Structured Fluids as Microreactors for Flavor Formation by the Maillard Reaction

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Thermal reactions of cysteine/furfural and cysteine/ribose mixtures were studied in model systems to gain more insight into the influence of structured fluids such as L_2 microemulsions and cubic phases on the generation of aroma compounds. Formation of 2-furfurylthiol from cysteine/furfural was particularly efficient in L_2 microemulsions and cubic phases compared to aqueous systems. The reaction led to the formation of two new sulfur compounds, which were identified as 2-(2-furyl)-thiazolidine and, tentatively, *N*-(2-mercaptovinyl)-2-(2-furyl)thiazolidine. Similarly, generation of 2-furfurylthiol and 2-methyl-3-furanthiol from cysteine/ribose mixtures was strongly enhanced in structured fluids. The cubic phase was shown to be even more efficient in flavor generation than the L_2 microemulsion. It was denoted "cubic catalyst" or "cubic selective microreactor". The obtained results are interpreted in terms of a surface and curvature control of the reactions defined by the structural properties of the formed surfactant associates.

Keywords: *Microemulsion; cubic phase; structured fluids; Maillard reaction; formation of thiols; flavor precursors; 2-furfurylthiol*

INTRODUCTION

Maillard reactions, for example, thermally induced reactions of amino acids and reducing sugars, have been studied for a long time, also with respect to their potential to generate flavors. It should be emphasized that the thermal reaction between cysteine and carbohydrates leads to the formation of >200 volatile compounds (Mulders, 1973; Farmer et al., 1989; Mottram and Whitfield, 1995). Of particular interest is the generation of sulfur-containing aroma compounds such as 2-furfurylthiol (FFT) and 2-methyl-3-furanthiol (MFT). Both compounds are potent odorants with unique sensory properties and were determined by aroma extract dilution analysis (AEDA) as major contributors to the aroma of a wide variety of food products including coffee (Holscher et al., 1990), cooked beef (Gasser and Grosch, 1988), and roasted sesame seeds (Schieberle, 1993). It was also shown that FFT and MFT belong to the key impact compounds of heated cysteine/ribose mixtures (Hofmann and Schieberle, 1995). Quantitation of these compounds by stable isotope dilution assays in dry-heated and aqueous reaction systems revealed a strong influence of the reaction conditions on the concentrations of these potent odorants (Schieberle and Hofmann, 1998). Particularly, the formation of FFT was strongly enhanced under the conditions of dry heating, which reflected roasting conditions. Other parameters affecting their generation, such as pH dependence, have also been studied (Schieberle and Hofmann, 1996), as well as the effectiveness of different sugar-derived degradation products as precursors (Hofmann and Schieberle, 1996). Furfural, a thermal pentose sugar degradation product, was shown to be an intermediate in the formation of FFT (Münch et al., 1997) and was chosen in our study to gain more insight into the influence of structured media on the generation of aroma compounds. The use of model systems is the primary tool to investigate the effect of structured fluids on the Maillard reaction.

Structured fluids are generally composed of microstructures dispersed in a homogeneous phase. Much attention was given in the past to association colloids, that is, aggregates formed by amphiphilic molecules (Hiemenz, 1986; Larsson, 1994; Laughlin, 1994) such as micelles, vesicles, microemulsions, mesophases, and macromolecule self-assemblies.

Monoglycerides were used in this work as surfactant for the generation of association colloids used as microreactors for the Maillard reactions. Monoglycerides consist of a single acyl chain (hydrophobic tail), which is attached to a glycerol moiety (hydrophilic headgroup). The headgroup is only weakly hydrated. The acyl chain of the monoglycerides may differ in the degree of unsaturation: It can be totally saturated or have either one (e.g., oleic acid) or two (e.g., linoleic acid) double bonds. When dispersed in water, monoglycerides are known to exhibit a rich polymorphism; that is, they form up to six distinct phases depending on the water content and the temperature (Krog, 1997; Briggs et al., 1996; Boyle and German, 1996). The degree of unsaturation mainly determines at which temperature the different phases are formed. For instance, with the saturated monoglycerides the cubic phase is formed only at high temperatures (>70−80 °C), whereas in the presence of unsaturated monoglycerides, it is formed at room temperature (see Figure 1). Moreover, the formation of a microemulsion phase (isotropic fluid) at high temperatures is best achieved with unsaturated monoglycerides. The structures of the different phases have been investigated by a variety of techniques, such as small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS), and microscopy. Because they have both a

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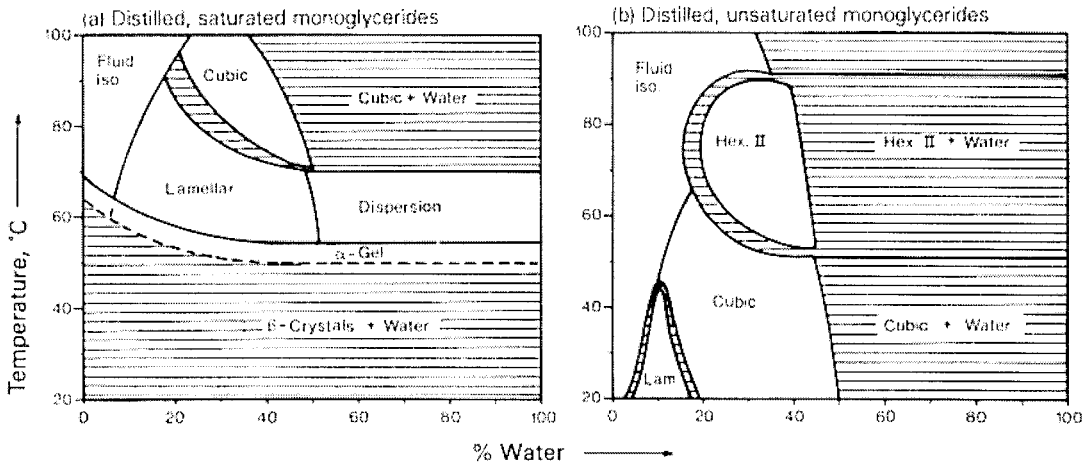

