Structuring of Edible Oils by Long-Chain FA, Fatty Alcohols, and Their Mixtures

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ABSTRACT: Homologous series of fatty alcohols and FA with chain lengths ranging from 16 to 22 carbons were evaluated for their oil-structuring potential by texture profile analysis (TPA). FA, fatty alcohols, and their mixtures were found to structure sunflower oil and several vegetable oils at levels as low as 2% (w/w) for the pure ingredients. Mixtures of fatty alcohols and FA with the same chain lengths, at 5% (w/w) in sunflower oil, showed a synergistic effect below 20°C at the composition ratios of 7:3 and 3:7 (w/w). This synergistic effect in the 7:3 stearyl alcohol/stearic acid mixture was due to effects on the microstructure of the composite material. The larger number of small crystals observed in the mixture was attributed to effects on the crystallization kinetics as a result of minimal interfacial tension at the specific 1:3 and 3:1 molecular ratios.

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KEY WORDS: Crystallization, crystal size distribution, microstructure, organogel, stearic acid, stearyl alcohol, synergistic effect, texture profile analysis.

Many food or home and personal-care products are composite materials consisting of a continuous phase and at least one dispersed phase. The dispersed phase may consist, for example, of emulsion droplets or crystalline particles. The dispersed phase can form a network throughout the continuous phase if its phase volume exceeds a critical value (which is different for droplets and crystals, and will also depend on the presence of interactions between dispersed-phase elements and on their shape and size distribution). In such systems, the network will contribute to the rheological characteristics of the composite.

In general, edible oils are structured using TAG hardstocks. Margarine is a well-known example of such a system. Aggregation (flocculation) as a result of Van der Waals interactions between the fat crystals in the oil phase leads to the formation of a fat crystal network, which determines consistency, mouthfeel, oil exudation, and emulsion stability in the food product (1,2). These hardstocks generally contain high levels of saturated FA, which are undesirable for nutritional and health reasons, and alternatives would be welcome. Unfortunately, very few edible alternatives to these TAG structuring are known. Some data are available on structuring using MAG (3) and sterol mixtures (4).

Low-M.W. gelators of organic liquids, which form so-called "organogels," are an interesting class of alternative structuring agents. These systems are usually prepared by warming a mixture until the solid "gelator" dissolves and subsequently cooling it below the gelation or crystallization temperature (5). The properties of organogels are determined by both thermodynamic considerations (solubility) and kinetic aspects (crystallization kinetics), as crystal size and shape will depend strongly on the kinetic properties of the crystallization process (6) of gelator crystallization. Unfortunately, most gelator molecules described in the literature can be dismissed as completely unsuitable for use in foods. Recently, however, a system that comes very close to being applicable was described in the patent literature, i.e., mixtures of fatty alcohols and FA in TAG oils (7). Specifically, a mixture of behenic acid and stearyl alcohol was described as a solidifying agent in canola oil.

The present paper is intended to study the oil-structuring potential of FA, fatty alcohols, and their mixtures in more detail. Characterization was done by means of microscopy and the texture profile analysis (TPA) method. The synergistic effect in mixtures with the same chain lengths received special attention.

MATERIALS AND METHODS

Palmitic acid (98%), stearic acid (97%), eicosanoic acid (99%), 1-hexadecanol (96%), and 1-octadecanol (95%) were purchased from Acros Organics (Geel, Belgium). Behenic acid (97%), 1-eicosanol (95%), and 1-docosanol (97%) were purchased from Fluka (Buchs, Switzerland). All the structuring agents were used without further purification. The abbreviations C_n-OH and C_n-acid, with n = 16 to 22, will be used for the n-alcohols and the n-FA, respectively (Table 1). Unilever Research Vlaardingen supplied the sunflower, soybean, and rapeseed oils.

Sample preparation. The structuring agent was mixed with vegetable oil at room temperature and heated until dissolution of the solutes was complete (between 60 and 80°C, depending on the sample). The solution was allowed to cool at room temperature to about 40°C with mechanical stirring and was subsequently transferred to a plastic tub and stored at 5°C to crystallize at rest. Two tub sizes were used, 20 and 125 g.

