

Effect of Surfactant Structure on the Pasting Properties of Wheat Flour and Starch Suspensions

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ABSTRACT

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Systematic studies were performed on the effect of the surfactant alkyl chain length (10–16 carbon atoms) and the head group charge/structure (anionic, cationic, nonionic) on the pasting properties of wheat flour and starch aqueous suspensions by means of a Rapid Visco Analyser (RVA). An excellent agreement was observed between the effect of surfactants on the onset temperature of the pasting process (PT) and the time to reach peak viscosity (t_{peak}) of wheat flour and wheat starch suspensions. Moreover, a correlation was found between the effect of different surfactants on these two parameters. With the exception of the cationic

surfactants (alkyl trimethyl ammonium bromides), the effect of surfactants (alkyl sulfates, maltosides, monoglycerides, and sucrose esters) was found to be strongly dependent on the surfactant chain length. Shorter chain surfactants (C10–C12) induced an earlier pasting, while longer chain surfactants (C14–C16) had the opposite effect. The effect of surfactants on PT and t_{peak} of flour suspensions was enlarged when the surfactant concentration was increased from $\approx 1\%$ to 15% (w/w) on a dry starch basis.

When heated above a characteristic temperature in an excess of water, native starch granules undergo gelatinization. This process, which can be regarded as the disruption of the molecular order within the granule (loss of granule birefringence and crystallinity), results in the swelling of the starch granules and the leaching of the linear fraction of the starch polysaccharides (amylose). In concentrated aqueous suspensions of native starch, temperature-induced swelling and amylose leaching lead to the formation of viscous pastes. These pastes are usually regarded as composite materials built up from a continuous polysaccharide phase with swollen starch granules as fillers. A sharp increase of the suspension viscosity, which is usually of a few orders of magnitude, takes place at the so-called pasting temperature (PT) and characterizes the onset of the pasting process.

Surfactants (amphiphilic surface active molecules) are well known for their ability to affect different aspects of the starch gelatinization process and to ultimately modify the properties of starch-based products. In practice, surfactants are usually added to starch suspensions to modify their pasting properties as well as the viscosity and viscoelastic behavior of the resulting pastes and gels.

The presence of native amphiphilic molecules as polar lipids (lysophosphatidyl choline, digalactosyl diglycerides, and free fatty acids) has been suggested to be associated with the higher pasting temperatures of wheat starches of high lipid contents (Eliasson et al 1981). It has also been related to the restricted amylose leaching of wheat and other cereal starches in comparison to other nonlipid-containing starches (Doublier 1987). On the other hand, numerous studies have shown that the effect of added surfactants on the PT of starch suspensions can be diverse. In this sense, early studies by Osman and Dix (1960) already suggested the existence of a relation between the surfactant effect, the length of the hydrocarbon chain and the number of hydrocarbon chains in the surfactant molecule. Furthermore, the influence of the surfactant chemical structure has become evident from differences found in the type and extent of the effects produced by different surfactants. In this respect, typical food-grade surfactants such as long chain (C14–C18) saturated monoglycerides (Krog 1973; Nierle and El Baya 1990), esters of sucrose (Deffenbaugh and Walker 1990), and

lactic acid derivatives (sodium and calcium stearyl lactylate) (Krog 1973) have been found to induce an increase in the PT of suspensions of wheat and other cereal starches. The extent of this effect was different for different surfactants and, in some cases, strongly concentration dependent (Deffenbaugh and Walker 1990; Nierle and El Baya 1990). Exceptions of this general trend have been reported for C18:0 alkyl glycerol-1-ethers (Nierle and El Baya 1990) and a propylene glycol fatty acid (C16) monoester (Promodan PVK) (Deffenbaugh and Walker 1990), which produced slight reductions in the PT of starch suspensions.

Despite the great deal of work that has been done in this area, there are no clear-cut conclusions about how the surfactant chemical structure influences the overall effect of surfactants on the onset of the pasting process. One important obstacle stems from the very different experimental conditions used in different studies, which makes direct comparisons impossible. This is primarily due to the fact that the granule swelling and amylose leaching, which are the processes that lead to the viscosity increase (pasting), are nonequilibrium processes. As shown in different studies, the outcome of such a process is extremely sensitive to test conditions, in particular to the heating rate used (Doublier 1987; Doublier et al 1987). Furthermore, this dependence is affected by the type of starch and its concentration in solution (Doublier et al 1987). In addition, the degree of susceptibility of different starches to the presence of a given surfactant is not the same, which suggests that conclusions drawn from analysis of one starch are not directly applicable to other starches (Deffenbaugh and Walker 1990; Kim and Walker 1992).

Investigations of the effects of surfactants on the pasting properties of starch have often involved the use of food-grade emulsifiers. Such emulsifiers are usually mixtures of different molecular species and therefore the exact molecular structure of the additive cannot be assessed. Moreover, the use of different surfactant concentrations in different studies makes assessing and comparing the effects of different surfactants from available data in the literature an unfeasible task.

This study focuses on the effect of surfactants on the pasting properties of wheat starch, in particular on the onset temperature of the pasting process (PT). For this purpose, suspensions of wheat flour and wheat starch were used, which also allows correlation of the effect of surfactants on both systems.

By performing systematic variations of the surfactant structure while keeping other relevant experimental parameters constant, this work seeks not only to assess the influence of surfactant structure on the PT, but also to gain insight on the possible mechanisms behind the effects they induce on the PT. A good understanding of the processes that trigger pasting and the way surfac-

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tants may affect them is of paramount importance if such a task is to be undertaken. Special attention is therefore paid to such processes, with a brief review on the current knowledge on the role they play in the pasting of starch.

Granule Swelling, Amylose Leaching, and the Pasting Process of Starch Suspensions

The properties of starch pastes depend not only on the properties of the dispersed and the continuous phase (deformability of the swollen granules and polysaccharide concentration) but also on the interaction between the two phases (Eliasson and Bohlin 1982; Eliasson 1986; Doublier et al 1987).