Figure 1. Phase diagrams of distilled monoglyceride products from Danisco Ingredients: (a) from hydrogenated lard (Dimodan P); (b) from sunflower oil (Dimodan LS); adapted from Danisco Ingredients, technical paper TP3-1e.

hydrophobic site (tail region) and a hydrophilic site (headgroup region including the solubilized water region), they are capable of dissolving both water-soluble and oil-soluble compounds (Engstrom, 1990; Ericsson et al., 1991).

Of particular interest is the cubic phase, which has a bicontinuous structure. It is generally described as two interpenetrating networks of water channels separated by a curved bilayer, extending in three dimensions [forming the so-called infinite periodic minimal surface (Larsson, 1989)]. The water pore diameter has been shown to be ~5 nm for the fully swelled phase. The curved bilayer structure gives rise to a very large interfacial area (~400 m^2/g), which is an excellent entrapment medium (Ericsson et al., 1991). The solubilization capacity for organic compounds was found to be governed by various factors but mostly by the curvature of the interface and the degree of water swelling (Ericsson et al., 1983, 1991; Razumas et al., 1996; Caboi et al., 1997).

Bicontinuous cubic phases are optically isotropic and completely transparent and have a consistency like gels, exhibiting the highest viscosity of all of the mesophases formed (Larsson, 1989; Fontell, 1990). Cubic phases can be also in equilibrium with an excess of water (they do not transform into other phases upon contact with water, see Figure 1), which is particularly interesting as a matrix system for a controlled release of drugs and eventually for flavor compounds. In certain cases, even stereoselectivity of organic reactions was achieved at such interfaces (Holmberg, 1994).

Much has been written on the solubilization capacity of cubic phases and on their potential as delivery systems (Burrows et al., 1994; Osborne and Ward, 1995; Chang and Bodmeier, 1997). However, their potential as microreactors for the thermal generation of aromas has not yet been studied. The aim of this work was to compare, on a quantitative basis, the reaction products of cysteine/furfural and cysteine/ribose model systems performed in two different structured fluids, that is, a cubic phase and a microemulsion phase, and in an aqueous medium under the same conditions. The influence of the structured phases on the thermal reactions is discussed.

EXPERIMENTAL PROCEDURES

Chemicals. L-Cysteine, D-ribose, furan-2-aldehyde (furfural), 5-methylfurfural, 5-ethyl-4-methyl-3-hydroxy-2(5*H*)-furanone (abhexon), and 3-acetyl-2,5-dimethylthiophene were obtained from Fluka (Buchs, Switzerland). Dimodan LS (sunflower oil monoglyceride, >98%) and Dimodan PV (saturated vegetable oil monoglyceride, >98%) were kindly provided by Danisco Ingredients (Braband, Denmark). Water used in these experiments was twice distilled.

Model Reactions. L-Cysteine (2 mmol) and furfural (2 mmol) were dissolved in a phosphate buffer (10 mL; 0.5 M; pH 5.0). The cubic phase was prepared by introducing 1 g of this solution and 4 g of melted (60 °C) Dimodan PV (saturated monoglyceride) into a Pyrex tube (i.d. = 1.5 cm). After vigorous stirring (Vortex), the tube was placed in an oil bath at 140 °C for 1 min and stirred again to form a homogeneous cubic phase. Finally, this system was thermally treated for 4 h at 100 °C. To obtain a microemulsion (isotropic fluid) at this temperature, Dimodan PV was replaced by the unsaturated monoglyceride product Dimodan LS ($C_{18:2}$ = 67% and $C_{18:1}$ = 21%; Krog, 1998). As reference, an identical thermal treatment was applied to 1 g of the buffer solution containing the reactants. After heating, the mixture was cooled and 4 g of melted Dimodan PV was added in order to have similar workup conditions for the isolation of volatiles.

In a second series of experiments, L-cysteine (6.67 mmol) and D-ribose (20 mmol) were dissolved in a phosphate buffer (10 mL; 0.5 M; pH 5.0). Cubic phase samples were prepared by introducing 2 g of this solution and 8 g of melted (60 °C) Dimodan PV into a Pyrex tube (i.d. = 2 cm). Finally, this system or 2 g of buffer solution alone (reference) was thermally treated following the same procedure as mentioned above.

Isolation of Volatiles from the Reaction Mixtures. The aqueous reference samples were first transformed into a cubic phase by adding melted Dimodan PV (4 g) to the reaction system to ensure maximal similarity in the reaction mixtures before sample cleanup. After cooling, the mix was extracted with diethyl ether (three times, total of 50 mL). The slurries were combined and submitted to the vacuum transfer system described by Sen et al. (1991) using only two cold traps immersed in liquid nitrogen. Once the sample was entirely frozen in liquid nitrogen, the vacuum was opened, the sample thawed, and the solvent together with other volatiles transferred into the cold traps at 100 mPa during 1.5 h, thus separating them from the monoglycerides. A high vacuum was avoided to minimize carry-over of monoglycerides into the cold traps. The distillate containing the aroma compounds was then dried over anhydrous Na_2SO_4 and concentrated to 2 mL on a Vigreux column (50 cm × 1 cm) and finally to 0.5 mL under a gentle stream of nitrogen.

Quantification of Volatiles. *(i) Furfural/Cysteine Reaction.* The diethyl ether used for the isolation of volatiles was spiked with benzylmercaptan as internal standard (5 or 10 μg).

