Theoretical Aspects of Surfactants in Relation to Their Use in Breadmaking¹

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ABSTRACT

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The physical chemistry of food grade surfactants used in breadmaking is discussed in relation to their functionality as dough conditioners and crumb softeners. A general survey of surface activity of surfactants and their ability to form lyotropic, mesomorphic phases in water is followed by a discussion

of how surfactants may interact with the components of flour: starch, proteins, and lipids. The formation of ordered surfactant-water structures in the dough may play a vital part in the function of dough conditioners and crumb softeners.

Surfactants in the form of monoglycerides and diglycerides have been used in the food industry since about 1921, and some industrial production of food grade surfactants has taken place for more than 50 years. Today the food industry annually uses approximately 100,000 tons of fat-derived surfactants, of which monoglycerides and their derivatives total about 75% on a volume basis

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0009-0352/81/03015807/\$03.00/0 ©1981 American Association of Cereal Chemists, Inc. Cereal-based foods produced in the industrialized parts of the world are one of the major markets for surfactants, which are used as dough conditioners; as crumb softeners in bread, buns and rolls; and as aerating agents in cake systems. Furthermore, surfactants are used as emulsifiers in emulsions (coffee whiteners, margarines, spreads), as amylose-complexing agents in starch-based foods (processed potatoes), as aerating agents in toppings and whipping creams, or as crystal-modifiers in fats.

CHEMICAL STRUCTURE

Most surfactants consist of hydrophobic fatty acid chains esterified to a hydrophilic polar group that can originate from different types of polyvalent alcohols, such as propylene glycol,

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glycerol, sorbitan, or sucrose. Furthermore, the polar group can be modified by esterifying it with organic acids, such as lactic, acetic, citric, succinic, diacetyl tartaric acid (DATA), etc. Ethoxylated sorbitan esters or ethoxylated monoglycerides (EMG) are nonionic, very hydrophilic surfactants. The anionic stearoyl lactylates are esters of lactic acid and fatty acids, usually partially neutralized in the form of sodium stearoyl-2-lactylate (SSL) or calcium stearoyl-2-lactylate.

The fatty acids esterified to the polar group may be blends with chain lengths from C_{12} to C_{20} depending on the type of hydrogenated or unhydrogenated fats (edible lard or tallow, sunflower oil, soya bean oil, etc.) or fatty acids used in the manufacture of the surfactants.

Both the fatty acid chain length and the degree of unsaturation are important for the functional properties of the surfactants. The manufacture of food surfactants has recently been described by Birk Lauridsen (1976) and van Haften (1979). Chemical specifications of the surfactants used in the baking industry (Table I) are available from Food Chemical Codex, 2nd ed., FAO Food and Nutrition paper (1978) or from the E.E.C. Council Directive of 25 July 1978 (1978), which gives specific criteria of purity for emulsifiers, stabilizers, etc.

SURFACE ACTIVITY

Surfactants are amphiphilic substances that, because of their chemical structure, possess both hydrophilic and lipophilic properties.

When surfactants are added to an oil or a water phase, they adsorb in one or more layers at the interphase between oil and water. In terms of energy, this adsorption at the interphase is a more favorable situation than a complete solution of the surfactant in either the oil or the water phase is. Surfactants reduce the interfacial tension (Fig. 1) and promote the emulsification of the two liquids. Furthermore, the emulsion stability is increased. In bread or cake shortenings, emulsifiers give a better distribution of the shortening in the dough, probably because of reduced surface tension of the fat.

The surface activity of emulsifiers is closely related to their chemical structure. The so-called hydrophilic/lipophilic balance (HLB) of an emulsifier depends on the hydrophilicity of the polar group in relation to the lipophilicity of the fatty acid group. Figure 1 shows that surfactants with a small polar group (low HLB), such as monoglycerides or propylene glycol esters, have less effect on the interfacial tension than do surfactants with a large polar group (high HLB), such as SSL, DATA esters, or polysorbates. HLB, as defined by Griffin (1954), is expressed on a numerical scale ranging from 0 to 20.

Davies (1957) has suggested allocating HLB numbers to the various hydrophilic and lipophilic components of the surfactant molecule and calculating the HLB value of the molecule. Such calculations must be considered with special caution, however,

because industrially produced surfactants are always mixtures of homologous components and are not fully represented by a single molecular formula.