TPA. The structuring potential of the various components was evaluated with a TA-XT2i texture analyzer from Stable Micro Systems Ltd. (Godalming, Surrey, United Kingdom) by

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TABLE 1
Physical Properties of n-Alcohols and n-FA

Common name	Systematic name	Abbreviation	m.p.[a] (°C)	Melting enthalpy[b] (kJ/mol)
Palmitic acid	Hexadecanoic acid	C_{16}-acid	61.8	54.9
Stearic acid	Octadecanoic acid	C_{18}-acid	68.8	61.3
Arachidic acid	Eicosanoic acid	C_{20}-acid	75.4	69.2
Behenic acid	Docosanoic acid	C_{22}-acid	81.0	
Palmityl alcohol	1-Hexadecanol	C_{16}-OH	49.3	34.7
Stearyl alcohol	1-Octadecanol	C_{18}-OH	59.5	66.6
Arachyl alcohol	1-Eicosanol	C_{20}-OH	66.1	73.7
Behenyl alcohol	1-Docosanol	C_{22}-OH	72.5	86.0

[a] Data from the *CRC Handbook of Chemistry and Physics*, edited by D.R. Lide, CRC Press, Boca Raton, FL, 1994.
[b] Data from the web site http://webbook.nist.gov/chemistry/
[c] Data from Reference 18.

using the TPA method. The sample was penetrated twice with a 12.7-mm diameter stainless-steel cylindrical probe (using a 25-kg load cell) in two consecutive up-and-down motions, and the resulting force (measured in compression) was recorded in grams as a function of time. The speed and distance of penetration were set to 2.0 mm/s and 10 mm, respectively. The pretest speed was set to 2.0 mm/s, and recording (acquisition rate of 0.01 s) was triggered automatically by a force of 5 g.

For the 125-g samples, three TPA measurements were taken on the same sample. As more measurements were performed on the same sample, the hardness value decreased. Hence, an average TPA curve was calculated using the software Texture Expert Exceed (version 2.13, Stable Micro Systems Ltd.). The hardness, defined as the maximum peak force during the first compression cycle, was determined from this average TPA curve.

A 125-g tub was used for experiments investigating aging and the effect of storage temperature. All other samples were prepared in a 20-g tub where only a single measurement could be done owing to the cost of raw materials. The reproducibility on three different 20-g samples was good, as indicated in the plots by an error bar representing the SD. The reproducibility for the systems C_{18}-OH, C_{18}-acid, and the C_{18}-acid/C_{18}-OH mixture was considered to be similar to that of the other compositions, for which only one 20-g sample could be prepared. This should be kept in mind when evaluating the results of other compositions. The hardness as a function of C_{18}-OH and C_{18}-acid concentrations was found to be quantitatively and qualitatively similar in both tubs. In the case of mixtures, the hardness was found to be only qualitatively comparable.

Microstructure. Crystal morphology was observed under crossed polarized light using a LM Zeiss Axioplan microscope. Under crossed polarized light, the oil phase, which is optically isotropic, appears completely dark and the presence of needle-like crystals is noticed by a bright white reflection.

RESULTS AND DISCUSSION

Structuring with pure components. Figures 1A and 1B show the hardness of organogels as a function of the concentration of the pure components. All samples were stored for 1 d at 5°C. Both the n-alcohols and n-FA had the potential to structure sunflower oil at concentrations as low as 2% (w/w). The increase in hardness was approximately linear, and an estimate of the solubility plus the percolation threshold of the components in sunflower oil could be determined from the $y = 0$ intercept. The structuring observed at low concentrations down to 2% was attributed to particles forming a network. The increase in hardness with increasing concentration was due to an increase in solids. At a constant temperature, the solubility was constant. Furthermore, we observed that, in general, the n-alcohols yielded harder products than the FA at the same concentration, with the exception of palmitic acid.

