \delta$  (open symbols) as a function of oscillatory frequency for starch gels, without adding emulsifier ( $\blacktriangle$ ,  $\triangle$ ), in the presence of LEC ( $\blacksquare$ ,  $\square$ ) and in the presence of SSL ( $\blacklozenge$ ,  $\lozenge$ ) (1% w/w, based on dry starch): (A) 10% (w/w); (B) 40% (w/w) starch. Mechanical spectra have been recorded after the thermal treatment in situ on the rheometer, at 20 °C and 1% strain amplitude.

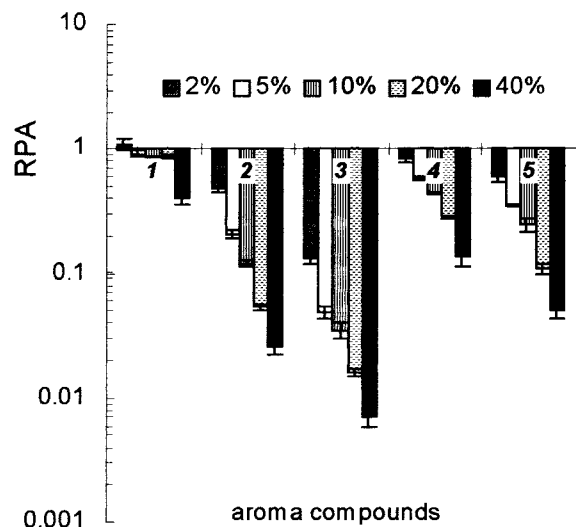
the elastic character of the gel (**Figure 3A**). However, at higher starch contents it has a negative effect on starch network development—lower moduli, higher frequency dependence, and higher  $\tan \delta$ , meaning a general reduction of the elastic character of the system (**Figure 3B**).

As previously mentioned for the nongelatinized starch dispersions, the volatile compounds had no significant effect on the rheological properties of the gelatinized starch dispersions (results not shown).

**Effect of Nongelatinized Starch Granules on Aroma Extraction.** Preliminary experiments (results not shown) of headspace analysis at different temperatures and equilibrium times were used to optimize the experimental conditions, to assume that the analysis for each sample was performed for gas-liquid systems at equilibrium.

Release of the aldehyde compounds from nongelatinized starch dispersions was investigated as a function of starch concentration and the presence of emulsifiers.

The relative retention capability of the starch dispersions is shown in **Figure 4** for starch concentrations between 2 and 40% (w/w). The degree of retention depends on the compound properties and on starch concentration. Retention of the aroma compounds clearly increases due to the presence of starch in the aqueous dispersions and increases with starch concentration.

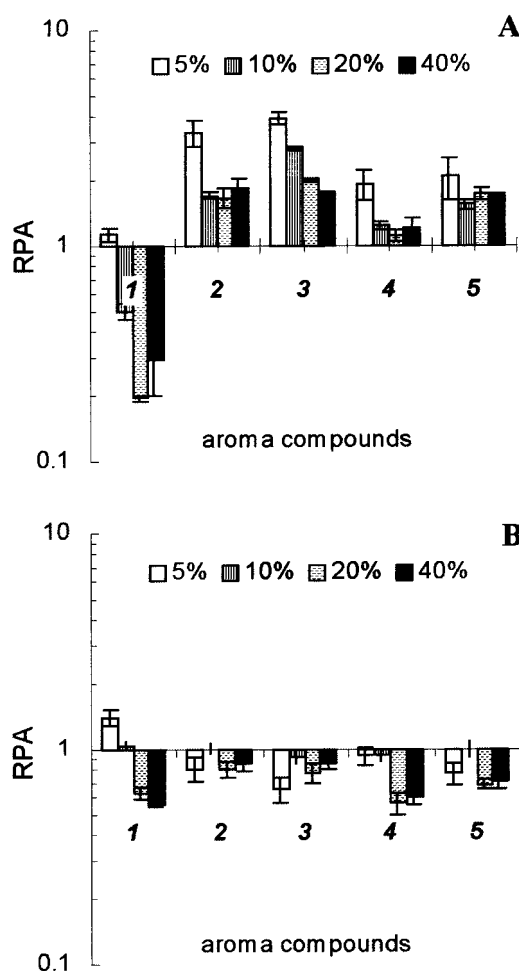


**Figure 4.** Relative peak areas (RPA) for the aroma compounds extracted by SPME from aqueous nongelatinized starch dispersions with different starch concentrations (2–40%). Aroma compounds: 1, hexanal; 2, nonanal; 3, decanal; 4, *trans*-2-nonenal; 5, (*E,E*)-2,4-decadienal. Error bars represent one standard deviation about mean values of triplicate measurements.