Emulsion stability depends on a number of factors, such as droplet size, viscosity of the continuous phase, surface tension, and the formation of protecting films around the dispersed droplets.

Adsorbed emulsifier molecules at an oil (O)/water (W) interface can form various types of films that depend on the packing

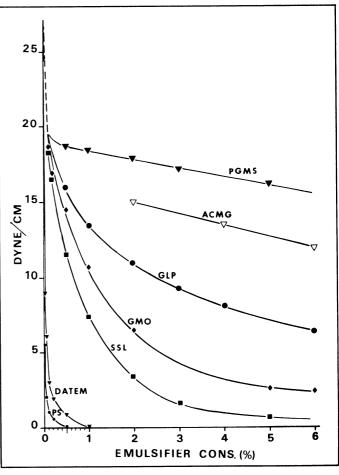


Fig. 1. Interfacial tension between soybean oil and water at 50° C. Measured by the Du Nouy ring technique. PGMS = distilled propylene glycol monostearate, ACMG = acetylated monoglycerides with acetylation degree of 0.7, GLP = lactylated monoglycerides, GMO = distilled monoglycerides from sunflower oil, SSL = sodium stearoyl-2-lactylate, DATEM = diacetyl tartaric acid ester of monoglycerides, PS = polysorbate 60 (from Krog 1977).

TABLE I
Specifications of Dough Conditioners/Crumb Softeners

	European Economic Community Regulation Number	U.S. Food and Drug Agency			
		Standardized Products Limitations ^a (%)	Nonstandardized Products		
Products			Limitations (%)	Reference ^b	
Monoglycerides and diglycerides	E.471	No limit	G.M.P.°	182.4505	
Diacetyl tartaric acid esters of monoglycerides	E.472e	No limit	G.M.P.	182.4101	
Sodium stearoyl-2-lactylate	E.481	0.5	P.T.E.d	172.846	
Calcium stearoyl-2-lactylate	E.482	0.5	0.5	172.844	
Succinylated monoglycerides	***	0.5	0.5	172.830	
Polysorbate 60	Annex II	0.5	0.5	172.836	
Ethoxylated monoglycerides	•••	0.5	0.5	172.834	

^aCode of Federal Regulations 21 (136.110).

^bCode of Federal Regulations.

^cGood manufacturing practice.

^dAmount not greater than that required to produce intended physical or technical effect.

conditions of the emulsifier hydrocarbon chains. In gaseous films, the molecules are oriented flat along the interface and can move independently. This gives a low surface pressure and no intermolecular cohesion between the surfactant molecules. In liquid expanded films, the surfactant molecules are packed closely together and considerable cohesive forces are found between the hydrocarbon chains, even though they are in a liquid, highly disordered state, horizontally oriented towards the interface. In liquid condensed films, the molecules are packed closely together, and strong cohesive forces exist between the hydrocarbon chains, which are oriented vertically towards the interface in a liquidlike state with a limited degree of mobility. Solid condensed films are similar to liquid condensed films, but the hydrocarbon chains of the surfactant molecules are in a crystalline state as in the α polymorphic form of fats (Davies and Rideal 1963, Lutton et al 1969, Tanford 1973).

The surface pressures of these films increase in order from gaseous to liquid expanded to liquid condensed to solid condensed. Emulsion stability increases in the same order because of the ability of condensed interfacial films to protect against the coalescence of dispersed droplets (Shaw 1970).

Boyd et al (1972) studied emulsion stability in relation to HLB values of mixed emulsifiers. Optimum emulsion stability is found when a lipophilic emulsifier and a hydrophilic emulsifier are mixed in a specific molar ratio. The rate of coalescence was lowest when the two emulsifiers were mixed in a ratio giving HLB 3.8 for W/O emulsions and 12 for O/W emulsions.

Furthermore, both the elasticity and the viscosity of the interfacial film are important factors in preventing coalescence of emulsion droplets.

The packing conditions of fatty acid hydrocarbon chains in bulk solutions of surfactants forming lamellar mesophases are closely related to the packing conditions of hydrocarbon chains in liquid condensed films. Therefore, information on how surfactants are adsorbed at O/W interfaces can be obtained by studying low-angle X-ray data of lamellar mesophases of surfactants in water. The optimum molar ratio of mixed emulsifiers that provides condensed packing conditions of the hydrocarbon chains has thus been found by low-angle X-ray diffraction studies on bulk solutions of surfactant blends (Boyd et al 1974, Krog 1974).