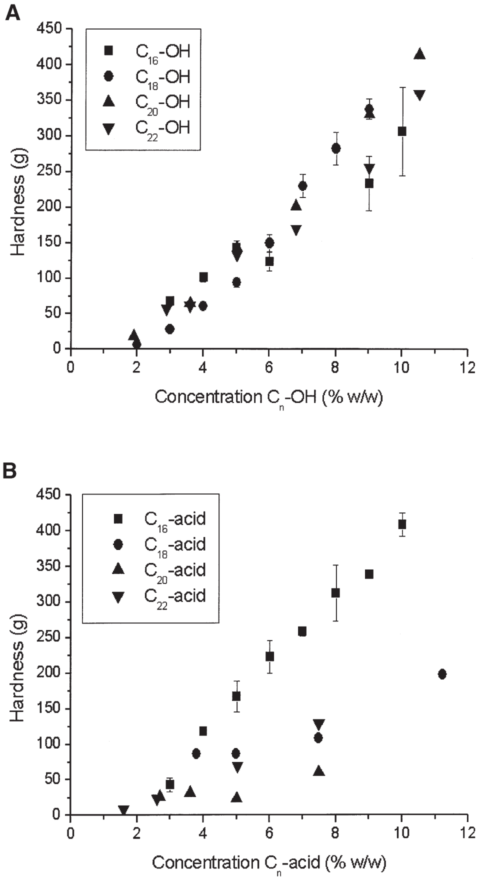

FIG. 1. Hardness of the pure components as a function of their concentrations in sunflower oil at 5°C. (A) n-Alcohols; (B) n-FA (20-g tub).

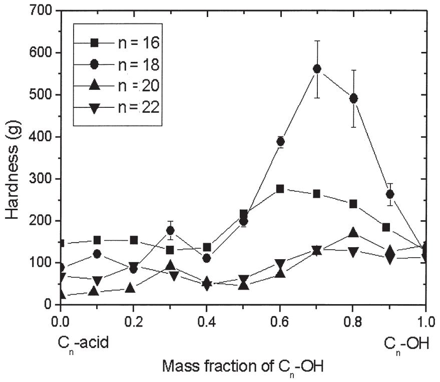

FIG. 2. Hardness at 5°C of mixtures of n-alcohols and n-FA with the same chain lengths at 5% (w/w) in sunflower oil (20-g tub). Error bars indicate SD.

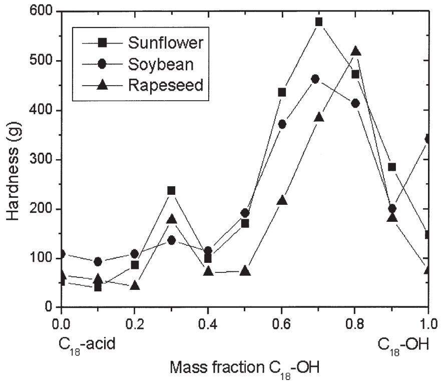

FIG. 4. Hardness at 5°C of mixtures of C_{18}-OH/C_{18}-acid at 5% (w/w) in different vegetable oils (125-g tub).

Structuring with binary mixtures (same chain lengths). Figure 2 shows the hardness of a mixture of FA and n-alcohols with the same chain lengths at a total concentration of 5% (w/w) in sunflower oil. All samples were stored for 1 d at 5°C. A common pattern appeared in the existence of two maxima in the curves at mixing ratios close to 7:3 and 3:7 (w/w). This synergistic effect was most pronounced for the stearyl alcohol/stearic acid (n = 18) binary mixture. For the C_{18}-OH/C_{18}-acid ratio with the most pronounced synergistic effect, a number of samples were produced at different total concentrations. At a total concentration of 7.5% (w/w), hardnesses greater than 1000 g could be obtained; at 2.5% a viscous and pourable solution was obtained without any hardness; and at 1.25% phase separation occurred, with crystals forming only a white layer at the bottom of the oil phase. In the composition range between 4:6 and 8:2 in the C_{18}-OH/C_{18}-acid mixture, more opaque samples were obtained than for the pure components.

Effect of storage temperature and aging. Figure 3 shows the effect of storage temperature on the hardness of stearic acid, stearyl alcohol, and stearyl alcohol/stearic acid (7:3) at 5% (w/w) in sunflower oil. The samples were stored 1 wk at 5°C following their preparation, and then for 2 wk at constant storage temperatures ranging from 5 to 40°C. A clear difference between the pure components and the mixture was noticeable. A synergistic effect between the components in the mixture began to take place at a temperature of 20°C. Above this temperature, the mixture behaved like the pure alcohol. This behavior is typical of gelling behavior, where the dispersed gelling agents begin to interact with each other and create a network at a specific temperature. As the temperature is decreased, more crystals are formed and the hardness increases. Looking at the pure components, we observed that the hardness of the fatty alcohol-based system was generally higher than the hardness of the acid-based system. At higher temperatures an inversion occurred, as the hardness of the fatty alcohol-based system decreased faster with temperature than did the FA-based system.

