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On the effect of surface active agents and their structure on the temperature-induced changes of normal and waxy wheat starch in aqueous suspension. Part I. Pasting and calorimetric studies

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Abstract

Pasting and calorimetric studies of normal and waxy wheat starch were performed in the presence of a series of ionic (sulphates, trimethyl ammonium bromides) and non-ionic (monoglycerides, maltosides) short (12 carbon atoms) and long (16 carbon atoms) *n*-alkyl chain surfactants. With the exception of the alkyl ammonium bromides, all of the short chain surfactants lower the pasting temperature (PT) in normal wheat starch, while the long chain surfactants have the opposite effect. Contrary, regardless of their chain length, all ionic surfactants lower the PT in waxy wheat starch while the non-ionic surfactants induce small, sometimes almost negligible changes in the PT. Calorimetric studies revealed the absence of a direct connection between the effect of surfactants on the onset of the starch gelatinization transition and the PT. However, in the presence of all surfactants, except the alkyl ammonium bromides, the PT of normal wheat starch was found to lie within or very close the temperature range within which the dissociation of the amylose–surfactant complexes takes place. Waxy wheat starch, in contrast, pasted at temperatures that fell within the temperature range of the starch gelatinization transition. This is taken as evidence of the existence of a correlation between the PT and the dissociation of the amylose–surfactant complexes.

Keywords: Surfactants; Starch gelatinization; Starch pasting; Wheat starch; Waxy wheat starch

1. Introduction

The temperature-induced gelatinization of starch is regarded as the water-mediated, irreversible disruption of the various types of order within the starch granule. As a consequence of this loss of order, swelling of starch granules is increased substantially and the starch polysaccharides, specially amylose (AM), can be exuded. The swelling and polysaccharide-leaching characteristics of starch granules in water are responsible for the thickening properties of starch. Surfactants (i.e., amphiphilic surface active molecules, also termed polar lipids when referring to nature's own surfactants) are well-known for their ability to affect these properties as well as the different aspects of the temperature-induced gelatinization of starches.

The effect of typical food grade emulsifiers on the granule swelling/AM-leaching properties of starch has been extensively studied, traditionally by means of viscometric techniques (e.g., Brabender viscoamylograph or Rapid Visco-Analyzer). These techniques monitor the changes in viscosity of concentrated (>6% w/v) aqueous suspensions of starch granules subjected to defined temperature regimes under mechanical shear. The same as fundamental rheological methods, viscometric techniques are sensitive to differences in the swelling state of starch granules.

The granule swelling/AM-leaching vs. temperature profiles of wheat and other cereal starches have been found two exhibit two stages (Eliasson, 1985a; Eliasson, 1986a).

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During the first stage (~60–75 °C), granule swelling due to water uptake and the leaching of AM are rather limited. During the second one (~75–95 °C), extensive swelling and AM-leaching take place. The dramatic viscosity increase that defines the onset of pasting [i.e., the pasting temperature (PT)] in typical viscometric "pasting profiles" is the result of the extensive swelling/AM leaching that takes place during that second stage (Doublier, 1987; Takahashi & Seib, 1988).

Food-grade surfactants such as linear, long alkyl-chain (14 to 18 carbon atoms) saturated monoglycerides (Azizi & Rao, 2005; Krog, 1973; Nierle & El Baya, 1990a), esters of sucrose (Deffenbaugh & Walker, 1990), and lactic acid derivatives [sodium and calcium stearoyl lactylates (SSL and CSL, respectively)] (Krog, 1973; Azizi & Rao, 2005) have been found to delay the onset of the pasting (i.e., restrict granule swelling/AM-leaching) of suspensions of wheat and other cereal starches.

Studies of granule swelling/AM-leaching patterns of starch granules under equilibrium conditions (long contact times at a given temperature) in the presence of long-chain monoglycerides (18 carbon atoms in the alkyl chain) (Eliasson, 1985a; Roach & Hoseney, 1995) and SSL (Eliasson, 1985a; Roach & Hoseney, 1995) have also reported restricted granule swelling (swelling occurring at higher temperatures than in the control sample). On the other hand, shorter-chain monoglycerides like glycerol monocaprate (Roach & Hoseney, 1995) and non-food grade surfactants as sodium dodecyl sulfate (SDS) (Eliasson, 1985a; Svensson, Autio, & Eliasson, 1998) have been reported to have the opposite effect (swelling occurring at lower temperatures than in a control sample).