(ii) Ribose/Cysteine Reaction. The diethyl ether was spiked with the following amounts of standard compounds: 350 μg

of 5-methylfurfural for quantitation of MFT, FFT, and furfural; 350 μg of 5-ethyl-4-methyl-3-hydroxy-2(5*H*)-furanone (abhexon) for quantitation of 4-hydroxy-5-methyl-3(2*H*)-furanone (norfuraneol); and 4.7 μg of 3-acetyl-2,5-dimethylthiophene for quantitation of bis(2-methyl-3-furyl) disulfide (MFT−MFT).

Quantitation in both reactions was based on the ratio of peak areas using the FID trace and was not corrected for possible differences in FID responses and recovery yields of internal standard and analyte.

High-Resolution Gas Chromatography (HRGC) and HRGC Mass Spectrometry (HRGC-MS). An HP5890 GC equipped with a DB-1701 fused silica capillary column (J&W, Folsom, CA; 30 m × 0.32 mm × 0.25 μm) was used. By means of a Valco valve, the effluent (He used as carrier gas; 80 kPa) was split to an FID and an FPD detector, both kept at 250 °C. An aliquot (1 μL) of the concentrated samples was injected in the splitless mode using an HP-7673A autosampler. Identification of compounds was performed using an HP-5890 series 2 GC with a DB-5 capillary column (J&W; 30 m × 0.32 mm × 0.25 μm) connected to a Finnigan MAT SSQ 7000 mass spectrometer. Mass spectra in the electron impact mode were generated at 70 eV and in the chemical ionization mode at 150 eV with isobutane as reagent gas. The GC oven temperature was programmed from 20 °C (2 min) at 70 °C/min to 50 °C (2 min), at 6 °C/min to 180 °C, and finally at 20 °C/min to 240 °C (10 min). Linear retention indices (RI) were calculated according to the method of van den Dool and Kratz (1963).

RESULTS

Furfural and Cysteine as Precursors of FFT. In the first series of experiments, cysteine was heated with furfural. Maillard reactions are often studied at elevated temperatures of 140−180 °C. In our study 100 °C was chosen due to the necessity to stay in the cubic phase region of the Dimodan PV (80−120 °C) and to avoid the use of pressurizable reaction vessels.

The cubic phase of the Dimodan PV/water system (80:20), used in this study, reverses to an L_2 microemulsion at temperatures >120 °C (Krog, 1998). It is also known that cubic to hexagonal and hexagonal to L_2 phase transition temperatures decrease for unsaturated monoglycerides, such as Dimodan LS. Thus, by keeping the monoglyceride/water at a constant ratio (80:20) and maintaining the temperature at 100 °C, we could obtain a reversed microemulsion phase by replacing Dimodan PV with Dimodan LS (Figure 1).

Reaction in Water. Figure 2 shows GC/FPD chromatograms of volatile compounds obtained from cysteine/furfural mixtures reacted in different media (water, microemulsion, and cubic phase).

In the aqueous phase (Figure 2A), besides the standard benzylmercaptane, only two sulfur compounds were detected in trace amounts. One compound was identified as FFT on the basis of its the retention index (RI) and MS spectra. It is the expected product from the reaction of furfural with cysteine.

Reaction in Structured Fluids. The yield of FFT was significantly increased in both the microemulsion and the cubic phase. In addition, two new compounds were detected in relatively large amounts (Figure 2B,C) with RI values of 1521 and 1997 on a DB-1701 gas capillary column.

On the basis of MS/EI (Figure 3) and MS/CI, these two molecules were identified as 2-(2-furyl)thiazolidine (RI = 1521) and, tentatively, *N*-(2-mercaptovinyl)-2-(2-furyl)thiazolidine (RI = 1997). To confirm these structures, 2-(2-furyl)thiazolidine was prepared from furfural and cysteamine in aqueous solution by heating an equimolar mixture (20 mmol each) at 100 °C for 1 h (Figure 4). The mass spectrum of the synthesized compound was in good agreement with the spectrum of the unknown compound at RI = 1521.

Both compounds, *N*-(2-mercaptovinyl)-2-(2-furyl)thiazolidine and 2-(2-furyl)thiazolidine, as well as FFT were quantified in the three systems investigated (Table 1). On the basis of the relative peak areas to the internal standard benzylmercaptane, ∼2 μg of FFT was generated in the aqueous reaction system. Under the same conditions ∼9 μg of FFT was generated in a microemulsion and ∼12 μg in the cubic structure, resulting in a 6-fold increase compared to the aqueous system.

The same trend was observed for 2-(2-furyl)thiazolidine and *N*-(2-mercaptovinyl)-2-(2-furyl)thiazolidine, for which the cubic phase as matrix gave the highest amounts of 240 and 123 μg, respectively. In the aqueous solution, 2-(2-furyl)thiazolidine was detectable in only one sample, whereas *N*-(2-mercaptovinyl)-2-(2-furyl)-thiazolidine could not be detected under the experimental conditions. These results indicate that the cubic structure is the most efficient matrix for the generation of these three volatile compounds under the chosen reaction conditions. Moreover, the ratio of the amount for each compound formed in the cubic phase and in the microemulsion differed significantly. Compared to the microemulsion, the amount of *N*-(2-mercaptovinyl)-2-(2-furyl)thiazolidine was 10 times higher in the cubic phase, whereas ratios of about 1.3 and 6 were observed for FFT and 2-(2-furyl)thiazolidine, respectively. Possible reasons for the different reaction yields will be discussed later.