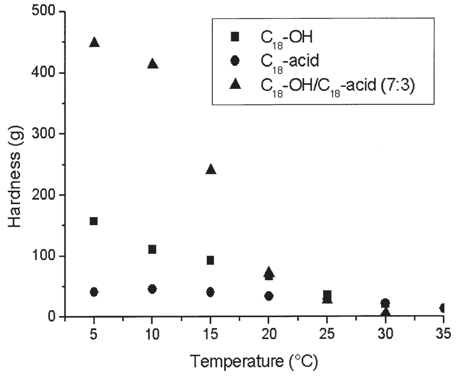

FIG. 3. Effect of storage temperature on the hardness of stearic acid, stearyl alcohol, and stearyl alcohol/stearic acid (7:3) at 5% (w/w) in sunflower oil (125-g tub).

For ideal solutions, the solubility can be calculated from the Hildebrand equation (9), which can be written as

$$\ln x = \frac{\Delta H_f}{R_g}\left(\frac{1}{T_m}-\frac{1}{T}\right) \qquad [1]$$

where x is the mole fraction of solute at temperature T in Kelvin, R_g the gas constant in J/mol·K, ΔH_f the molar heat of fusion in J/mol, and T_m the melting temperature of the solute in Kelvin. Assuming that this equation is valid in our system for the physical properties of C_{18}-OH and C_{18}-acid (see Table 1), at any given temperature above 5°C the acid would have more solids than the alcohol. If, in the range of solids considered here, the structure arises from primary bonds between the crystals, the structuring potential of C_{18}-OH per solids is greater than that for C_{18}-acid, and the inversion at high temperatures is due to the dissolution of C_{18}-OH.

The hardness of separate 125-g samples stored at 5°C was followed as a function of time. The structure, as characterized by hardness, was maintained for 1 mon of storage. No posthardening or postsoftening was observed.

Structuring of different oils. Figure 4 shows that the synergistic effect observed for the C_{18}-OH/C_{18}-acid binary mixture in sunflower oil at 5°C also occurred with soybean oil and rapeseed

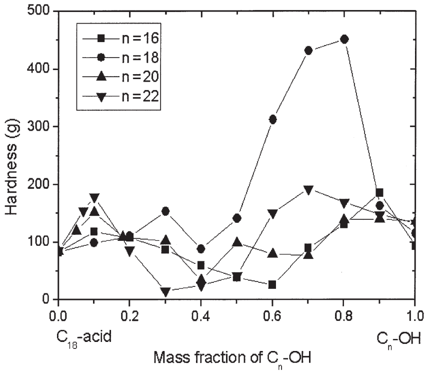

FIG. 5. Hardness at 5°C of mixtures of n-alcohols with different chain lengths and stearic acid at 5% (w/w) in sunflower oil (20-g tub).

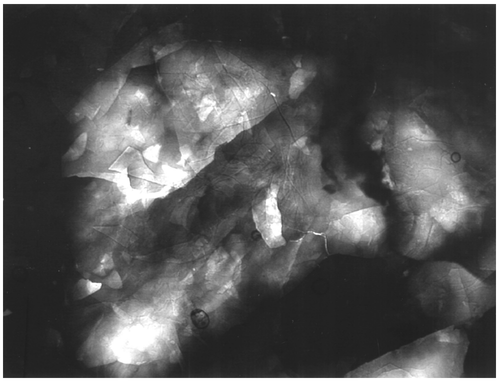

FIG. 7. Micrograph of C_{18}-OH at 5% (w/w) in sunflower oil after 1 d at 5°C (width 1900 µm).

oil. The synergistic effect was thus independent of the oil. Furthermore, one can observe that the hardness of stearyl alcohol at 5% in soybean oil was much higher than was the case for the two other vegetable oils. This effect illustrates that soybean oil had solids contributing to the structure at 5°C. Soybean oil contains 11% saturated palmitic FA, as does olive oil, and thus partially crystallizes at 5°C, as it would when refrigerated by a consumer. Rapeseed and sunflower oils contain only 4.3 and 6.7% palmitic FA, respectively.