A recent systematic investigation of the effect of surfactant structure [head group and chain length (from 10 to 16 carbon atoms)] on the pasting properties of wheat starch revealed that the effect of a series of anionic and non-ionic *n*-alkyl surfactants on the PT as well as other pasting parameters (e.g., time required to reach maximum viscosity) was controlled to a great extent by the surfactant chain length (Mira, Eliasson, & Persson, 2005). Short alkyl chain surfactants (10 and 12 carbon atoms) induced an earlier pasting than in the control sample, while longer-chain surfactants (14 and 16 carbon atoms) had the opposite effect. An increase in surfactant concentration was found to affect the magnitude of the effect produced by the surfactant but not the characteristic pattern of the effect itself.

The effect of surfactants on the swelling/AM-leaching properties of granular starch has usually been related to their ability to form helical inclusion complexes with AM and the characteristics of such complexes (Biliaderis & Tonogai, 1991; Deffenbaugh & Walker, 1990; Eliasson, 1985a). However, none of the theories proposed to date can fully account for the chain-length-dominated effect of some surfactants on the PT.

The present study seeks to further explore the possible mechanisms behind the chain-length dependence of the effect of surfactants on some of the pasting properties of wheat starch. In order to do this, changes which take place when wheat starch is heated up to 95 °C in excess water in the presence of a series of selected short (C_{12}) and long *n*-alkyl chain surfactants (C_{16}) are studied. Information on the granule swelling/AM-leaching process is indirectly obtained by means of viscometric studies carried out a different heating rates. Thus, the swelling/AM-leaching properties of the starch are assessed under the non-equilibrium (thermal and physicochemical) and mechanical shear conditions often encountered in practical applications.

Information on the events taking place on a molecular level in the system is sought by means of calorimetry. In this respect, the effect of surfactants on the thermal transitions associated to the starch gelatinization has been extensively studied (Biliaderis & Tonogai, 1991; Eliasson, 1994; Eliasson, 1985b; Eliasson, 1986b; Evans, 1986; Ghiasi, Varriano-Marston, & Hoseney, 1982; Svensson et al., 1998; Villwock, Eliasson, Silverio, & BeMiller, 1999). However, with the exception of the many studies which have aimed at the characterization of the AM–surfactant complexes, the effect of the surfactant structure (head group and chain length) on the thermal transitions associated with the gelatinization of starch has not been systematically investigated.

Additional insight on the possible interaction mechanisms involved in the processes studied is sought through the use of both normal and waxy wheat starch. Compared to normal wheat starches, waxy wheat has a much lower AM content (~0–3% compared to ~30% AM) (Chakraborty et al., 2004; Soulaka & Morrison, 1985; Yoo & Jane, 2002), thus being potentially very useful for disentangling effects due to interactions between surfactants, amylose, and amylopectin (AMP).

2. Experimental section

2.1. Materials

The two wheat starches used in this study were prime starches prepared from flour. The normal wheat flour used was a commercial flour milled from the Swedish winter wheat cultivar Gnejs provided by Nord Mills (Sweden). The waxy wheat flour was kindly provided by Dr. Craig F. Morris (USDA/ARS Western Wheat Quality Laboratory, Pullman, WA, USA). This flour was milled (Buhler MLU-202) from a spring habit, hexaploid waxy wheat, produced from a cross of 'Bai Huo' and 'Kanto 107' grown in California in 1997.

2.1.1. Starch preparation

Prime starch was extracted from flour according to a gluten washing procedure based on the method of Wolf Wolf (1964). A stiff dough ball was prepared by mixing 100 g of flour with 70 mL of distilled water and then aging at room temperature for 2 h. The starch was then washed from the dough ball by kneading it by hand, under a stream of distilled water, over a metal sieve with mesh opening of

76 µm. The collected starch slurry was packed by centrifugation at 2300*g* for 15 min. The upper, pigmented fraction (containing mainly small starch granules, protein and endosperm cell walls) was then removed with a spatula. The prime starch was further purified by resuspending it in distilled water, centrifuging it and scraping off any remaining tailings. The resulting prime starch was then spread out and air-dried under ambient conditions. Three to four batches of starch were isolated following this procedure and then combined. Starch moisture content was taken as weight loss after heating at 120 °C for 2 h and was found to be 11.0% and 11.6% for normal and waxy wheat starch, respectively.

2.1.2. Surfactants

A series of *n*-alkyl chain surfactants (monoglycerides, sodium sulphates, trimethyl ammonium bromides, and maltosides) were used in this study. In all cases, surfactants with both 12 and 16 carbon atoms in the alkyl chain (hereafter referred to as "short-" and "long-chain" surfactants, respectively) were included. The molecular weight (M_W), structure, type of surfactant (based on the charge of the polar head group), critical micelle concentration (cmc) at 40 °C, as well as the respective abbreviations used throughout this article are all summarized in Table 1.