A hypothetical pathway for the generation of 2-(2-furyl)thiazolidine from furfural (**I**) and cysteine (**II**) is displayed in Figure 5. The first step in the reaction is the addition of cysteine to the carbonyl group of furfural. The subsequent elimination of a molecule water gives rise to a Schiff base (**III**). This compound may undergo decarboxylation, resulting in product (**IV**). This intermediate can finally form a five-membered ring by addition of the nucleophilic sulfur to the imine, which leads to the formation of 2-(2-furyl)thiazolidine. Compound **III** may also first cyclize to compound **IIIb** and subsequently lose CO_2. The 2-(2-furyl)thiazolidine may then react with mercaptoacetaldehyde, released from cysteine upon Strecker degradation, to finally give rise to the tentatively identified *N*-(2-mercaptovinyl)-2-(2-furyl)thiazolidine.

Ribose/Cysteine Reaction. This system was chosen because many parameters influencing flavor generation such as pH, water activity, and temperature have already been studied (Hofmann and Schieberle, 1995) and because of the importance of C5 sugars in the formation of meatlike and savory flavors. In the following, we selectively determined potent odorants that could be identified under the analytical conditions rather than giving an entire view of volatiles generated.

The sensory properties of the reaction flavor obtained in the aqueous system were compared with those of the cubic phase sample by using a laboratory panel. The reaction carried out in the cubic phase was found to have a more intense overall flavor with a strong rubber, eggy, roast chicken-like aroma. The aroma of the aqueous reaction was evaluated after transformation of the solution into a cubic phase system in order to have similar volatile−matrix interactions. This mixture was weak in aroma, reminiscent of meat and lard with some burnt character.

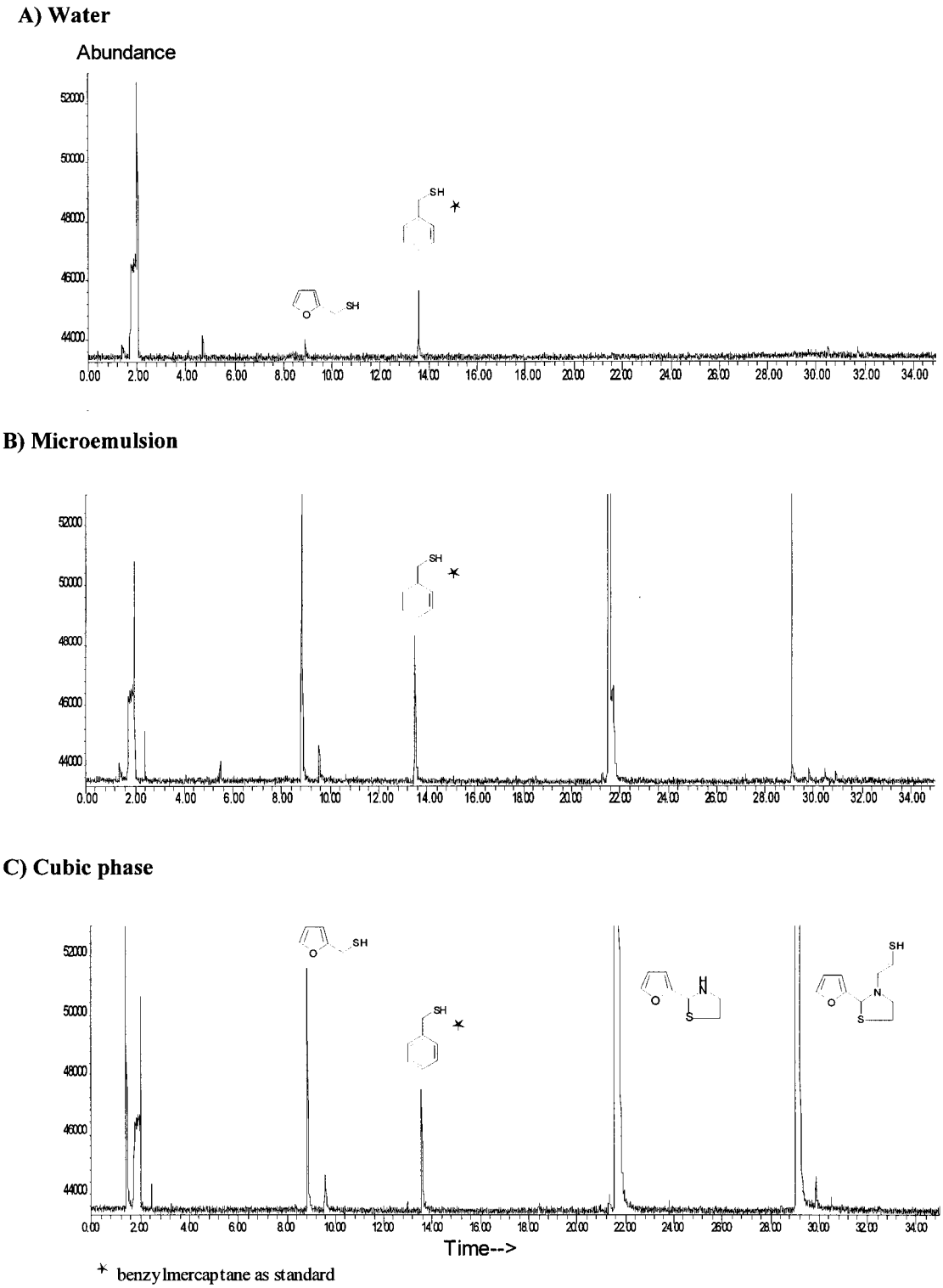

Figure 2. GC/FPD chromatogram (DB-1701 capillary column) of volatile compounds generated from the reaction of furfural/cysteine in (A) water, (B) microemulsion, and (C) cubic phase. The internal standard benzylmercaptane is indicated by ★.