Generally, the effect of starch concentration on the volatile headspace extraction was statistically significant ( $P < 0.05$ ). The aldehydes with higher chain length were retained the most and showed very low headspace quantities, with values reduced to 0.7% for decanal and the more concentrated starch dispersions. These values are similar to those reported for microcellular starch foams prepared from gelatinized starch (15), although in this case the higher retention was observed for the more polar compounds. In contrast, much lower retention degrees have been reported for starch powders, at low moisture and room temperature (16). The unsaturated compounds showed lower retention when compared with their saturated homologues. It seems that linear and more hydrophobic compounds diffuse more easily into the granules and/or undergo more extensive adsorption at the granule surface.

Starch granules are semicrystalline relatively dense particles characterized by heterogeneity in shape, size, structure, and composition. Some peculiarities of the granule surface might be relevant for volatile retention, namely, the reported porous structure (40) and the presence of small protrusions (10–50 nm) (41). The high capacity for retention by the nongelatinized starch granule in aqueous dispersion might be related to the porosity of the native starch granules, associated with slight swelling and partial hydration. Also, the surface composition of the starch granule may play an important role, namely, in adsorption phenomena and as the first barrier to any compound that might penetrate the granule. The surface of starch granules is composed predominantly of carbohydrate material (42), but the minor components, mainly lipids and proteins, are known to be present near and at the surface at higher concentrations than are found in the bulk analysis of starch (43, 44). Surface lipids, despite their quite low levels, may play an important role in adsorption phenomena, especially for the more hydrophobic compounds. The formation of inclusion assemblies is unlikely to occur, at least outside the granule, because no appreciable amount of amylose has been leached out under these conditions.

Whether the primary effect is due to adsorption at the granule surface or penetration into the granules, or even a combination of the two factors, is not known, but the former explanation appears to be more plausible. In fact, it has been shown that



**Figure 5.** RPA for the aroma compounds extracted by SPME from aqueous nongelatinized starch dispersions with different starch concentrations (5–40%) and with emulsifiers (1% w/w, based on dry starch): (A) SSL; (B) LEC. The legend for the volatiles is the same as in Figure 4.

water and some small polar compounds may penetrate the granule but that hydrophobic molecules do not penetrate the granules to any significant extent (45). The higher retention observed for the higher chain and hydrophobic aldehydes can thus be explained by adsorption at the granule surface.

Retention was also affected by the presence of emulsifiers. The presence of SSL causes a decrease in the aldehyde retention, except for hexanal, when compared with the retention profile of the starch dispersions without emulsifier (Figure 5A). The effect of SSL, reducing the retention capability of the starch, is more pronounced as the starch concentration decreases. The most affected compounds were those more retained in the absence of SSL, that is, those which probably have interacted more extensively with the starch granules. This emulsifier is considered to be a good complexing agent, and it is also capable of film formation at the granule surface. A decrease in granule penetration or availability of superficial binding sites, or even some competition effects for inclusion or surface binding sites between volatile and emulsifier, may explain the observed effects on the compound's retention. It must be recalled that this emulsifier also had an appreciable effect on the rheology of the system. It could be expected that the effect of promoting a higher structured system would cause an increase in retention, resulting from a simple effect of decreasing the mass transfer rate throughout the aqueous phase. However, if this explanation can be proposed for the hexanal retention profile, the same