All surfactants used were analytical grade reagents and used as received. Alkyl maltosides (C_{n+1}Malt) were purchased from Anatrace (Maumee, OH), sodium hexadecyl sulphate (C_{16}Sulph) from Lancaster (Morecambe, UK) and the rest of the surfactants from Sigma Chemicals (Schnelldorf, Germany).

2.1.3. Surfactant concentration

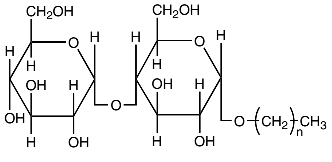
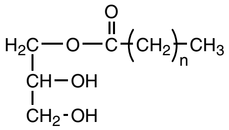
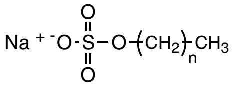
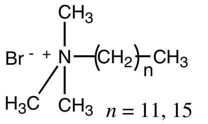
All studies were carried out at a surfactant concentration of 1.02×10^{-4} moles of surfactant/g of starch on a wet basis (wb) which corresponds to weight concentrations in the range of 3% to 6% w/w wb. This concentration corresponds to surfactant concentrations in solution of 10.2 and 34.0 mM for the pasting and calorimetric studies, respectively.

2.2. Methods

2.2.1. Viscometry

The pasting properties of the different starch–surfactant combinations were studied using a Rapid Visco Analyser (RVA) (series 4, Newport Scientific, Warriewood NSW, Australia). Viscosity changes in the suspensions were followed as the samples were heated from 40 to 95 °C and kept

Table 1
List of surfactants used

Surfactant group	Structure	Abbreviation	M_W		cmc[a] (mM)		Type
			C_{12}[c]	C_{16}[c]	C_{12}[c]	C_{16}[c]	
Maltosides	 *n* = 11, 15	C_{n+1}Malt[b]	510.6	566.7	0.17 (20 °C)	6×10^{-4}[d](–)	Non-ionic
Mono-Glycerides	 *n* = 10, 14	C_{n+2}Glyc[b]	274.4	330.5	–[e]	–[e]	Non-ionic
Sodium sulphates	 $Na^{+}\,{}^{-}O\text{-}S(=O)_2\text{-}O\text{-}(CH_2)_n\text{-}CH_3$ *n* = 11, 15	C_{n+1}Sulph[b]	288.4	344.5	8.60 [f]	0.52[f]	Anionic
Trimethyl ammonium bromides	 *n* = 11, 15	C_{n+1}TAB[b]	308.3	364.5	16.5[f]	1,16 [f](45 °C)	Cationic

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[a] cmc, critical micelle concentration in aqueous solution. Values correspond to a temperature of 40 °C unless otherwise stated in parentheses with the cmc value.

[b] *n*, number of CH_2 groups in the alkyl chain of the surfactant (see the schematic of the surfactant molecular structure in the table).

[c] C_{12} and C_{16} refer to the length of the surfactant alkyl chain (i.e., 12 and 16 carbon atoms, respectively).

[d] Data from manufacturer's catalog [Anatrace, Maumee, OH (http://www.anatrace.com/downloads.htm)].

[e] Above their Kraft temperature (<50 °C for C_{12}Glyc and ≈ 70 °C for C_{16}Glyc), monoglycerides exist as diluted surfactant–water blends, which in the case of longer chain monoglyerides (i.e., C_{16}Glyc), may be solutions of liposomes (Krog et al., 1983).

[f] Data from Mukerjee and Mysels (1971).

at that temperature for 5 min. Heating rates of 1.5 and 6.5 °C/min were used. The rotating speed of the paddle (i.e., shearing conditions) along the pasting program was the same as used in standard pasting programs (160 rpm).

Suspensions of starch (2.5 g, wb) in distilled water or surfactant solutions (25 mL) were prepared directly in the RVA sample containers to yield 10% w/v wb starch suspensions. Surfactant solutions were also directly prepared in the RVA sample container. These solutions were heated to 40 °C (the initial temperature of the pasting programs) before the addition of starch. Surfactants with high Krafft temperatures (i.e., C_{16}Sulph, C_{16}Malt, C_{12}, and C_{16}Glyc) were heated to 70 °C until homogeneous solutions were obtained and then quickly cooled back to 40 °C before the addition of starch.

Viscosity values along the pasting program were collected every 4 or 8 s and reported in cP. The different pasting parameters were obtained from the curves (viscosity vs. time/temperature) by means of the instrument analysis software. The temperature at which the samples begin their rapid viscosity building phase, i.e., the pasting temperature (PT), corresponds to the temperature at which the rate of change in viscosity reaches an arbitrarily-set value of 4 cP/s for a heating rate of 6.5 °C/min and 1.3 cP/s for a heating rate of 1.5 °C/min. The peak viscosity (η_{PEAK}) and time to peak (t_{PEAK}) parameters correspond, respectively, to the maximum viscosity value attained by the sample along the pasting program and the time at which this value is reached. Most tests were conducted in duplicate.