FORMATION OF LYOTROPIC. MESOMORPHIC PHASES

When surfactant crystals are mixed with water and the temperature is above the so-called Krafft point (Tc), the hydrocarbon chains transform from the solid state to a liquidlike state; at the same time, water penetrates through the layers of polar groups and a liquid-crystalline mesophase is formed (Fig. 2). If the temperature is further increased, the lamellar structure may break down and other mesophases may be formed, ie, cubic or hexagonal. The schematic structures of the lamellar, hexagonal, and cubic mesophases are shown in Fig. 3.

On cooling below the T_c, the hydrocarbon chains crystallize again, normally in the α -crystalline form with hexagonal chain packing. The same volume of water may still be located between the lipid bilayers, and a gel structure consisting of bimolecular lipid layers alternating with water layers is formed as shown in Fig. 2. Such surfactant-water gels comprise an important active physical state in which the surfactant reacts optimally with water-soluble components, like amylose, or with dispersed gluten proteins. The mesomorphic behavior of monoglycerides in water has been investigated by Lutton (1965), Larsson (1967), and Krog and Larsson (1968). Of the liquid crystalline mesophases, the lamellar mesophase is the most interesting. The surfactant molecules are arranged in bimolecular lipid layers with the polar groups in contact with the water layers. The lamellar phase may be diluted with up to more than 95% water, provided the swelling conditions of the water layer are carefully controlled with regard to ion concentration and pH (Krog and Borup 1973). In the hexagonal II mesophase, the hydrocarbon chains form the continuous phase and the polar groups are oriented towards the cylindrical aggregates of water. This mesophase cannot swell in excess of approximately 40% water. If more water is present, a two-phase system or an emulsion is formed. This also applies to the cubic phase of monoglycerides.

In the model of the cubic phase, shown in Fig. 3, water is enclosed in spherical units arranged in a three-dimensional pattern. This structure has recently been reevaluated by Lindblom et al (1979), who suggest that the water aggregates are separated by lipid bilayer units in such a way that both the lipid phase and the water phase are

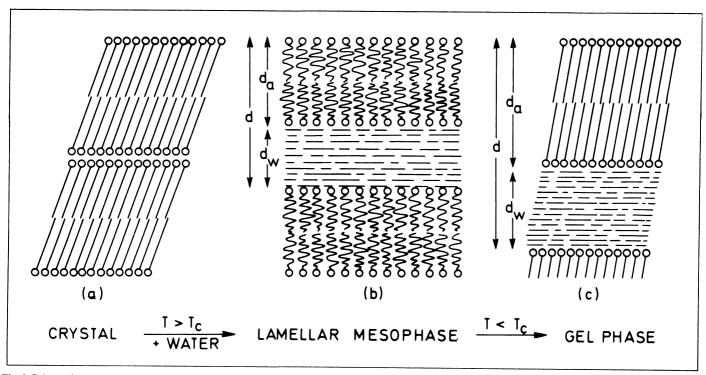


Fig. 2. Schematic model showing swelling of a surfactant crystal (a), and formation of a liquid-crystalline lamellar mesophase (b) at temperature (T) above the Krafft point (T_c), and, on subsequent cooling below T_c, the formation of an α-crystalline surfactant-water gel phase (c). d = X-ray Bragg spacing, d_a= calculated thickness of bimolecular lipid layer, d_w = calculated thickness of water layer (from Krog and Birk Lauridsen 1976).

continuous. Binary phase diagrams of saturated monoglycerides and unsaturated monoglycerides in water are shown in Fig. 4. The phase behavior of some important food surfactants in water has been reviewed by Krog and Birk Lauridsen (1976). EMG as well as polysorbates and anionic surfactants like DATA esters, SSL, and succinylated monoglycerides form ordered structures in water at ambient temperature. EMG and polysorbates form hexagonal I (middle) mesophases in water, which on further dilution break down into micelles. DATA esters, SSL, and succinylated monoglycerides form lamellar liquid crystalline or gel phases (as shown in Fig. 2b and c), depending on the temperature and provided the pH is above 5-6.