Structuring with binary mixtures (different chain lengths). Figure 5 shows the hardness of mixtures of stearic acid (C_{18}-acid) and n-alcohols with different chain lengths (n = 16 to 22) at a total concentration of 5% (w/w) in sunflower oil. All samples were stored for 1 d at 5°C. A synergetic effect was quite evident in the C_{18}-OH/C_{18}-acid mixture compared with the FA/fatty alcohol combinations of the other chain lengths. In the latter systems, positive and negative effects were observed on the structuring behavior. The hardnesses of the mixtures increased or decreased compared with the pure compounds. In these systems, a pronounced minimum in hardness was observed. The minimum shifted toward the component with the shortest chain length, which was also the component with the lowest m.p. (C_{16}-OH; see Fig. 5 and Table 1). In the composition range in C_n-OH/C_{18}-acid between 4:6 and 8:2 (where n = 16 to 22), more opaque samples were obtained than for the pure components.

In the case of mixtures, the amount of solids will depend on the phase diagram and, in particular, on the solid–liquid equilibrium curve. In the case of a eutectic system, the m.p. of the eutectic component is below that of the pure components. Thus, fewer solids are expected when the composition is eutectic. The FA/n-alcohol systems behave in an eutectic manner (10). This explains the fact that a minimum in hardness was observed for a particular ratio. Furthermore, in a eutectic system, an increase in the difference between the m.p. of two substances will shift the eutectic toward the axis of the lower-melting substance. This shift in the minimum of hardness, which happened in our binary mixtures, led us to conclude that these systems also behaved in a eutectic manner in the presence of oil.

The particular case of the 7:3 C_{18}-OH/C_{18}-acid mixture at 5% in sunflower oil (where, surprisingly, a maximum in hardness was observed close to the theoretical eutectic ratio of 7:3) was investigated further by polarized light microscopy.

Figures 6–8 show the microstructures of C_{18}-acid, C_{18}-OH, and the 7:3 C_{18}-OH/C_{18}-acid mixture, respectively, at 5% in sunflower oil after 1 d of storage at 5°C. The acid has well-defined lozenge-shaped crystals of about 200 µm in size. The

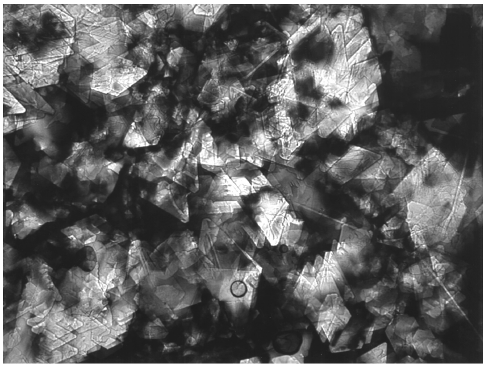

FIG. 6. Micrograph of C_{18}-acid at 5% (w/w) in sunflower oil after 1 d at 5°C (width 1900 µm).

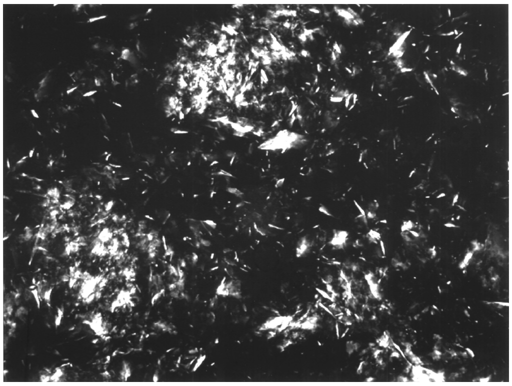

FIG. 8. Micrograph of C_{18}-OH/C_{18}-acid (7:3) mixture at 5% (w/w) in sunflower oil after 1 d of storage at 5°C (width 1900 µm).

crystals form agglomerates where the lozenges are stacked on top of each other. The alcohol shows a large fractured agglomerate of platelet-like crystals of about 1800 μm. In contrast, the mixture shows a large number of small crystals with a size of about 80 μm. The microstructure of the mixture explains why the hardness of the sample was higher than that of the pure components. It has been shown (11) that the ratio of surface area to average crystal length in a wax crystal network can be altered by varying the cooling rate of the mineral oils that act as a solvent. The yield stress increases with decreasing particle size, which is consistent with the behavior for flocculated colloidal gels.