2.2.2. Differential scanning calorimetry (DSC)

Calorimetric studies were performed under experimental conditions similar to the ones chosen for the pasting experiments. The same surfactant concentration (moles of surfactant/g starch) and heating rates were thus used in both cases.

The thermal transitions associated with the gelatinization of starch were examined with a DSC (DSC 821^{e}, Mettler-Toledo, Switzerland) of the heat flux type. Starch samples in hermetically sealed 40 μL aluminium pans (Mettler-Toledo, Switzerland) were heated from 20 to 120 °C at a heating rate of 6.5 °C/min. An empty aluminium pan was used as a reference sample.

Starch (ca. 10 mg) was weighed into the sample pans to which distilled water or a surfactant solution (30 μL in either case) was added so that a 33% w/v wb starch suspension was obtained (i.e., starch:water ca. 1:3 wb). Before sealing and reweighing the sample pans, the suspensions were carefully mixed with the aid of a pin to guarantee an even water distribution in the sample.

Water and surfactant solutions were at room temperature when added to the starch. Surfactants with high Krafft temperatures (i.e., C_{16}Sulph, C_{16}Malt, C_{12}, and C_{16}Glyc) were heated to 70 °C until homogeneous solutions were obtained and then quickly cooled back to the desired temperature of addition.

The temperatures and enthalpies of the different endothermic transitions observed in the DSC traces, were determined by means of the instrument analysis software. The reported onset temperatures (T_{O}) correspond to the point at which a straight line drawn up the leading edge of the endotherm intersects the baseline and the peak temperatures (T_{PEAK}) to the point of maximum endothermic heat flow relative to the baseline. Enthalpy values (ΔH) are calculated by estimation of the area under the endotherm with a fitted straight baseline. These values are reported on a dry starch basis. All tests were conducted at least in triplicate.

2.2.3. Statistical analysis

Analysis of variance (ANOVA) with significance defined at $p < 0.05$ was performed on the viscometry and calorimetry data. Significant differences among mean values were determined by Tukey's test using a family-wise error level of 0.05.

3. Results and discussion

3.1. Pasting studies

3.1.1. Normal wheat starch

The results from the pasting studies of normal wheat starch in the presence of short- and long-chain surfactants are shown in Figs. 1A and B and in Table 2. In the presence of short-chain surfactants, the pasting curves of normal wheat starch are characterized by lower pasting temperatures (PT), shorter times to reach peak viscosity (t_{PEAK}) and higher peak viscosities (η_{PEAK}) than in the control sample (see ΔPT, Δt_{PEAK}, and $\Delta\eta_{\mathrm{PEAK}}$ in Table 2, respectively). The extent of the changes induced in these properties is found to be different for the different surfactants. The greatest ability to reduce PT is shown by the cationic surfactant C_{12}TAB, the shortest time to reach peak viscosity (t_{PEAK}) is found in the presence of C_{12}Malt and the highest η_{PEAK} in the presence of C_{12}Sulph.

In the presence of all the long-chain surfactants, with the exception of C_{16}TAB, the pasting temperature of the suspensions is found to be higher than in the control sample, the extent of the increase induced by the different surfactants being similar. On the other hand, the peak viscosity (η_{PEAK}) is found to be increased by all the long-chain surfactants except C_{16}Sulph, for which the η_{PEAK} is actually reached further along the pasting profile (data not shown). As for the effect of the long chain surfactants on t_{PEAK}, a variety of effects are encountered and no apparent trends can be identified. Thus, in comparison to their short-chain counterparts, all the long-chain surfactants but C_{16}TAB are found to have a very distinctive effect on the PT while they have a somewhat similar effect (in type and extent) on the η_{PEAK}.

It is worth noting that despite the differences observed between the effects of short- and long-chain surfactants, a common, interesting feature can be recognized in the pasting curves of normal wheat starch in the presence of all surfactants. In most cases, the presence of surfactants results in a much steeper viscosity rise after the PT, the anionic surfactants C_{12}TAB and C_{16}Sulph being the only exceptions. The steepness of the initial viscosity rise in the pasting curve reflects the temperature range over which granules swell. It is thus clear from the shape of the pasting curves, that in the presence of most of the surfactants studied the whole population of starch granules exhibits a more homogeneous behaviour, swelling over a narrower temperature range.