Table II shows X-ray data (Krog 1975) of a lamellar monoglyceride-water phase, the corresponding gel phase, a hexagonal II phase of SSL-water, and a hexagonal I phase of polysorbate 60-water. The structure of the hexagonal I phase is not shown in Fig. 3, but it is the reverse of hexagonal II. This means the surfactant molecules are arranged in cylindrical aggregates, with the polar groups facing the outer continuous water phase. The data in Table II show that the surface area per molecule of surfactant exposed to the water phase increases from 32 (Å)² for monoglycerides to 138 (Å)² for polysorbate 60.

TABLE II
X-Ray Data of Surfactant-Water Phases

Type of Phase	X-ray Spacing (Å)	Lipid Bilayer Thickness (Å)	Water Layer Thickness (Å)	Specific Surface in Contact with Water (Å) ²
Monoglyceride-water 60:30 w/w, lamellar				
phase, 60°C	63.8	38.1	25.7	32.0
60:40 w/w, gel				
phase, 25°C	93.9	54.9	39.0	22.0
Sodium stearoyl-2- lactylate-water 58:42 w/w, hexagonal II phase, 60° C	59.5	19.2	40.3	42.6
Polysorbate 60-water 60:40 w/w, hexagonal I phase, 45° C	77.1	62.7	14.4	138.0

From Krog 1975.

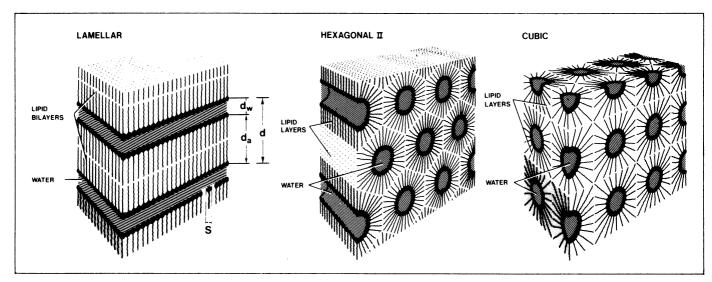
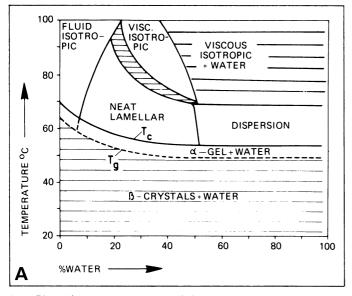


Fig. 3. Schematic structure models of the lamellar, hexagonal II, and cubic mesophases. d = X-ray Bragg spacing, $d_a = \text{calculated thickness of bimolecular}$ lipid layer, $d_w = \text{calculated thickness of water layer}$, S = area per molecule surfactant in contact with water (from Krog 1975).



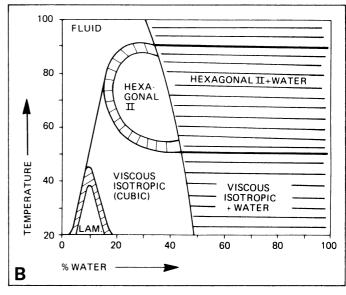


Fig. 4. Phase diagrams: A, saturated, distilled monoglyceride (DIMODAN PM)-water; B, unsaturated, distilled monoglyceride (DIMODAN LS)-water. Hexagonal II = reversed hexagonal.

SURFACTANTS AS DOUGH CONDITIONERS

The role of wheat flour lipids in combination with surfactants in breadmaking has been studied by many researchers. An excellent review on this complicated subject has been given by Chung et al (1978).

The binding of lipids, native flour lipids as well as surfactants, to the starch fraction and the gluten fraction in doughs has been studied primarily by using solvent extraction methods. The lipids extracted from the gluten fraction are generally characterized as free lipids, bound lipids, and strongly bound lipids, depending on the polarity of the solvents used to release the lipids. Little is known about molecular interactions between a surfactant and the individual gluten proteins. Based on lipid binding studies, Hoseney et al (1970) have suggested that flour free polar lipids (glycolipids) are bound to glutenin by hydrophobic bonding and to gliadin by hydrogen bonding or electrostatic bonds. The simultaneous binding of surface-active lipids to both gliadin and glutenin may contribute to increased gas retention ability of gluten. Several models for lipid interaction with gluten proteins and starch have been demonstrated (Chung et al 1978).