The volatiles formed in the cubic phase and in water were monitored by GC/FID (Figure 6) and GC/FPD (Figure 7). The FPD chromatograms evidenced the differences between the two samples indicating generation of higher amounts of sulfur-containing compounds in the cubic system.

A multiple standard addition method was used to quantify six compounds in the reaction mixtures that were identified by comparison with the corresponding reference compounds based on RI on two capillary columns of different polarities (DB-5 and DB-1701) and their MS/EI spectra. Three compounds, covering the range of chemical and physical properties of the volatiles generated in the Maillard reaction, were chosen as internal standards (see Experimental Procedures). Possible differences in recovery yield of the analyte and the standard were not taken into account for the calculation of concentrations.

Similarly to the reaction of cysteine/furfural, there was a significant increase in the concentration of FFT

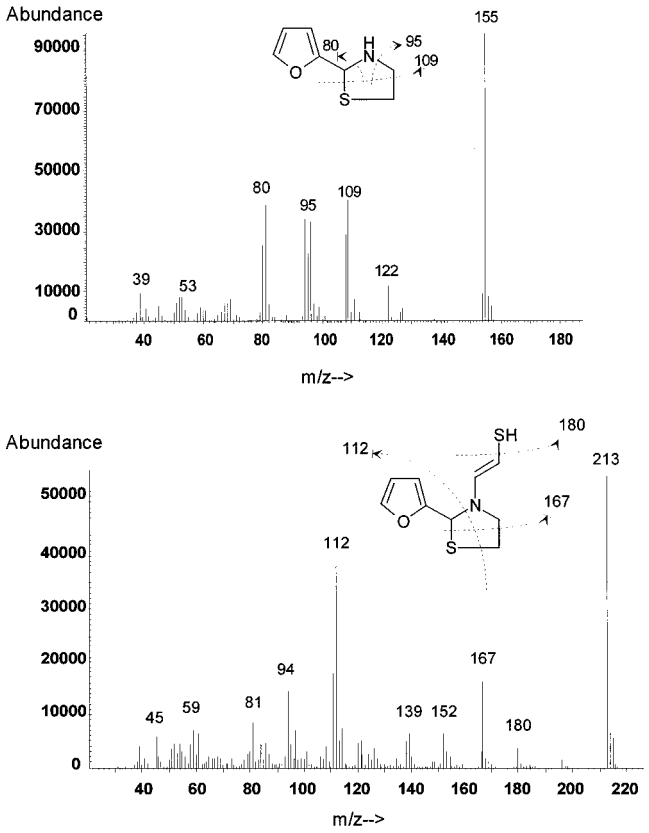

Figure 3. Mass spectra (MS/EI) of 2-(2-furyl)thiazolidine and tentatively identified *N*-(2-mercaptovinyl)-2-(2-furyl)thiazolidine.

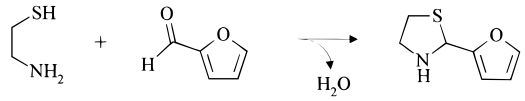

Figure 4. Synthesis of 2-(2-furyl)thiazolidine from cysteamine and furfural.

Table 1. Amounts of Volatile Reaction Products Generated from Furfural and Cysteine Solubilized in Different Matrices

	amount[a] (μg)		
matrix	2-furfuryl-thiol	2-(2-furyl)thi-azolidine	*N*-(2-mercaptovinyl)-2-(2-furyl)thiazolidine
water	1.8	nd[b]	nd[b]
microemulsion	8.7	42	11.7
cubic phase	11.6	240	123

[a] Mean values of duplicates (SD < 20%). [b] Not detected.

in the cysteine/ribose reaction mixture carried out in the cubic phase compared to the reaction in water, in which only trace amounts were detected (see Table 2). The detection limit under the given conditions was ~0.5 μg/5 g of cubic phase sample. The potent odorant MFT was detected only in the cubic phase system. The absence of this compound in the reference is surprising, but not contradictory to the findings in the literature (Hofmann and Schieberle, 1995). Indeed, this compound was detectable in the reference when the reaction system was directly extracted with diethyl ether, that is, no cubic phase was formed before extraction, and when the isolation of volatiles was done by vacuum distillation. The losses and poor recovery during isolation from the cubic phase also explain that some of the other odorants reported by Hofmann and Schieberle (1995) could not be detected, although they may have been formed.