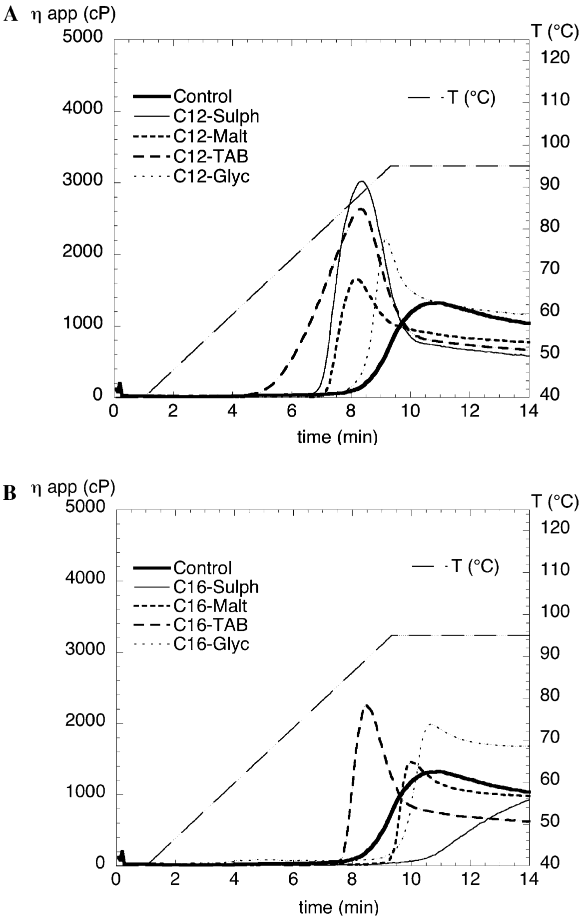

Fig. 1. Pasting profile of normal wheat starch (10% w/v wb) in the presence of (A) short-chain and (B) long-chain surfactants. Heating rate 6.5 °C/min.

3.1.2. Waxy wheat starch

Fig. 2 and Table 3 show the pasting curves and characteristic pasting parameters of waxy wheat starch in the presence of short- and long-chain surfactants.

The pasting profile of waxy wheat starch (Figs. 2A and B) is characterized by a low PT and a high η_{PEAK} followed by a dramatic reduction in viscosity (i.e., high breakdown), which are the typical pasting features of waxy wheat

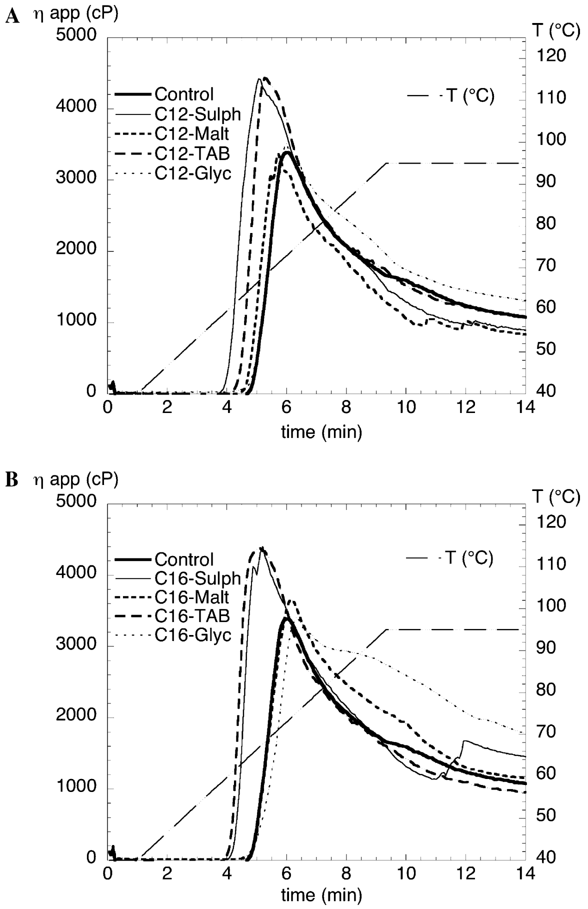

Fig. 2. Pasting profile of waxy wheat starch (10% w/v wb) in the presence of (A) short-chain and (B) long-chain surfactants. Heating rate 6.5 °C/min.