Another theory for lipid interactions with gluten is the well-known Grosskreutz model for the gluten structure (Grosskreutz 1961). Here the lipids are suggested to be present in a bimolecular lipid layer that separates platelets of protein units. Based on low-angle X-ray scattering of gluten protein solutions, the conclusion was drawn that the protein platelets have a diameter of 10,000 Å and a thickness of 70 Å. The lipid bilayer separating the protein units was estimated on the basis of the occurrence of an X-ray diffraction line about 48-50 Å. Stutz et al (1973) suggested that surfactants in the form of stearoyl lactylates (calcium stearoyl-2-lactylate or SSL) interacted with gluten proteins in a way similar to that of the Grosskreutz lipid bilayer.

Larsson (1979) has pointed out, however, that one single lipid bilayer cannot give a sharp diffraction line. Only a multilayered mesophase with a strict periodicity in at least one dimension, such as the lamellar mesophase has, can give a sharp diffraction line. The X-ray line is significantly broadened when the size of the ordered region is reduced to a thickness below 1,000 Å perpendicular to the corresponding diffraction plane.

According to Larsson (1979), the only reasonable explanation for an X-ray spacing near 50 Å is that it originates from a lipid, liquid-crystalline phase with a lamellar structure. This theory is further supported by recent studies on the phase behavior of isolated wheat flour lipids in water by Carlson et al (1978); those studies showed that wheat lipids form liquid-crystalline phases in

TABLE III
Amylose Complexing Effect of Surfactants

Type of Surfactant	Amylose Complexing Index ^b	
Distilled monoglycerides from		
Hydrogenated		
Lard (65% monostearin, 30% monopalmitin)	92	
Soybean oil (85% monostearin)	87	
Unhydrogenated		
Lard (45% monoolein)	35	
Soybean oil (55% monolinolein)	28	
Acetylated monoglycerides	0	
Mono-diglycerides, saturated (50% monoester)	42	
Organic acid esters of monoglycerides		
Lactylated monoglycerides	22	
Succinylated monoglycerides	63	
Diacetyl tartaric acid esters	49	
Propylene glycol monostearate (90% monoester)	15	
Sorbitan monostearate	18	
Polysorbate 60	32	
Sodium stearoyl-2-lactylate	72	
Calcium stearoyl-2-lactylate	65	
Lecithin (from soybean oil)	16	

^a From Krog 1971.

water. Ternary phase diagrams of wheat and gluten lipids (Carlson et al 1979b) show the presence of two liquid-crystalline phases, the lamellar type and the hexagonal II type. Larsson (1979) examined lipids from flours with good and poor baking performance and found some relationship between the ability of the lipids to form a lamellar phase in water and the baking quality of the flour. This indicates that the liquid-crystalline state is important for the functionality of flour lipids.

Surfactants that are most effective as dough conditioners (ie, SSL, EMG, DATA ester, Polysorbate) are all able to form lamellar mesophases or gel structures in water at dough mixing temperatures. We are therefore tempted to assume that the functionality of native flour polar lipids and of added surfactants is related to their ability to form ordered structures of lamellar type similar to biological membranes in the water phase of the dough.

MacRitchie (1977) and Larsson (1979) have supported the theory that polar lipids, including surfactants active as dough conditioners, function as foam stabilizers in the dough. According to this concept, the polar lipids are concentrated in the aqueous phase of the dough surrounding the gas bubbles in ordered structures similar to the mesophase structures of bulk solutions of isolated wheat lipids in water. Addition of surfactants (dough conditioners) to a dough may act in a similar way and support the native flour lipids in their foam-stabilizing function.

In principle, surfactants can function as dough conditioners in two ways. First, surfactant molecules can interact by means of hydrophobic and/or hydrophilic binding (electrostatic or hydrogen bonds) to gluten proteins. According to this concept, the added surfactant must be soluble in the water phase of the dough on a molecular level in order to perform as a dough conditioner. Second, surfactants can interact in bulk form with the water phase of the dough, forming associated lipid-water structures together with flour free polar lipids. The structure of the lipid-water mesophases may be of the lamellar type, allowing the high degree of molecular freedom seen in biological membranes. Bimolecular lipid layers may associate with both polar and nonpolar surfaces of protein aggregates or stabilize air-water interfaces.