**Table 3.** Pearson Correlation Coefficients among Relative Peak Areas (RPA) and Some Rheological Parameters for Aldehydes Extracted from Nongelatinized Starch Dispersions, with or without Emulsifiers

volatile RPA	rheological parameters					
	$\eta_a/\text{Pa}\cdot\text{s}$	$\eta^*/\text{Pa}\cdot\text{s}$	$G'/\text{Pa}$		$G''/\text{Pa}$	$\tan \delta$
	$\dot{\gamma} = 31 \text{ s}^{-1}$	$\omega = 31 \text{ rad/s}$	$\omega = 31 \text{ rad/s}$	$\omega = 31 \text{ rad/s}$	$\omega = 31 \text{ rad/s}$	$\omega = 31 \text{ rad/s}$
hexanal	-0.756 <sup>a</sup>	-0.711 <sup>a</sup>	-0.411	-0.758 <sup>a</sup>	-0.687 <sup>b</sup>	-0.129
nonanal	-0.566	-0.659 <sup>b</sup>	-0.308	-0.693 <sup>b</sup>	-0.644 <sup>b</sup>	-0.325
<i>trans</i> -2-nonenal	-0.595	-0.706 <sup>b</sup>	-0.213	-0.724 <sup>a</sup>	-0.694 <sup>b</sup>	-0.474
decanal	-0.478	-0.595 <sup>b</sup>	-0.211	-0.626 <sup>b</sup>	-0.581 <sup>b</sup>	-0.381
( <i>E,E</i> )-2,4-decadienal	-0.519	-0.643 <sup>b</sup>	-0.227	-0.660 <sup>b</sup>	-0.635 <sup>b</sup>	-0.439

<sup>a</sup> Correlation is significant at the 0.01 level. <sup>b</sup> Correlation is significant at the 0.05 level.

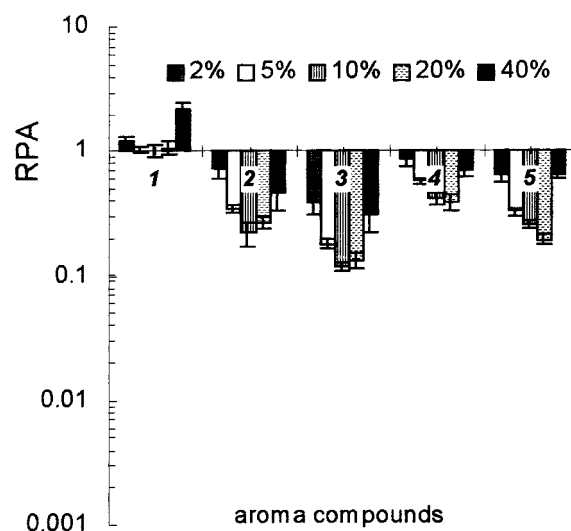
would not be true for the other compounds, where more specific effects related to emulsifier–starch interactions are probably playing more important roles. However, for higher starch concentrations, the increasing viscous character of the system may also contribute to the increased retention when compared with the lower granule concentrations.

LEC had less influence on the rheological properties of the starch dispersions but some effect on the retention of volatile compounds, probably due to its hydrophobic characteristics (Figure 5B), allowing the direct binding of volatiles.

Linear correlations between the RPA, obtained for the starch systems in the presence or absence of emulsifier, and the rheological parameters were investigated (Table 3). A significant inverse correlation for the apparent viscosity values was obtained only for the relative headspace values of hexanal. No significant correlations were obtained with the  $\tan \delta$  values, a parameter directly related to the relative viscous/elastic character of the system. Significant negative correlations were obtained with complex viscosity and the viscoelastic moduli. Interestingly, only the rheological parameters measured at high shear rate or oscillatory frequency show a significant correlation with the aroma retention. For most cases, no significant correlations have been obtained when rheological parameters measured under conditions where the fragile granule-to-granule interactions were not destroyed were considered, that is, at low shear rate or frequency. An example of this behavior is given for  $G'$  in Table 3. These findings may be related, not only to the effect of the viscous and elastic properties of the matrices on volatile retention but, indirectly, to the important role of the amount of non-interacting starch granules in the observed retention profiles.

Although it has long been supposed that the nongelatinized starch granules act as inert particles, we have demonstrated considerable indirect evidence that these entities can interact with volatiles in a significant manner.