The idea that the initial viscosity increase observed in pasting profiles of concentrated starch suspensions is related to reaching a certain volume fraction of swollen granules has received wide acceptance throughout the years (Bagley and Christianson 1982; Doublier 1987; Batley and Curtin 2000). Good agreement between granule swelling-solubility (amylose leaching) and pasting profiles under the same pasting conditions (shearing and heating rate) for a series of cereal and legume starches has been reported by Doublier (1987). In the same study, the dramatic viscosity increase in pasting profiles of starch pastes of different botanical origin was reported to coincide with a certain volume fraction of swollen granules. This volume fraction was ≈ 0.7 – 0.8 depending on the pasting procedures (Doublier 1987). However, the existence of very high volume fractions of swollen granules at the PT does not necessarily imply that the viscosity increase observed is completely governed by friction between granules. The corresponding concentrations of leached amylose in solution at volume fractions of 0.7 – 0.8 (as predicted by the reported solubility indexes in the same study by Doublier) are >1 – 1.5% , w/w, which is approximately the entanglement concentration of amylose in solution (c^*) (Gidley and Bulpin 1989). Beyond this concentration, gel formation will occur owing to entanglements between polysaccharide molecules,

implying that the continuous polysaccharide phase could also be expected to contribute to the overall viscosity increase of the starch paste at the PT.

The granule swelling and amylose leaching processes have been shown to be highly correlated (Doublier et al 1987; Tester and Morrison 1990) and they cannot be expected to be altered independently. In consequence, the PT of starch based suspensions can, for the sake of simplicity, be considered as a parameter directly linked to the swelling and amylose leaching processes. This reasoning allows direct interpretations of the effects of any additive on the PT, without making it necessary to previously ascertain the extent to which the swollen granules or the polysaccharide phase contribute to the viscosity rise at the early stages of the pasting process. As a consequence, the effect of surfactants on the PT could be interpreted on the basis of the changes they induce on the swelling-amylose leaching process responsible for triggering the pasting process. Higher pasting temperatures would thus result from delayed or restricted swelling and amylose leaching, while lower pasting temperatures would result from the opposite effect.

Results from numerous studies on the effect of surfactants on the swelling-solubility patterns of starch granules under equilibrium conditions (long contact times at a given temperature) seem to support the idea of the existence of a connection between the surfactant structure (especially the chain length) and the overall effect on the swelling behavior of starch. In this regard, SDS (an anionic surfactant with 12 carbon atoms in the *n*-alkyl chain) has been reported to favor the early swelling of wheat starch granules (swelling at lower temperatures than in a control sample) (Eliasson 1985; Svensson et al 1998). Increased swelling of wheat starch granules with respect to a control sample has also been reported to be produced by glycerol monocaprate (a nonionic surfactant with an alkyl chain with 10 carbon atoms) (Roach and Hosoney 1995). On the other hand, longer chain monoglycerides (18 carbon atoms

TABLE I
List of Surfactants

Surfactant Group	Structure	Type	Abbreviation	cmc ^a (mM)			
				R = 9	R = 11	R = 13	R = 15
Maltosides		Nonionic	C(R+1)-Malt	1.8 ^b (20°C)	0.17 ^b (20°C)	0.01 ^b (20°C)	6×10^{-4} (—)
Monoglycerides		Nonionic	C(R+1)-Glyc	— ^c	— ^c	— ^c	— ^c
Sucrose esters		Nonionic	C(R+1)-Suc	— ^c	0.34 ^d (27°C)	0.026 ^d (20°C)	0.055 ^d
Sulfates		Anionic	C(R-1)-Sulf	33.47 ^d	9.18 ^d	2.43 ^d	0.52 ^d (40°C)
Trimethyl ammonium bromides		Cationic	C(R+1)-TAB	70 ^d (40°C)	17.3 ^d	4.2 ^d	1.5 ^d

^a Critical micelle concentration in aqueous solution. Values are at 50°C unless otherwise stated in parentheses with the cmc value.

^b From manufacturer's catalog (Anatrace, Maumee, OH [http://www.anatrace.com/downloads.htm]).

^c Above their Kraft temperature ($<50^\circ\text{C}$ for C10, C12, and C14-Glyc and $\approx 70^\circ\text{C}$ for C16-Glyc), monoglycerides exist as diluted surfactant-water blends, which in the case of longer chain monoglycerides (C14–C16), may be solutions of liposomes (Krog et al 1983).

^d Critical micelle concentrations of aqueous surfactant systems (Mukerjee and Mysels 1971).

in the alkyl chain) have delayed the granule swelling (swelling occurring at higher temperatures than in the control sample) (Eliasson 1985; Roach and Hosenev 1995), the same as sodium stearoyl lactylate (SSL) (an anionic surfactant with 17 carbon atoms in the alkyl chain) (Eliasson 1985).

Based on the findings reported in the present study, the theories proposed to date to explain effects produced by different surfactants on the PT and swelling-leaching processes are discussed and reconsidered. Also, new hypotheses are considered and different approaches are put forward.

MATERIALS AND METHODS

The pasting properties of aqueous suspensions of wheat flour and wheat starch were investigated in this study. The wheat flour used was a commercial flour milled from Swedish winter wheat cultivar Tarso provided by Nordmills (Sweden). As reported by the producer, the average content of protein and ash for this flour is 11.5 and 0.55% on a dry matter basis, respectively. The starch content in the flour as determined by the method of Ewers (1909) was 69.5%. The wheat starch used was a commercial sample of C☆Gel 2006 supplied by CereStar (Sas van Gent, The Netherlands). This starch sample exhibited the typical bimodal size distribution of wheat starches with one peak at $\approx 2.8 \mu\text{m}$ (0.71 volume [%]) and the other at $\approx 20 \mu\text{m}$ (11.07 volume [%]) as determined by a light-scattering instrument (Mastersizer model 2000, Malvern Instruments Inc., UK) as described elsewhere (Raeker et al 1998; AACC 2000). Average water contents of flour and starch (taken as weight loss after heating at $120^\circ\text{C} \pm 5^\circ\text{C}$ for 2 hr) were 15 and 11.5%, respectively. Distilled water was used in all the experiments.