SURFACTANTS AS CRUMB SOFTENERS

The crumb-softening effect of surfactants is closely related to their effect as starch-complexing agents. The mechanism of starch complexing and its effect on crumb softening and staling rate of bread have been reviewed by Knightly (1973).

The linear amylose fraction of starch forms a helical structure in the presence of a complexing agent, which can be a saturated monoglyceride. The helix is stabilized by the fatty acid hydrocarbon chain that fulfills the hydrophobic solvation requirements of the helix. Once the helical complex is formed, it is generally insoluble in water. Carlson et al (1979a) showed that the hydrocarbon chain conformation inside the amylose helix seems to

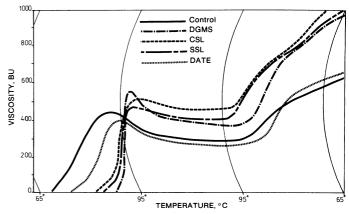


Fig. 5. Amylograph curves of wheat starch. Surfactants were added at the 0.5% level, starch basis. **DGMS** = distilled saturated monoglycerides, **CSL** = calcium stearoyl-2-lactylate, **SSL** = sodium stearoyl-2-lactylate, **DATE** = diacetyl tartaric acid esters of monoglycerides (from Krog 1973).

^bMilligrams of amylose precipitated by 5 mg of surfactant.

be ordered as in the crystalline state, and their results indicate that the polar group is not included in the helix. Kim and Robinson (1979) reported that the amylose-surfactant complex significantly impedes β -amylolytic degradation of amylose. Furthermore, they found that complexes formed by ethoxylated surfactants (EMG or polysorbate 60) were not insoluble in water.

The complexing effect of monoglycerides with different chain lengths was studied by Lagendijk and Pennings (1970) and Krog (1971). Optimum complexing effect was found with saturated monoglycerides having a chain length from C₁₄ to C₁₈. One mole of amylose reacts with approximately 20 moles of glycerol monopalmitate to form an insoluble complex in water. The precipitated complex still has considerable iodine affinity, indicating free spaces in the amylose chain that can be occupied by iodine. If 1 mole of amylose is reacted with 100 moles of glycerol monopalmitate, the iodine affinity of the complex would be reduced to zero.

Comparison of the complexing abilities of various surfactants shows that saturated, distilled monoglycerides are the most effective (Table III).

A good correlation between the amylose-complexing index and the crumb-softening effect in bread was found by Krog and Nybo Jensen (1970) and Lagendijk and Pennings (1970).

When monoglycerides are added to a bread dough in the form of β -crystalline hydrates, the thin β -crystals adsorb to the surface of starch granules during dough mixing. During the baking process, the β -crystals of monoglycerides transform first into the α -crystalline state and then into a liquid crystalline phase, in which form the monoglycerides are active in amylose complex formation. This may take place at temperatures of about 50° C and well before the starch granules begin to gelatinize. The swelling of starch granules in bread is therefore delayed and the amount of free amylose formed is diminished by the reaction with surfactants, resulting in a softer crumb structure. Because reduced swelling of starch granules makes more water available for the gluten phase, it may indirectly influence the moisture distribution between starch and gluten (Willhoft 1973).

Figure 5 shows the influence of various surfactants on amylograph curves of wheat starch. The pasting temperature is delayed most by distilled monoglycerides. This is possibly related to their amylose-complexing effect (Krog 1973).

How much surfactants can influence the retrogradation of amylopectin, a major factor in the complicated bread staling process, is not quite clear.

CONCLUSION

The function of surfactants in breadmaking is obviously complex, and this is especially true for the dough-conditioning effect of surfactants. To understand their function, both the chemical and physical properties of surfactants should be considered. Surfactants added to a dough system in a crystalline form must go into solution in the aqueous phase of the dough before they can react with flour constituents on a molecular or bulk phase level. The interactions of surfactants with water and their associations into ordered, mesomorphic structures should therefore be taken into consideration. Surfactants may form ordered lipid-water structures together with flour lipids during dough mixing. From such structures lipid bilayers may be exposed to gluten proteins (modifying their rheological properties), to air/water interfaces (stabilizing the gas bubble structure during fermentation), or to starch granules (delaying their gelatinization). Finally, the ordered lipid-water structures may be a vehicle for molecular interactions between surfactants and protein or starch components.

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