Table 2
Pasting temperature (PT), time to reach peak viscosity (t_{PEAK}) and peak viscosity (η_{PEAK}) of normal wheat starch suspensions (10% w/v wb) in the presence of surfactants

Surfactant	PT (°C)	ΔPT	t_{PEAK} (min)	Δt_{PEAK}	η_{PEAK} (cP)	$\Delta\eta_{\mathrm{PEAK}}$
–	87.55 ± 0.26^{a}	–	10.78 ± 0.08^{a}	–	1312 ± 13^{a}	–
C_{12}Sulph	77.97 ± 0.51^{b}	−9.58	8.35 ± 0.04^{bcdg}	−2.42	3011 ± 71^{b}	1699
C_{12}TAB	66.38 ± 1.24^{c}	−21.18	8.33 ± 0.00^{cdg}	−2.44	2620 ± 15^{c}	1308
C_{12}Malt	79.88 ± 0.11^{d}	−7.68	8.20 ± 0.00^{d}	−2.58	1624 ± 57^{dh}	312
C_{12}Glyc	85.20 ± 0.00^{e}	−2.35	9.17 ± 0.05^{e}	−1.61	2214 ± 8^{egi}	902
C_{16}Sulph	94.68 ± 0.46^{fhi}	7.13	13.00 ± 0.00^{f}	2.22	796 ± 66^{f}	−516
C_{16}TAB	82.75 ± 0.21^{g}	−4.80	8.47 ± 0.00^{g}	−2.31	2215 ± 71^{gi}	903
C_{16}Malt	93.73 ± 0.32^{h}	6.18	9.97 ± 0.05^{h}	−0.81	1585 ± 180^{h}	273
C_{16}Glyc	93.05^{ih}	5.50	10.67^{a}	−0.11	1990^{i}	678

Heating rate 6.5 °C/min.
See Table 1 for the abbreviations used to refer to the different surfactants.
ΔPT, Δt_{PEAK}, and $\Delta\eta_{\mathrm{PEAK}}$ denote the difference between the respective pasting parameter in the presence and absence (control) of surfactant.
Reported values are means ± standard deviation of duplicates (values with no standard deviations reported correspond to tests that were carried out once). Values within the same column followed by the same letter are not significantly different ($p \leqslant 0.05$).

Table 3
Pasting temperature (PT), time to reach peak viscosity (t_{PEAK}) and peak viscosity (η_{PEAK}) of waxy wheat starch suspensions (10% w/v wb) in the presence of surfactants

Surfactant	PT (°C)	ΔPT	t_{PEAK} (min)	Δt_{PEAK}	η_{PEAK} (cP)	$\Delta\eta_{PEAK}$
–	64.07 ± 0.23^{a}	–	6.0 ± 0.00^{a}	–	3399 ± 28^{a}	–
C_{12}Sulph	58.00 ± 0.71^{be}	−6.07	5.03 ± 0.05^{bf}	−0.97	4382 ± 56^{bcde}	983
C_{12}TAB	60.77 ± 0.45^{cd}	−3.30	5.29 ± 0.04^{ce}	−0.71	4317 ± 99^{cde}	918
C_{12}Malt	62.88 ± 0.04^{a}	−1.19	5.73 ± 0.00^{d}	−0.27	3346 ± 23^{a}	−53
C_{12}Glyc	64.20 ± 0.00^{a}	0.13	6.07 ± 0.09^{ag}	0.07	3496 ± 18^{a}	97
C_{16}Sulph	60.03 ± 0.25^{de}	−4.04	5.20 ± 0.00^{e}	−0.80	4370 ± 45^{de}	971
C_{16}TAB	59.22 ± 0.66^{e}	−4.85	5.07 ± 0.00^{f}	−0.93	4405 ± 15^{e}	1006
C_{16}Malt	64.70 ± 0.00^{a}	0.63	6.13 ± 0.00^{g}	0.13	3344 ± 434^{a}	−55
C_{16}Glyc	63.80^{a}	−0.27	6.33^{h}	0.33	3402^{a}	3

Heating rate 6.5 °C/min.
See Table 1 for the abbreviations used to refer to the different surfactants.
ΔPT, Δt_{PEAK}, and $\Delta\eta_{PEAK}$ denote the difference between the respective pasting parameter in the presence and absence (control) of surfactant.
Reported values are means ± standard deviation of duplicates (values with no standard deviations reported correspond to tests that were carried out once). Values within the same column followed by the same letter are not significantly different ($p \leqslant 0.05$).

varieties (Abdel-Aal, Hucl, Chibbar, Han, & Demeke, 2002; Chakraborty et al., 2004; Grant et al., 2001; Kim, Johnson, Graybosch, & Gaines, 2003). The more rapid and extensive swelling of waxy starch granules with respect to normal ones is usually attributed to the existence of a more loosely bound internal structure which is associated to the lack of AM as well as to the low contents of internal lipid (Grant et al., 2001; Tester & Morrison, 1990).