Analytical-grade samples of surfactants commonly used in food applications (sucrose esters, monoglycerides) as well as nonfood surfactants (sodium sulfates, trimethyl ammonium bromides, maltosides) were chosen for this study. In each case, the number of carbon atoms in the alkyl chain was systematically varied so that the overall length of the surfactant hydrophobic tail varied between 10 and 16 carbon atoms ($R = 9, 11, 13, \text{ and } 15$ in Table I). All surfactants were purchased from Sigma Chemical (Schnell-dorf, Germany) with the exception of the alkyl maltosides (Anatrace, Maumee, OH), sucrose monomystirate (C14-Suc) (Greyhound Chromatography and Allied Chemicals, Merseyside, UK), and sodium hexadecyl sulfate (C16-Sulf) (Lancaster, Morecambe, UK). The molecular structures, types (based on the charge of the polar head group), and critical micelle concentrations (cmc) of the surfactants used are summarized in Table I.

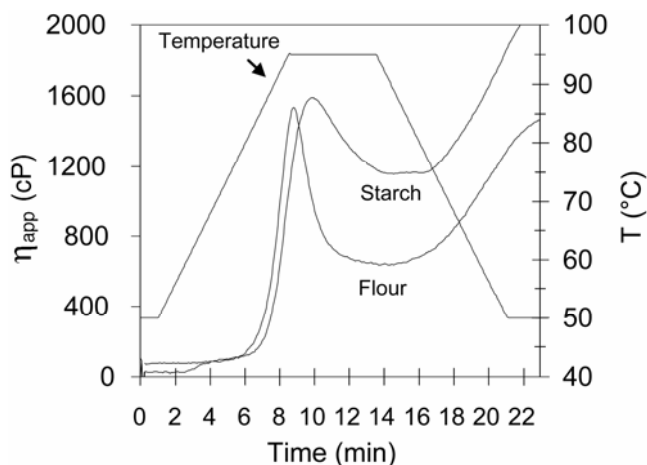


Fig. 1. RVA curve (apparent viscosity vs. time/temperature) of wheat flour and wheat starch aqueous suspensions (0.09 starch/water ratio)

Preparation of Wheat Flour and Starch Suspensions

Dispersions of flour (3.50 g, wb) or starch (2.59 g, wb) in distilled water (25 mL) were prepared directly in the Rapid Visco Analyser (RVA) sample container to yield a 14% (w/w) flour and a 10% (w/w) starch suspension, which both correspond to a starch-to-water weight ratio of 0.09 on a dry starch basis (dsb).

To prepare such dispersions, flour or starch was added to water or aqueous surfactant solutions. The temperature of these solutions was 50°C (the initial temperature of the RVA pasting program). After addition of starch or flour, the suspensions were then homogenized by jogging a paddle blade through the sample up and down several times.

The effect of surfactant concentration on pasting properties of flour was studied in the concentration range 0.5–15% (w/w) dsb. This corresponds approximately to a range of 1.02×10^{-5} to 3.1×10^{-4} mol of surfactant/g of dry starch, which in turn corresponds to surfactant concentrations in solution of 0.9–25 mM.

Evaluation of Pasting Properties of Suspensions

Changes in the viscosity of wheat flour and starch aqueous suspensions under controlled temperature changes were studied using a Rapid Visco Analyser (series 3, Newport Scientific, Narrabeen, Australia). The RVA is essentially a heating and cooling viscometer especially configured for testing starch-based products that has proved useful for evaluating the pasting and cooking properties of starch-based suspensions and assessing the effects of different additives (Deffenbaugh and Walker 1990; Nierle and El Baya 1990).

Starch and flour suspensions were subjected to a 23-min pasting program during which the samples were kept at 50°C for 1 min, heated at $6^\circ\text{C}/\text{min}$ to 95°C (pasting region), kept at that temperature for 5 min (hold region), and then cooled down again to 50°C (set-back region) at the same rate. High mixing speed (960 rpm) was used during the first 10 sec of the program to thoroughly homogenize the sample. Afterwards, milder shear conditions (160 rpm) were applied throughout the process.

The temperature at which the samples began their rapid viscosity building phase, known as the pasting temperature (PT), was obtained from the RVA curves. This value, as determined by means of the instrument controlling and analysis software, corresponds to the temperature at which the rate of change in viscosity reaches an arbitrarily set value, in our case $4\text{cP}/\text{sec}$.

Other relevant parameters of the pasting, hold and setback regions of the RVA curves such as the maximum or peak viscosity (η_{peak}), time required to reach η_{peak} (t_{peak}), breakdown (η_{break}), and final viscosity (η_{final}) were also obtained from the pasting curves.

Temperature is recorded by the RVA at 4-sec intervals to the nearest 0.2°C . This temperature corresponds to the temperature of the heating block and not of the sample, which can lag several degrees behind. Such temperature lag depends on the heating-cooling rate and the apparent viscosity of the starch sample (Hazleton and Walker 1996). Nevertheless, the viscosity of different suspensions at PT should be similar, as at this point, the viscosity has just started to rise. Therefore, in accordance with the temperature lag for a heating rate of $6^\circ\text{C}/\text{min}$ (Hazleton and Walker 1996), the actual sample pasting temperatures can in all cases be expected to be 1.5°C lower than those reported here.

All tests were conducted in triplicate. The standard deviations of the pasting temperatures and times reported, which are $\approx 0.5^\circ\text{C}$ and 0.1 min, respectively, are represented as error bars in the figures. The standard deviations of viscosity values are reported in the respective tables.

RESULTS AND DISCUSSION

Pasting Curves and Pasting Temperature

The pasting curves for the studied wheat flour and starch suspensions are shown in Fig. 1. These curves show the evolution of the apparent viscosity (η_{app}) of the suspension as a function of

time and temperature. Both curves exhibit the general features usually shown by concentrated starch-based suspensions (>8% [w/w] starch) subjected to such heating-cooling programs as reported and described elsewhere (Doublier 1987; Deffenbaugh and Walker 1989, 1990; Keetels et al 1996). Furthermore, at 50–95°C, the dramatic increase of the suspension viscosity, which characterizes the onset of the pasting process and defines the pasting temperature, is clearly seen.