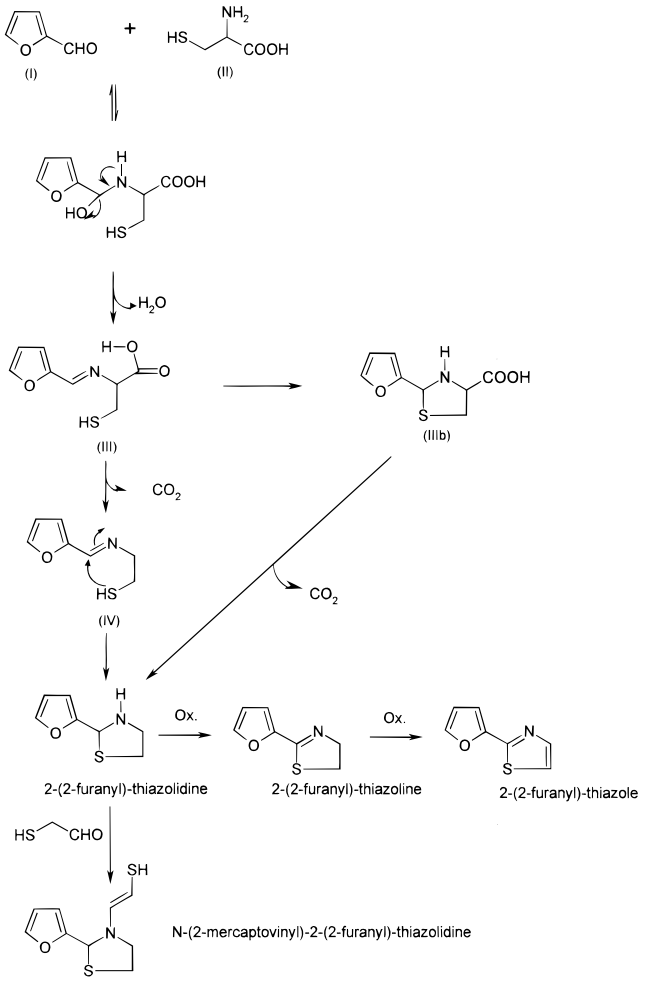

Figure 5. Hypothetical reaction pathway leading from cysteine and furfural to 2-(2-furyl)thiazolidine and *N*-(2-mercaptovinyl)-2-(2-furyl)thiazolidine.

Besides MFT and FFT, the formation of their precursors norfuraneol and furfural was favored in the cubic phase, being formed in ~2.5-fold higher amounts. These two compounds were recently found to be the key intermediates in the formation of thiols from C5 sugars (Hofmann and Schieberle, 1998).

The occurrence of 8.3 μg of MFT−MFT indicates that ~50% of the MFT was dimerized. The dimer could have been formed either during the Maillard reaction itself or afterward during the isolation procedure. Because MFT is very unstable in water and some organic solvents (Hofmann et al., 1996), we assume that the presence of the dimer is at least partly due to artifacts. Partitioning of MFT into the hydrophobic chain region of the cubic phase could be the reason for its enhanced generation.

DISCUSSION

This work clearly demonstrates that structured fluids, such as association colloids, strongly influence the thermal generation of volatiles from cysteine/furfural and cysteine/ribose mixtures. Various hypotheses will be discussed in an attempt to gain a first understanding of these phenomena.

Water Activity. The Maillard reaction is known to be dependent on water activity (Bell and Labuza, 1994).

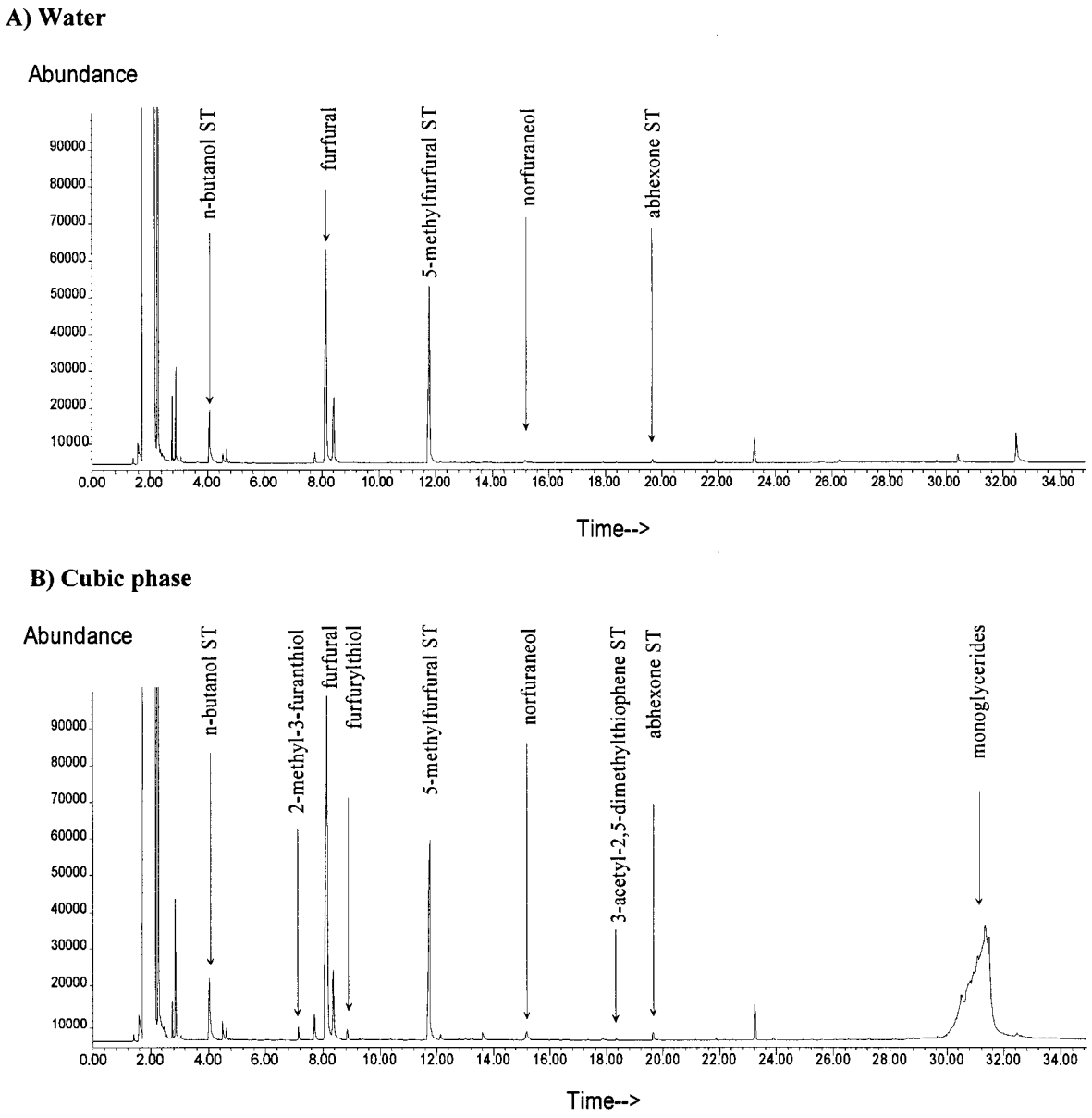

Figure 6. GC/FID chromatogram (DB-1701 capillary column) of volatile compounds generated from the reaction of ribose/cysteine in (A) water and (B) cubic phase.