As observed in Fig. 2A and B, the addition of surfactants brings about rather minor changes in the pasting of waxy wheat starch. Moreover, in contrast to what was observed in normal wheat starch, ionic and non-ionic surfactants are found to have distinctively different effects regardless of their chain length (see Table 3). The non-ionic surfactants (alkyl-Malt and alkyl-Glyc) are found to have either a very small or an insignificant effect on any of the pasting properties (PT, η_{PEAK} and t_{PEAK}) of the waxy wheat starch. On the other hand, the ionic surfactants (alkyl-TAB and alkyl-Sulph) lower the PT, tend to shorten the t_{PEAK} and increase η_{PEAK}. Furthermore, the changes induced by short- and long-chain ionic surfactants are of similar magnitude.

If results from pasting studies of normal and waxy wheat starch are contrasted, a very interesting trend can be identified. Compared to waxy wheat starch, the effect of most surfactants on the PT of normal wheat starch (i.e., changes with respect to control sample) is not only greater but also governed by the surfactant chain length to a certain extent. In the case of waxy wheat starch, the effects of surfactants on PT seem to be governed by the nature of the head group (charged or non-charged), the surfactant chain length having no apparent effect.

3.1.3. Heating rate effect

Table 4 summarizes the pasting parameters of normal wheat starch in the presence of surfactants when pasting is induced using a heating rate of 1.5 °C/min. The use of a slow heating rate such as this one, favours the attainment of equilibrium (thermal and physicochemical) in the system while at the same time exposes the suspension to more prolonged agitation and mechanical shear. The starch samples used for these experiments, though prepared from the same flour samples, belong to a different set of isolated batches.

Table 4
Pasting temperature (PT), time to reach peak viscosity (t_{PEAK}) and peak viscosity (η_{PEAK}) of normal wheat starch suspensions (10% w/v) in the presence of surfactants

Surfactant	PT (°C)	ΔPT	t_{PEAK} (min)	Δt_{PEAK}	η_{PEAK} (cP)	$\Delta\eta_{PEAK}$
–	88.78 ± 0.04^{a}	–	38.27 ± 0.00^{a}	–	574 ± 13^{a}	–
C_{12}Sulph	75.10 ± 0.00^{b}	−13.68	29.87 ± 0.19^{bc}	−8.40	2761 ± 6^{b}	2188
C_{12}TAB	66.03 ± 1.03^{c}	−22.75	29.80 ± 0.10^{c}	−8.47	2361 ± 20^{c}	1788
C_{12}Malt	77.50 ± 0.21^{d}	−11.28	28.80 ± 0.00^{d}	−9.47	1496 ± 4^{d}	922
C_{12}Glyc	84.07^{e}	−4.71	32.53^{e}	−5.73	2051^{e}	1477
C_{16}Sulph	94.98 ± 0.04^{fi}	6.20	44.00 ± 0.00^{f}	5.73	766 ± 27^{f}	192
C_{16}TAB	80.05 ± 0.00^{g}	−8.73	30.73 ± 0.09^{g}	−7.53	2152 ± 35^{g}	1578
C_{16}Malt	91.35 ± 0.00^{hi}	2.57	36.67 ± 0.00^{h}	−1.60	1144 ± 4^{h}	570
C_{16}Glyc	93.15^{i}	4.38	37.73^{i}	−0.53	1296^{i}	722

Heating rate 1.5 °C/min.
See Table 1 for the abbreviations used to refer to the different surfactants.
ΔPT, Δt_{PEAK}, and $\Delta\eta_{PEAK}$ denote the difference between the respective pasting parameter in the presence and absence (control) of surfactant.
Reported values are means ± standard deviation of duplicates (values with no standard deviations reported correspond to tests that were carried out once). Values within the same column followed by the same letter are not significantly different ($p \leqslant 0.05$).

Small differences between the two sets of batches were found to have a certain influence on the absolute values of the pasting parameters. Thus, the actual pasting parameters obtained for the starches at the two heating rates cannot be directly compared. However, it is yet valid and useful to make comparisons based on the changes that surfactant induce with respect to the control samples. Hence, if only changes with respect to the control sample are regarded, it can be observed that when pasting of normal wheat starch is induced using a heating rate of 1.5 °C/m the short- and long-chain surfactants bring about the same type of changes as the ones they induce when a faster heating rate is used. However, as expected, the magnitude of the changes is found to be different. In terms of PT and compared to what was observed at a faster heating rate, short-chain surfactants and C_{16}TAB are found to produce greater reductions in PT at lower heating rates (See Tables 2 and 4). The long-chain surfactants, on the other hand, effect somewhat smaller delays in the onset of pasting. It is also found that the magnitudes of the changes induced by surfactants (long- and short-chain) on η_{PEAK} are greater than the ones produced at faster heating rates, although the actual viscosity values are 100–1000 cP lower.