When compared with the starch suspension, the flour suspension exhibited a somewhat earlier onset of pasting (lower PT), shorter time to reach maximum viscosity (t_{peak}), and lower peak viscosities (η_{peak}) (Fig. 1, Tables II and III). Excepting these minor differences, the viscosity profiles of both suspensions along the pasting region of the RVA curve (50–95°C) were very similar.

Despite the fact that the flour and the starch used in this study come from the same botanical source (wheat), differences in granule size distribution, lipid content, percentage of damaged granules, as well as enzyme content are expected to exist between the starch present in the two systems. Assessing the extent to which these differences or the presence of flour components other than starch are responsible for the differences observed between the pasting curves of starch and flour suspensions is beyond the scope of this study. It suffices for our purpose to find and point

out that similarities between the two pasting curves seem to corroborate the fact that the starch fraction exerts a primary influence on the viscosity of flour hot pastes (Morris et al 1997).

Data retrieved from the hold and setback regions of the RVA curves of the flour and starch suspensions (in the absence and presence of surfactants) is also presented in Tables II and III. This data is presented for the sake of the completeness of this report, despite the fact that these properties and the effect of surfactants on them are not the focus of this study.

Effect of Surfactant Structure

The strong influence of surfactants on the pasting process became apparent when the pasting curves of wheat flour and starch suspensions in the presence of different surfactants were obtained. Figure 2A shows the PT of wheat flour suspensions in the presence of surfactants with different head groups and alkyl chain lengths.

As seen in Fig. 2A, the PT of the flour suspension in the presence of a given surfactant group increased as the number of carbon atoms in the surfactant alkyl chain increased from 10 to 16, the alkyl trimethyl ammonium bromides (alkyl-TAB) being the only exception. For the monoglycerides (alkyl-Glyc), that increase was linear in the range of chain lengths studied, while for

TABLE II
Flour Paste Viscosities Along the 23-min RVA Profile^a

Surfactant Group	Chain Length	Viscosity (cP)				
		Peak (η_{peak})	Breakdown (η_{break})	Trough	Final (η_{final})	Setback
—	—	1,503 ± 37	882 ± 21	621	1,439 ± 42	818
Alkyl-Malt	C10	1,797 ± 49	1,186 ± 35	612	1,341 ± 37	729
	C12	2,077 ± 78	1,333 ± 47	744	1,745 ± 106	1,001
	C14	2,076 ± 8	1,138 ± 1	939	2,345 ± 13	1,406
	C16	2,166 ± 2	1,116 ± 18	1,050	2,594 ± 3	1,545
Alkyl-Sulf	C10	2,162 ± 22	1,461 ± 25	701	1,619 ± 7	919
	C12	2,375 ± 46	1,569 ± 49	806	2,129 ± 49	1,323
	C14	2,384 ± 125	1,386 ± 71	998	3,197 ± 524	2,199
	C16	2,639 ± 17	1,463 ± 38	1,176	3,894 ± 39	2,718
Alkyl-TAB	C10	1,328 ± 4	863 ± 10	464	1,154 ± 13	689
	C12	1,509 ± 141	1,053 ± 116	456	1,108 ± 70	652
	C14	1,655 ± 47	1,157 ± 35	498	1,409 ± 38	911
	C16	1,687 ± 66	964 ± 21	723	2,208 ± 129	1,485
Alkyl-Suc	C10	1,753 ± 40	1,119 ± 6	634	1,451 ± 67	817
	C12	1,863 ± 21	1,357 ± 17	732	1,789 ± 18	1,057
	C14	1,480 ± 29	883 ± 11	597	1,381 ± 23	784
	C16	1,942 ± 17	1,073 ± 27	869	2,141 ± 73	1,272
Alkyl-Glyc	C10	2,053 ± 18	1,375 ± 7	678	1,678 ± 19	1,000
	C12	2,167 ± 46	1,121 ± 42	1,046	2,601 ± 79	1,555
	C14	2,059 ± 32	849 ± 13	1,209	3,002 ± 157	1,792
	C16	1,802 ± 51	698 ± 8	1,104	2,897 ± 157	1,793

^a Effect of nonionic, anionic, and cationic surfactants.

TABLE III
Starch Paste Viscosities Along the 23-min RVA Profile^a

Surfactant Group	Chain Length	Viscosity (cP)				
		Peak (η_{peak})	Breakdown (η_{break})	Trough	Final (η_{final})	Setback
—	—	1,616 ± 36	459 ± 23	1,156	2,153 ± 46	997
Alkyl-Malt	C10	1,611 ± 166	817 ± 110	912	1,994 ± 163	1,083
	C12	2,008 ± 6	1,089 ± 60	920	2,285 ± 11	1,366
	C14	1,835 ± 59	933 ± 34	902	2,716 ± 95	1,815
	C16	1,810 ± 34	832 ± 50	501	2,718 ± 90	1,716
Alkyl-Sulf	C10	2,396 ± 39	1,445 ± 8	951	2,002 ± 68	1,051
	C12	2,451 ± 14	1,619 ± 40	833	2,120 ± 20	1,288
	C14	2,320 ± 19	1,168 ± 5	1,152	4,199 ± 1	3,047
	C16	2,426 ± 38	567 ± 25	1,859	5,934 ± 55	4,075
Alkyl-TAB	C10	1,818 ± 103	851 ± 59	966	2,062 ± 12	1,096
	C12	2,070 ± 10	1,178 ± 23	892	1,719 ± 16	827
	C14	2,071 ± 39	1,259 ± 19	812	1,713 ± 48	901
	C16	1,950 ± 36	1,142 ± 38	808	2,501 ± 30	1,693

^a Effect of nonionic, anionic, and cationic surfactants.

the maltosides (alkyl-Malt), sucrose esters (alkyl-Suc), and sulfates (alkyl-Sulf), such linearity was only observed for 12–16 carbons, surfactants with alkyl chains with 10 and 12 carbons yielding very similar PT values. When compared with the PT of the control flour suspension, and again with the exception of suspensions in the presence of alkyl-TAB, suspensions with shorter chain surfactants (C10–C12) had lower PT while the suspensions with the longer chain surfactants (C14–C16) had a higher one. Thus, the onset of the pasting process took place earlier (at lower temperatures) when surfactants with 10 and 12 carbon atoms in the alkyl chain were present, while it was delayed (took place at higher temperatures) in the presence of surfactants with 14 and 16 carbons in the alkyl chain.