**Effect of Starch-Rich Gelatinized Matrices on Aroma Extraction.** The gelatinization of starch clearly affects the release profile of the aroma compounds. The relative retention capability of the starch dispersions is shown in Figure 6. Generally, relative to water, the retention of aroma compounds increases due to the presence of starch. Aldehydes with higher chain lengths were also retained the most, as previously observed for nongelatinized dispersions. Again, the degree of retention was dependent on the compound properties and on starch concentration. The exception was hexanal, the molecule with the lowest molecular weight studied. No significant effect on its retention was observed for starch concentrations lower than 40%. Furthermore, at 40% starch, and contrarily to the other compounds, the degree of retention for hexanal was about half that observed for water. Possibly, its relative polarity and small size impart higher mobility in the matrix, and its capability to specifically interact with the starch granules is reduced. It should

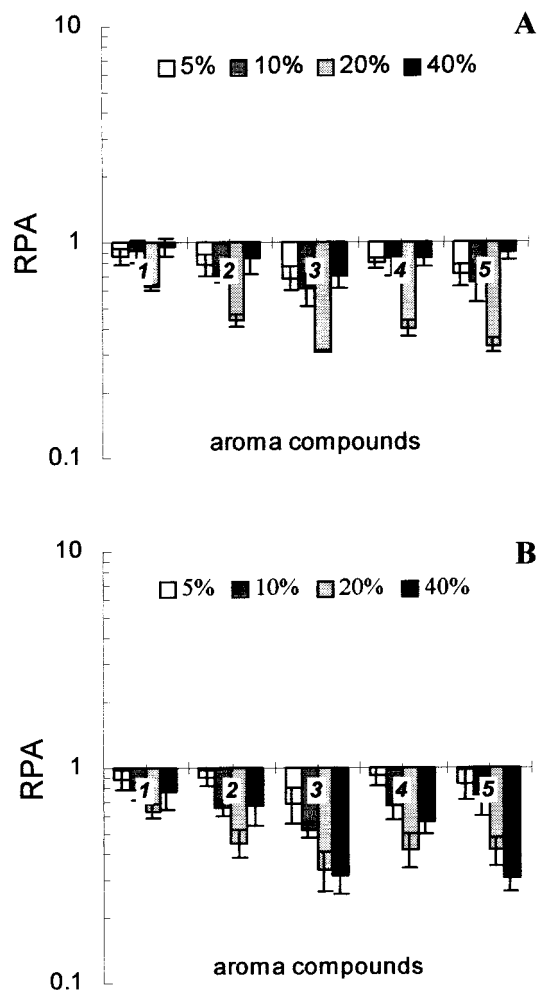


**Figure 6.** RPA for the aroma compounds extracted by SPME from aqueous gelatinized starch dispersions with different starch concentrations (2–40%). The legend is the same as in Figure 4.

also be noted that hexanal was the compound least affected in the case of the nongelatinized dispersions.

Gelatinization of the granules was found to decrease their capability for aroma retention (see Figures 4 and 6 for comparison), and starch concentration had a statistically lower effect on retention, when compared with the nongelatinized dispersions. Generally, the highest retention was observed at intermediate starch concentrations (10–20%). Starch granular integrity and/or the granule surface characteristics thus appear to be an important criteria in defining aroma release. The changes in granule structure occurring during gelatinization, namely, the decrease in crystalline zones and the leaching of granular components, will have an important effect on the native internal surface of the granule, defined by the capillary structure of the hydrated particle, and on the external granule surface, imparting a lower capability for adsorbing volatiles. Complexation with starch fractions and hindered mobility within the matrix may now play more important roles, but even so the relative retention capability is lower than for the nongelatinized dispersions.

The origin of the effect of starch concentration on volatile headspace release from the gelatinized systems may be interpreted as follows. For the more concentrated gels, the extent of granule swelling is limited by the available physical volume and water availability (46, 47). These restrictions mean that as starch concentration increases, the swelling of individual granules is reduced with a concomitant decrease in the leaching out of granular components, thus reducing the availability of polymeric material outside the granule. Also, a reduction in the



**Figure 7.** RPA for the aroma compounds extracted by SPME from aqueous gelatinized starch dispersions with different starch concentrations (5–40%) and with emulsifiers (1% w/w, based on dry starch): (A) SSL; (B) LEC. The legend is the same as in Figure 5.

number of binding sites may also occur due to granule-to-granule enhanced interactions. In addition, at high granule volume fraction, the lower amount of free water may cause reduced solubility of the volatiles, especially for the higher chain aldehydes, increasing partition coefficients between air and solvent, and thus a higher headspace concentration. These changes in matrix structure result in the observed decrease in volatile retention at the higher concentrations analyzed.