The microstructure of the mixture may have been caused by one of three effects: (i) heterogeneous nucleation, (ii) a higher nucleation rate, or (iii) crystal habit modification.

Morphological and kinetic observations have been made on the heterogeneous nucleation of long chain n-alcohol crystals from solution in the presence of vapor-deposited thin films of FA (12). The C_n-acid template accelerated the crystallization of C_n-OH when the n value of the template film was the same as or longer by 2 than that of the guest crystals.

Langmuir monolayers of FA/fatty alcohol mixtures were studied by means of isothermal and X-ray diffraction measurements and were shown to be completely miscible (13). Mixed monolayers of stearic acid/stearyl alcohol exhibited a minimum area per molecule at the 1:3 and 3:1 molecular ratios (14). This led to a decrease in interfacial tension at these particular ratios. According to the classical nucleation theory, a lower interfacial tension will result in a smaller critical radius and thus to a greater rate of nucleation. Aggregation and gelation does not occur immediately after a solution is cooled below the crystallization temperature. The kinetics of growth of the colloidal aggregates follows nucleation and growth laws (14–17). The classical equation for the homogeneous nucleation rate, *J*, can be written as follows:

$$J = J_{\max} \exp\left(-f \frac{\gamma^3 V_c^{\,2}}{\left(k_b T\right)^3 \left(\ln c / c_{\mathrm{eq}}\right)^2} \right) \qquad [2]$$

where $J_{\max}$ is the maximum nucleation rate, *f* a constant depending on the geometry of the critical nucleus, γ the interfacial free energy, V_c the molecular volume in the crystal lattice, k_b the Boltzmann constant, *T* the absolute temperature, *c* the concentration, and c_{eq} the equilibrium concentration. For a given system, $J_{\max}$ depends on the maximal molecular collision frequency and on the configuration of the nucleating molecules. The nucleation rate will be strongly dependent on the supersaturation ratio c/c_{eq} and the interfacial energy, γ. From Equation 2, a decrease in the interfacial energy or an increase in the supersaturation ratio will lead to a higher nucleation rate and thus to a decrease in the average crystal size. In the 7:3 C_{18}-OH/C_{18}-acid mixture, the supersaturation ratio was at a minimum; thus, the increase in the number of crystals must be attributed to an effect on the interfacial energy. In the case of lipids, for example, according to Ostwald's rule, the α-polymorph often nucleates before the β′ or β polymorphs despite the existence of a substantial undercooling of the two more stable polymorphs (β and β′). Thus, the nucleation of lipid polymorphs is kinetically controlled, and they are transformed into stable phases for thermodynamic reasons. This effect is often attributed to the α-polymorph having a lower interfacial tension but also results from changes on the pre-exponential factor $J_{\max}$.

The third possibility is that, during crystallization, the fatty alcohol and the acid act as surfactants. Crystallization phenomena and processes may be greatly affected by the addition of surfactants, which play an important role in nucleation and growth kinetics and can substantially modify both the habit (shape) and size distribution of crystal products (18). The nucleation rate of magnesium sulfate is known to be higher in the presence of SDS, probably reflecting a reduction of the solid surface free energy. A common observation with the addition of surfactants is the reduction of crystal size often associated with a decrease in growth rate (18).

Thus far, our results point to the fact that the predominant mechanism explaining the synergetic effect in the stearyl alcohol/stearic acid system in oil is the increase in nucleation rate due to the lowering of the interfacial energy. Furthermore, we have shown that the microstructure has a major impact on the hardness of a system. Further studies should focus on the initial stages of nucleation in these systems by looking, for example, at the possibility of mixed micelle formation before the onset of crystallization.

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