The effect of a group of nonionic (alkyl-Malt), cationic (alkyl-TAB), and anionic (alkyl-Sulf) surfactants on the PT of starch suspensions is shown in Fig. 2B. Interestingly, the same chain length dependence as for the flour suspensions is observed for the three groups of surfactants studied. Nevertheless, compared with their effect on the PT of flour, the ionic surfactants in general induced a much larger change in the PT of the starch suspension, while the nonionic surfactant group produced changes of the same magnitude.

The time required for the flour and starch suspensions to reach peak viscosity (t_{peak}) in the absence and presence of surfactants is shown in Fig. 3A,B. As observed in this figure, the shorter chain surfactants (C10–C12) of most surfactant groups induced shorter

t_{peak} , while the longer chains had either very little (C14) or the opposite effect (C16), inducing longer t_{peak} . Exceptions were the effect of alkyl-TAB on the t_{peak} of flour and starch suspensions and the alkyl-Malt on the t_{peak} of the starch suspension. Interestingly, despite minor differences, it can be observed that variation of t_{peak} of flour and starch suspensions in the presence of surfactants follow a pattern similar to the PT. This suggests that factors that govern the reaching of a viscosity maximum are related to the factors responsible for triggering the viscosity rise that defines the PT.

As for other pasting properties like the peak viscosity (η_{peak}) of the flour and starch pastes in the presence of surfactants, such correlation with the PT was not observed (Tables II and III). In this case, the effect of surfactants was not significantly chain length dependent. In most cases, all surfactants yielded higher peak viscosities than in the control flour or control starch suspension. The magnitude of the effect induced by different surfactant groups on the η_{peak} was very different, the surfactant head group seeming to play a major role. No general trends were observed when effects of different surfactants on the η_{peak} of wheat flour and starch suspensions were compared. However, in both systems, the alkyl sulfates (alkyl-Sulf) yielded the largest increase in η_{peak} .

The results shown in Figs. 2 and 3 demonstrate that, as far as the PT and the t_{peak} are concerned, a very good agreement is observed between the effect of the different surfactants on flour and starch suspensions. Despite differences in magnitude, the

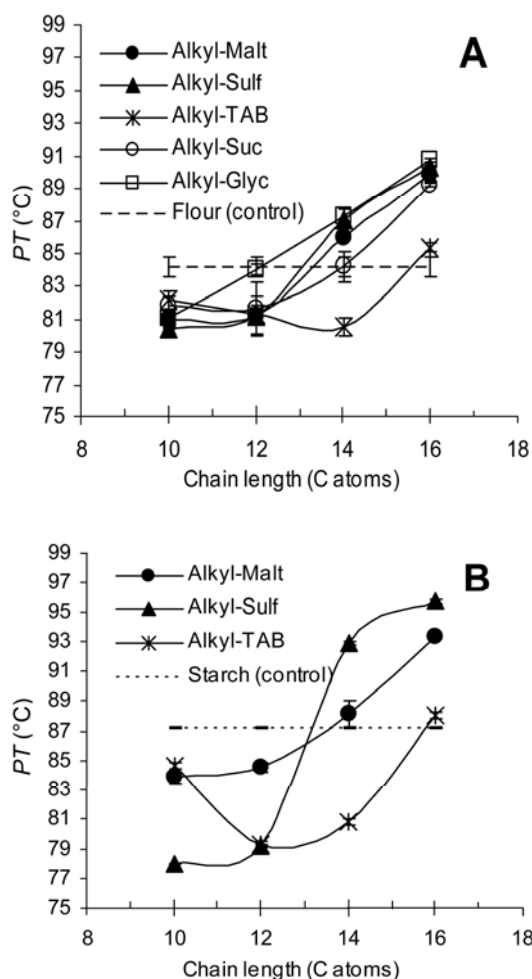


Fig. 2. Pasting temperature of (A) wheat flour suspensions (0.14 flour/water ratio) and (B) wheat starch suspensions (0.10 starch/water ratio) in the presence of surfactants with different head groups and alkyl chain length. (Surfactant concentration 4.1×10^{-5} mol of surfactant/g of dry starch or $\approx 1\%$ w/w, dsb).

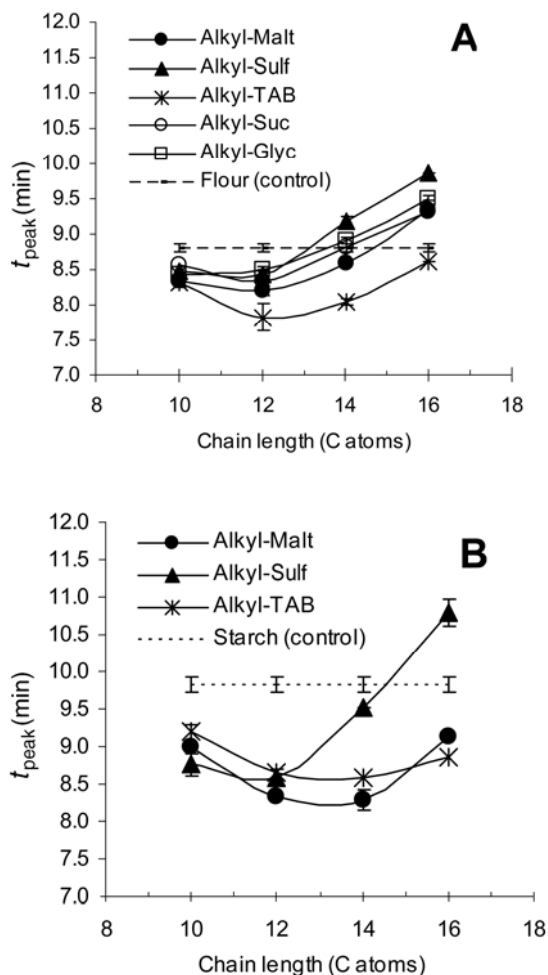


Fig. 3. Time to peak of (A) wheat flour suspensions (0.14 flour/water ratio) and (B) wheat starch suspensions (0.10 starch/water ratio) in the presence of surfactants with different head groups and alkyl chain length. (Surfactant concentration 4.1×10^{-5} mol of surfactant/g of dry starch or $\approx 1\%$ w/w, dsb).

effects of surfactants are indeed equivalent in most cases. Results obtained for flour could be extrapolated to starch suspensions and vice versa, indicating that interactions between surfactants and the starch fraction account for the effects these have on some of the pasting properties (PT and t_{peak}) of the flour suspension. Interestingly, the same does not seem to be true for the η_{peak} of starch and flour suspensions in the presence of surfactants.