Likewise, thermal flavor generation is influenced by water activity, as shown in dry-heated model systems of cysteine with different monosaccharides (Hofmann and Schieberle, 1998). In our study, however, both structured fluids (microemulsion and cubic phase) exhibited a water activity of ~1 and, consequently, the differences in the flavor formation cannot be explained by differences in macroscopic water activity.

Reaction pathways may, however, depend on water and reactant mobility and their availability to each other. In aqueous solutions, the reactants are totally free to interact, whereas in the investigated structured fluids the water is confined within cubic phase channels or the internal core of the microemulsion, respectively.

Often, it has been shown that rate enhancement is primarily due to an increase of reactant concentration in the water droplet (Holmberg, 1994; Tascioglu, 1996). In this study, furfural and cysteine were entirely solubilized in water before the different systems (cubic phase and microemulsion) were prepared, and their concentrations were based on the water content being identical in the systems. Furthermore, the partitioning of the reactants between the lipophilic and hydrophilic regions in the structured fluid phases lowers the actual concentration of the reactants in the water region. Nevertheless, we observed higher yields for FFT and MFT.

Role of the Surfactant—Water Interface. One of the possible mechanisms, which lead to the remarkable rate enhancement and to different product distribution, is the partitioning (compartmentalization) of the reactants at the surfactant−water interface or close to it, thus inducing a concentration gradient. Locally high concentrations at the interface are thought to strongly accelerate bimolecular reactions. Moreover, the close proximity of the reactants as well as their restrained movement within the interface will increase the frequency of molecular collisions (cage effect).

This hypothesis is quite coherent with previous results demonstrating that aspartame, a dimeric amino acid, is clearly solubilized at the interface of microemulsions (Furedi-Milhofer et al., 1999). Moreover, it was

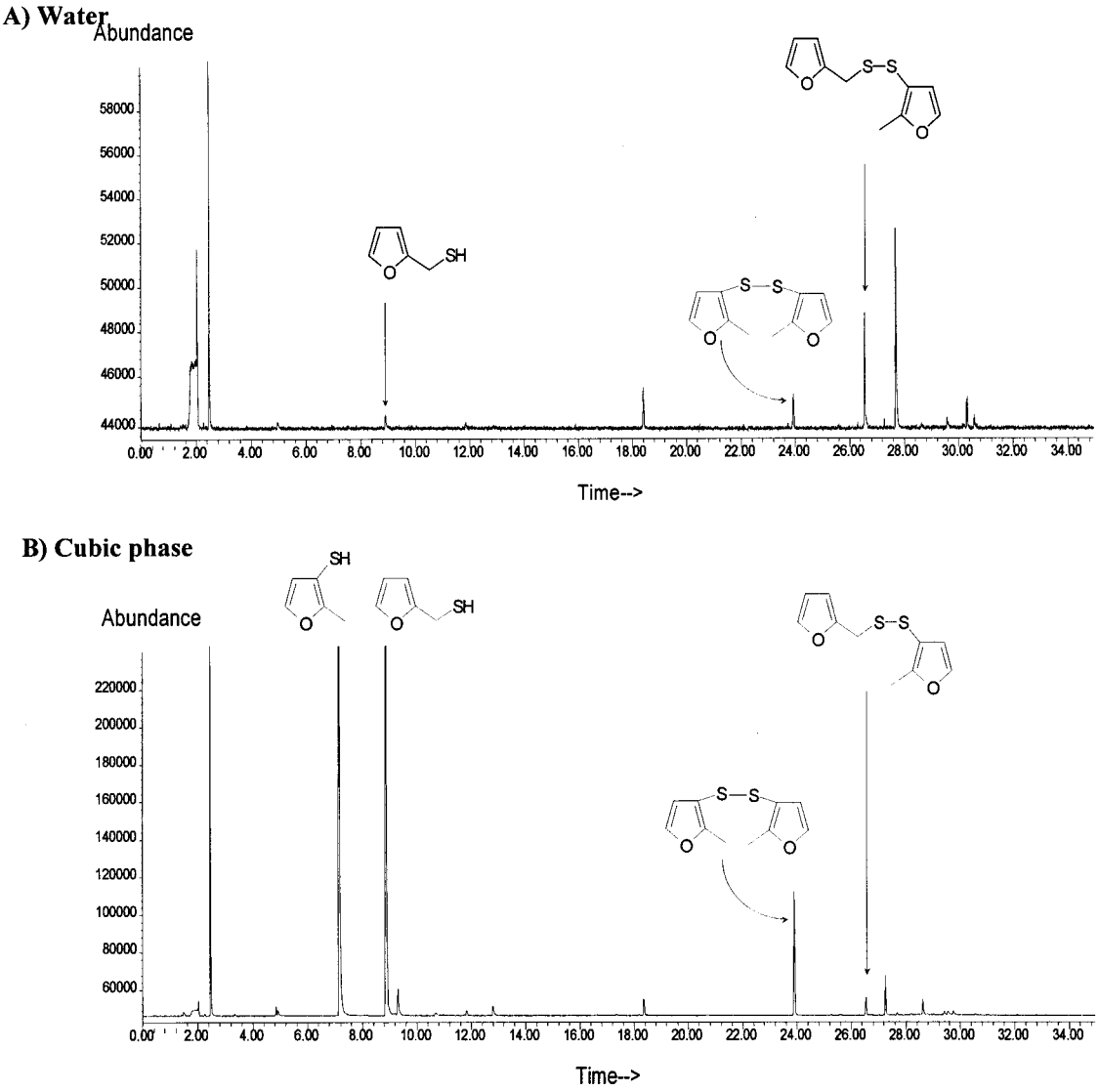

Figure 7. GC/FPD chromatogram (DB-1701 capillary column) of volatile compounds generated from the reaction of ribose/cysteine in (A) water and (B) cubic phase.