Contrarily to what has been observed for the nongelatinized starch dispersions, the presence of SSL and LEC increased the overall aroma retention (**Figure 7**) when compared with the starch alone. Interestingly, the effect of each was quite similar. The main difference between emulsifiers was observed at 40% starch. At this starch level, LEC still causes higher retention, whereas SSL causes a decrease in volatile retention.

It is known, despite some debate about the mechanism behind these effects, that certain emulsifiers such as SSL depress the swelling capability of starches during heating and decrease the leaching of the granule components, mainly amylose, delaying the deformation and collapse of starch granules (22, 24, 48, 49). The lower amount of material leached out from the starch granules can explain the less efficient network formation, observed in the rheological measurements, which is known to be mainly due to the amylose fraction dissolved during gelatinization of the granules. Therefore, because of a lower gelatinization degree occurring due to the presence of the

emulsifier, the higher granule integrity may explain the enhanced retention capability, in addition to the mechanisms responsible for volatile retention in the gels without emulsifier, as discussed above.

Considering the apparent similarity in the effects promoted by both emulsifiers, the effect of the emulsifiers on the matrix structure, a lower mass transfer rate and the direct binding of volatiles by the emulsifier, may be postulated to contribute to the higher observed retention. However, no significant correlations were obtained between the RPA and any of the rheological parameters analyzed, for either the gelatinized systems with or without emulsifiers. This suggests that other more specific effects, besides a simple physical hindrance to the volatile diffusion throughout the matrix, are influencing the retention behavior.

In fact, a well-founded explanation for the retention behavior of the gelatinized systems in the presence of emulsifiers is hard to achieve, and clearly more work is needed on this subject.

It is well-known that the structural organization of the starch gel depends on both the continuous matrix and the granules (acting as a filler) and on the interactions between components. Furthermore, the interactions between components may occur in several ways (29, 36, 50): direct granule-to-granule contact, granule–amylose/amylopectin interactions, and granule–amylose/amylopectin–granule interactions. The complexity of the system is increased by the presence of the emulsifier, affecting the balance between the different factors controlling the gel network. Despite these limitations, the results obtained enable some conclusions to be drawn and might be useful for further development on this subject.

It should be noted that, generally, from the rheological point of view, the effects of the two emulsifiers on the nongelatinized and gelatinized systems were quite different and must reflect the different interaction mechanisms between starch and emulsifier. The different structural organization of the system results in different volatile retention capabilities. In the case of the nongelatinized systems, the main effect of SSL was to increase the elastic character and structure of the system, causing a general decrease in volatile retention. In the case of the gelatinized systems, the main effect was the increase in viscous character of the system and a negative effect on starch network development. This was followed by a general increase in retention, even higher for LEC, which despite its lack of complexing ability caused a higher effect on the rheological behavior of the starch gels.

Therefore, it seems that factors contributing to a decrease in granule integrity and surface availability may also lead to a decrease in volatile retention. Factors that contribute to aggregation of the starch components and network perfection also decrease retention, whereas factors that hinder interactions among starch components (granules or leached material) cause enhanced retention capability.

## SAFETY

Sodium azide ( $\text{NaN}_3$ ) is hazardous and should be handled with care.

## ABBREVIATIONS USED AND NOMENCLATURE

$\eta^*$ , complex viscosity (Pa s);  $\eta_a$ , apparent shear viscosity (Pa s);  $\dot{\gamma}$ , shear rate ( $\text{s}^{-1}$ );  $\tan \delta$ , loss tangent ( $G''/G'$ );  $\omega$ , oscillatory frequency (rad/s);  $G'$ , storage modulus (Pa);  $G''$ , loss modulus (Pa);  $P$ , probability of incorrectly rejecting the null hypothesis; dwb, dry weight basis; FID, flame ionization detector; GC, gas

chromatography; LEC, lecithin; RPA, relative peak areas; SPME, solid-phase microextraction; SSL, sodium stearyl-2-lactylate.

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