Moreover, what is particularly remarkable about the results presented in Figs. 2 and 3 is the general effect most surfactants with a given chain length have on some pasting properties (PT and t_{peak}), regardless of the nature of their head group. The hydrophilic-lipophilic balance of surfactant molecules with a given chain length and different head group can indeed be widely different and, in consequence, so can their maximum monomer concentrations in solution (given by cmc) (Table I). Interestingly enough, differences of such nature did not have any major apparent influence; only the chain length of the surfactants seemed to determine the type of effect observed on the pasting properties studied.

Effect of Surfactant Concentration

Surfactants in solution are characterized by their ability to self-associate. Below the critical micelle concentration (cmc) surfactants exist as monomers, whereas at the cmc surfactant, micelles start to form and exist in equilibrium with monomers. Furthermore, a given surfactant can form a series of different association structures depending on the concentration in solution. The cmc of nonionic surfactants is generally much lower than that for ionic surfactants (Table I). In the first part of this study, surfactant concentrations of $\approx 1\%$ (w/w, dsb) were used to compare effects of different surfactants. Thus, at the early stages of the pasting process (when surfactant solutions were put in contact with starch granules) nonionic surfactants were well above their cmc, whereas some of the ionic surfactants (shorter chain) were below theirs. To further investigate whether the state of the surfactants in solution had an influence on their effect on the PT and t_{peak} of the suspensions, the pasting behavior of flour suspensions in the presence of surfactants at different concentrations was studied. In this case, the effect of maltosides with different chain lengths (C10–C16) as well as C12-Sulf and C12-TAB were investigated.

As observed in Fig. 4A, the lowering effect on the PT of the shorter chain surfactants (C10-Malt and C12-Malt) became more pronounced as the concentration was increased. The same relationship between the magnitude of the effect on the PT and the surfactant concentration does not seem to hold for the longer chain maltosides. Although in the presence of C14-Malt and C16-Malt, the PT of the suspension was always higher than the PT of the control flour within the whole concentration range studied, the increasing effect on the PT either became marginally smaller (C14-Malt) or just leveled off (C16-Malt) when the concentration was increased beyond a certain value.

The data shown in Fig. 4A reveal two interesting facts. First, they suggest that increasing the concentration of the nonionic surfactant in the system tends to affect the magnitude of the effect produced by the surfactant but not the type of effect itself (whether the surfactant lowers or increases the PT). Second, they show that the shorter chain length surfactants have an effect on PT that is more dramatically affected by changes in surfactant concentration.

Figure 4B shows the effect of the surfactant concentration on the PT of the flour suspension, this time for three surfactants with the same chain length but different head group charge and structure (C12-Sulf, C12-TAB, C12-Malt). The lowering effect of these three surfactants on the PT increased with surfactant concentration within the whole concentration range studied. Interestingly, no evident changes in this trend could be identified for the two ionic surfactants when their concentration in solution went beyond their cmc (1.1×10^{-4} and 2.1×10^{-4} mol of surfactant/g of starch for C12-Sulf and C12-TAB, respectively). The variation of the PT with the surfactant concentration was rather different from one

surfactant to the other, the effect of the C12-TAB being the most sensitive to concentration variations.

Preliminary experiments on the effect of short and long chain maltosides on the PT of starch suspensions (*unpublished data*) gave indications that increasing surfactant concentration produces the same type of effect on starch as on flour suspensions. These findings were not surprising, however, given the good agreement that had been found previously between the effects of different surfactants on the PT of flour and starch suspensions at lower concentrations (Fig. 2).

The effect of surfactant concentration on the t_{peak} is shown in Fig. 5A,B. Changes in t_{peak} as a function of surfactant concentration followed a pattern similar to that seen for the PT (Fig. 4A,B). The t_{peak} decreased almost linearly as the concentration of the shorter chain surfactants increased (C10–C12), while it increased and leveled off at rather low concentrations of the longest chain surfactant (C16). However, C14-Malt, which produced a slight increase in the PT that decreased marginally with concentration, had a markedly different effect on t_{peak} , which decreased in an almost linear fashion as the concentration of C14-Malt was increased.

The results found regarding the concentration effect of longer chain surfactants (C16-Malt) on the t_{peak} of flour and starch suspensions are in good agreement with that reported for mixtures of stearic (C18) and palmitic (C16) acid esters of sucrose on wheat, maize, and tapioca starches. All these surfactants produced a delay in the onset of the pasting (higher PT) that increased as the concentration was increased (Deffenbaugh and Walker 1990).