Table 2. Amount of Volatile Reaction Products Generated from Ribose and Cysteine Solubilized in Different Matrices

	amount[a] (μg)	
compound[b]	cubic phase	water
2-methyl-3-furanthiol (MFT)	18.4	nd[c]
2-methyl-3(*2H*)-furanone	36.7	13.1
furfural	874	351
2-furfurylthiol (FFT)	12.0	tr[d]
3-mercapto-2-pentanone	tr	nd[c]
norfuraneol	698	291
MFT−MFT	8.3	tr
MFT−FFT	tr	tr

[a] Mean values of duplicates (SD < 20%). [b] Compounds were identified by comparison with the reference compound based on retention indices on DB-5, DB-1701, and MS/EI spectra. [c] Not detected.

shown that even water-soluble molecules such as butanedione can induce a phase transition of the cubic phase into a lamellar phase due to interactions with the monoglyceride surfactant headgroup (Vauthey, 1998). Therfore, one may expect that cysteine, like aspartame or butanedione, will equally penetrate into the interface and will be localized or immobilized at the interface.

It has been shown in the literature that the release of H_2S from cysteine solution at pH 3−9 shows a first-order reaction enhanced by alkaline pH (Zheng and Ho, 1994). The activation energies are 31.3 and 29.4 kcal/mol for pH 3.0 and 9.0, respectively. On the other hand, H_2S release activation energies from glutathione were 18.8 and 19.9 kcal/mol at pH 3 and 9, respectively. Glutathione evolves H_2S more rapidly than cysteine. In this case, the negative charge of the carboxyl group is further away from the α-carbon than it is in cysteine (Zheng and Ho, 1994). Therefore, the hydrogen atom of the α-carbon is more readily abstracted. If cysteine is attracted to the surface, its negative charge will be embedded in the bilayer and will appear to be more distant to the α-carbon than it is in free cysteine. As a result, the pathway leading to the formation of FFT will become more favorable, as observed in our experiments.

Therefore, besides a concentration effect, the specific microenvironment at the surfactant−water interface may influence the transition state by lowering the activation energy (Tascioglu, 1996) and lead to a rate enhancement in the generation of volatiles.

Role of the Interfacial Area. Rate enhancement occurring in microemulsions is generally referred to as *microemulsion catalysis* (Rathman, 1996; Romsted et al.,

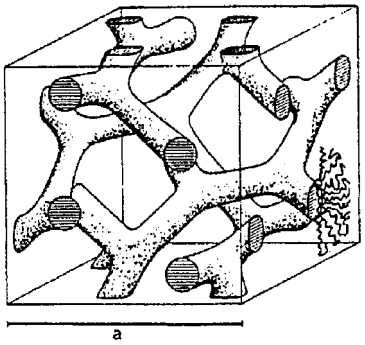

Figure 8. Structure of the bicontinuous cubic phase [adapted from Seddon (1990)].

1997). Tables 1 and 2 show the strong effect on the generation of volatile products in Maillard model reactions. Nevertheless, it has been shown in this work that flavor formation in cubic phases is even more efficient and yields higher amounts of key aroma compounds. We denominate this effect *cubic catalysis*; it can mainly be understood in terms of differences in the surfactant−water interface properties, such as interface area or curvature, assuming that the chemical reactions occur preferably at the interfacial layer.

It is well established that the three-dimensional structure of the cubic phase consists of water channels separated by a bilayer arranged in such a way that it forms a so-called infinite periodic minimal surface (see Figure 8). These result in a large interfacial area of ~400 m^2/g of cubic phase (Ericsson et al., 1991). On the other hand, assuming the formation of spherical droplets in the reversed microemulsion (L_2), a much smaller interfacial area is formed, which could explain the differences in flavor compounds generated between the two structured fluids. It is, however, not possible at this stage to predict how an increase in the interfacial area will influence the final production of the different volatile compounds. Moreover, the influence of the interface curvature is difficult to estimate. Indeed, very different yield ratios were obtained for FFT, 2-(2-furyl)-thiazolidine, and *N*-(2-mercaptovinyl)-2-(2-furyl)thiazolidine generated in the cubic phase compared to the microemulsion (Table 1).

Additional information on the binding constants of the reactants and the products is required to gain a more precise insight into the distribution of compounds between the aqueous phase and the interface.

CONCLUSIONS

Monoglycerides/water systems forming bicontinuous cubic phases as well as microemulsions have been used as "microreactors" for the generation of aroma compounds by the Maillard reaction.

It was shown that structured fluids which are organized on a nanometer scale can lead to remarkably higher yields of FFT and MFT as well as different aroma profiles in the thermal generation of volatile compounds. The flavor enhancement is partly due to an increase in the reaction yield of odor-active compounds and partly due to the wider variety of reaction products formed in these structured media. Cubic phases showed a significantly higher flavor enhancement than microemulsions. However, both structured fluids were significantly more efficient as a reaction medium than water.

It is postulated that the dominant factors affecting the reaction yield are the nature of the water/surfactant interface and its area. The present work highlights the potential of structured fluids in the thermal generation of flavors and opens up new avenues for enhanced flavor generation.

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