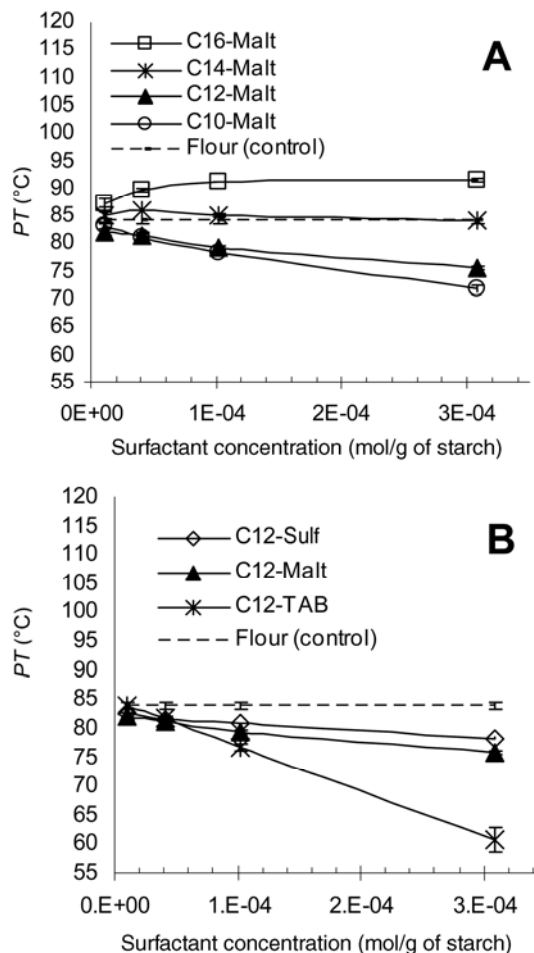


Fig. 4. Pasting temperature of wheat flour suspensions (0.14 flour/water ratio) in the presence of (A) alkyl-maltosides (C10–C16) and (B) C12-surfactants (sulfate, maltosides, and trimethyl ammonium bromides) as a function of surfactant concentration (≈ 0.5 – 15% w/w, dsb).

Interpreting the Effects of Surfactant on PT: Surfactant Structure and Concentration

The effect of surfactants on the PT can be interpreted on the basis of the changes they induce on the granule swelling-amylose leaching process that is thought to be responsible for triggering the pasting process. Results regarding the different effects induced by short and long chain surfactants on PT are indeed in good agreement with previously reported results of effects of some short and long chain surfactants on the swelling of starch granules at equilibrium conditions (Eliasson 1985; Roach and Hosney 1995; Svensson et al 1998). In this respect, the effects of surfactants on swelling and leaching properties of granular starch have usually been related to the formation and characteristics of the helical inclusion complexes formed between amylose and (polar) lipids (Eliasson 1985; Deffenbaugh and Walker 1990; Biliaderis and Tonogai 1991). Differences between the effects caused by C12-Sulf and C16/C18-Glyc on the granule swelling have been attributed to differences in solubility of a surface layer on the granules built of amylose-surfactant complexes (Eliasson 1985). High hydrophilicity of charged surfactant head groups was thought to be responsible for the high complex solubility which, in turn, was believed to favor water uptake by the granule. Poor water solubility of inclusion complexes of amylose and surfactants has been reported to be associated with the absence of electrostatic stabilization, either because the surfactant is nonionic or because the concentration of noncomplexed surfactant or added salt is sufficiently high to screen electrostatic effects (Egermayer et al 2003).

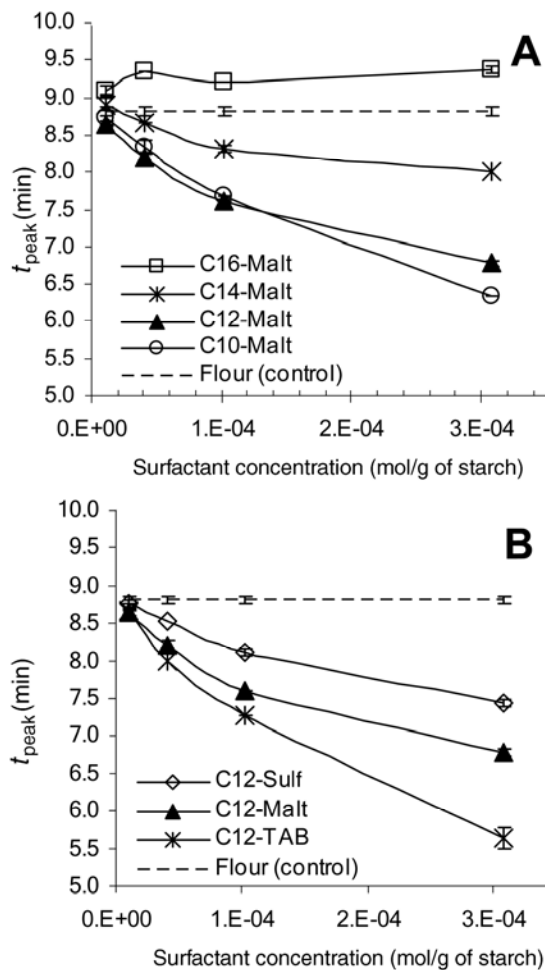


Fig. 5. Time to peak of wheat flour suspensions (0.14 flour/water ratio) in the presence of (A) alkyl-maltosides (C10–C16) and (B) C12-surfactants (sulfate, maltoside, and trimethyl ammonium bromides) as a function of surfactant concentration (≈ 0.5 –15% w/w, dsb).

Differences in complex solubility may seem a likely explanation for the different effects of some charged and noncharged surfactants on the swelling of starch granules. However, this approach fails to explain why a surfactant like SSL, an anionic surfactant with C17 alkyl chain, restricts granule swelling (Eliasson 1985), even though high solubility of the complex could be expected due the presence of a (negatively) charged head group. More importantly, it cannot account for the rather chain length dominated surfactant effects on the PT of flour and starch suspensions found in the present study. This raises the question whether any chain length dependent property of the complexes forming such surface layers can be responsible for the overall effect of surfactants on the PT found in this study. Some properties of the amylose-surfactant complex have been reported to depend on the alkyl chain length of the complexing agent. Thermal stability (melting temperature of complex) (Eliasson and Krog 1985; Kowblansky 1985), enthalpy of melting (Hoover and Hadziyev 1981; Godet et al 1993), and resistance to enzymatic attack (Eliasson and Krog 1985) of the complex formed with a series of surfactants with a given functional group have increased as the alkyl chain length of the complexing agent increased. However, such properties were also reported to be strongly head group dependent (Kowblansky 1985).

Even though the hypothesis of the formation of a surface layer of amylose-surfactant complexes seems feasible, the evidence presented here indicates that, on its own, it does not suffice to explain the most general aspects of the effect of surfactants on PT. Therefore, alternative possibilities should be considered.

A study by Gray and BeMiller (2001) showed that for common corn and potato starches swollen in water at room temperature, granule “accessibility” for a series of fluorescent fatty acyl amides with chain length of 6–16 carbon atoms seemed to depend on the alkyl chain length of the molecule. For common corn and potato starch, C14–C16 and C12–C16 compounds, respectively, were completely excluded from the granule interior and were found only adsorbed on the outer granule surface.

Differences in granule accessibility controlled by restrictions imposed by the surfactant alkyl chain length could be expected to occur during the very early stages of the RVA pasting cycle, when granules experience only a relatively limited water uptake. If so, these differences could explain to a certain extent the rather collective behavior exhibited by surfactants with different functional groups and a given chain length. If shorter chain (C10–C12) surfactants can (for whatever reason) access the granule interior easily, they can favor destabilization of granule internal structure either by steric or electrostatic effects. Longer chain surfactants (C14–C16) would be confined to the outer granule surface, where they may adsorb. Formation of a water insoluble outer surface layer through complex formation with partly leached amylose or by simple surfactant adsorption to the granule surface could thus be responsible for the granule restricted water uptake and amylose leaching.

On the other hand, the extent to which the swelling and leaching process of starch is affected by a surfactant of a given chain length can be expected to be related to the nature of its head group. Specific starch-surfactant interactions or granule destabilization mechanisms related to, for example, the presence of certain ions or counter ions could well account for the observed differences between the PT of flour and starch suspensions in the presence of an anionic, cationic, and nonionic surfactants with the same chain length (Fig. 1A,B). Interactions of such nature might be the reason behind the low PT of starch and flour suspensions in the presence of alkyl-TAB (even the longer chain ones). Such an effect was believed to be related to the presence of the bromide ion (Br^-), which had been reported to be particularly disruptive toward the crystalline regions of starch granules and therefore favored granule destabilization (Villwock et al 1999). Therefore, additional trial experiments where Br^- was added to the starch

suspensions as NH_4Br were performed. These experiments showed that counter ion effects are negligible at the concentrations used in this study (4.1×10^{-5} mol/g of starch), the differences in PT in the presence and absence of the ions being within the standard deviation. This indicates that the effect of the alkyl-TAB on PT is more likely related to the surfactant character of the molecules and the strong electrostatic interaction that keeps the counter ion bound to the surfactant head group. Nevertheless, the molecular mechanism behind this destabilizing effect is not yet clarified and further studies are needed.

Within the scope of the interpretation made here, larger effects of surfactants on the PT could be expected when increasing surfactant concentration because the presence of larger amounts of surfactants would enhance granule surface coverage or granule penetration and complex formation.

Apart from the ideas so far presented, there is yet another aspect of the starch-surfactants interactions that is worth taking into consideration when discussing the possible mechanisms behind the surfactant effect on the PT. These are the effects on the rheological properties of molecular solutions of the starch polysaccharides. In this respect, surfactants greatly influence the rheological behavior of starch gels. In most cases, the addition of (polar) lipids to starch gels has resulted in stronger and more elastic gels (i.e., higher storage modulus [G'] as well as lower phase shifts [δ]) (Biliaderis and Tonogai 1991; Eliasson and Kim 1995).

In the present study, it was found that in the presence of a given surfactant group, the final viscosity (η_{final}) of the starch and flour suspensions tended to be higher as the chain length of the surfactant was increased (Tables II and III). Furthermore, this was true for most of the surfactant groups studied.

As demonstrated by Langton and Hermansson (1989) at the final stages of a pasting profile similar to the one done in an RVA, most of the amylose has leached out to form a macromolecular solution in which the remains of disrupted amylopectin-rich granules are embedded. This implies that the η_{final} values retrieved from an RVA curve could be expected to reflect the degree or strength of the intermolecular association that takes place in the macromolecular network upon cooling. Assuming that is the case, our η_{final} data would be in agreement with previous studies that reported that upon addition of a given surfactant group the starch gels were stronger (higher G') and more elastic (the lower the δ the longer the alkyl chain length of the surfactant) (Eliasson and Kim 1995).

Based on the experimental evidence available, it is not possible to assess the extent to which the effect of surfactants on the rheological behavior of the solubilized amylose can be related to their overall effect on the onset of the pasting process. Moreover, even though the above mentioned aspect is not likely to be the main contributor to the effect of surfactant on the PT, further studies are necessary.

CONCLUSIONS

A very good agreement was observed between the effect of surfactants on the PT and t_{peak} of wheat flour and wheat starch suspensions. Despite differences in magnitude, the effects of surfactants on starch and flour suspensions were equivalent in most cases. In addition, correlation between the effect of different surfactants on these two pasting properties (PT and t_{peak}) was found. On the other hand, the same was not the case for other pasting properties such as the η_{peak} . The effect of surfactants on the PT and t_{peak} was strongly chain length dependent. The addition of surfactants with 10 and 12 carbon atoms in the alkyl chain induced an earlier pasting (lower PT than the control sample), while pasting was delayed (higher PT than in the control sample) by surfactants with 14 and 16 carbons in the alkyl chain. Such a trend was observed for all the surfactants studied, regardless of

their head group charge and structure, with alkyl trimethyl ammonium bromides (alkyl-TAB) being the only exception. Essentially, the same trends were found regarding the effects of different surfactants on t_{peak} . However, in the latter case, surfactants with 14 carbon atoms in the alkyl had a rather ambiguous effect, inducing in some cases marginal increases in t_{peak} and in others minor reductions.

The effect of surfactants on PT and t_{peak} of flour suspensions was enlarged when the surfactant concentration was increased from 1% to 15% (w/w) on a dry starch basis. The extent of such enlargement was different, depending on the surfactant chain length and head group. However, in all cases, an increase in surfactant concentration was found to affect the magnitude of the effect produced by the surfactant but not the type of effect itself (whether the surfactant lowers or increases the PT or t_{peak}).

Effects of surfactants on the PT were interpreted as due to their effects on the granule swelling and amylose leaching processes. Differences in solubility of a granular surface layer built of amylose-surfactant complexes cannot fully account for the chain length dependent effect of surfactants on the PT because complex solubility is strongly dependent on the surfactant charge rather than chain length. Differences in granule accessibility, which under certain conditions have been suggested to be controlled by surfactant chain length, may explain the rather collective behavior of surfactants with the same chain length.

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