Table 5 shows the pasting parameters of waxy wheat starch in the presence of surfactants when pasting is induced using a heating rate of 1.5 °C. In this case, the tendencies found regarding the effect of different surfactants are also the same as the ones found when a heating rate of 6.5 °C/min was used. The ionic surfactants (short- and long-chain) are thus found to induce the largest changes in the pasting parameters of waxy starch while the effect of the non-ionic surfactants is either smaller or simply insignificant (see ΔPT, $\Delta\eta_{\mathrm{PEAK}}$, and Δt_{PEAK} in Table 5). Compared to what was observed at faster heating rates, the magnitude of the changes observed at a heating rate of 1.5 °C/min tends to be greater.

Thus, in general, the use of different heating rates (1.5 and 6.5 °C/min) does not affect significantly the type of changes induced by surfactants on the pasting properties of normal and waxy starch. However, it cannot be ignored that for normal wheat starch lower heating rates resulted in larger depressions of the PT in the case of short-chain surfactants and somewhat smaller (and not larger) delays in PT in the case of the longer-chain surfactants. This could be partly due to a higher effective solid content in the starch suspensions in the presence of long-chain surfactants, as the higher the pasting temperature the more water will be lost due to the evaporation up to the moment at which pasting begins. On the other hand, this could also be related to the role that time and non-equilibrium aspects may play on the effect that surfactants have on the PT and other pasting properties of starch. The tendencies found in our investigation are in good agreement with the effect some short- and long-chain surfactants have been reported to have on the swelling of wheat starch granules at equilibrium conditions (Eliasson, 1985a; Roach & Hoseney, 1995; Svensson et al., 1998). Despite this, it would be premature to suppose that the trends found in this study regarding the effect of surfactant chain length would hold if swelling and leaching studies were carried out under conditions closer to equilibrium. Clearly, this would be a topic worth studying further.

3.2. Calorimetric studies

Figs. 3 and 4 show the DSC thermograms of normal and waxy wheat starches in the presence and absence of surfactants. In general, one, two or three distinctive endothermic transitions can be recognized in them. The single, well-defined transition associated to the gelatinization of starch in excess water (i.e., starch:water < 2:3) is seen in the DSC traces of the normal and waxy wheat starch in the temperature ranges 50–70 and 50–80 °C, respectively. The endotherm occurring at higher temperatures (>80 °C), associated with the dissociation transition of the amylose–lipid (surfactant) complex, can be recognized in the thermograms of normal wheat starch both in the absence and presence of surfactants. As expected, no evidence of such transition is seen in the thermograms of the waxy wheat

Table 5

Pasting temperature (PT), time to reach peak viscosity (t_{PEAK}) and peak viscosity (η_{PEAK}) of waxy wheat starch suspensions (10% w/v wb) in the presence of surfactants

Surfactant	PT (°C)	ΔPT	t_{PEAK} (min)	Δt_{PEAK}	η_{PEAK} (cP)	$\Delta\eta_{\mathrm{PEAK}}$
–	62.10 ± 0.21^{a}	–	19.27 ± 0.09^{a}	–	2836 ± 18^{a}	–
C_{12}Sulph	54.83 ± 0.11^{bg}	−7.28	15.73 ± 0.00^{bef}	−3.53	3729 ± 32^{bcef}	893
C_{12}TAB	58.43 ± 0.11^{c}	−3.68	16.93 ± 0.19^{c}	−2.33	3786 ± 30^{cef}	950
C_{12}Malt	60.85 ± 0.00^{deh}	−1.25	18.07 ± 0.28^{d}	−1.20	2758 ± 45^{a}	−78
C_{12}Glyc	60.85^{eh}	−1.25	18.67^{ad}	−0.60	3201^{dh}	365
C_{16}Sulph	55.70 ± 0.00^{fg}	−6.40	15.33 ± 0.19^{ef}	−3.93	3869 ± 33^{ef}	1033
C_{16}TAB	55.40^{g}	−6.70	15.33^{f}	−3.93	3715^{f}	879
C_{16}Malt	61.95^{ah}	−0.15	19.47^{a}	0.20	2217^{g}	−619
C_{16}Glyc	61.40^{h}	−0.70	19.73^{a}	0.47	3208^{h}	372

Heating rate 1.5 °C/min.

See Table 1 for the abbreviations used to refer to the different surfactants.

ΔPT, Δt_{PEAK}, and $\Delta\eta_{\mathrm{PEAK}}$ denote the difference between the respective pasting parameter in the presence and absence (control) of surfactant.

Reported values are means ± standard deviation of duplicates (values with no standard deviations reported correspond to tests that were carried out once). Values within the same column followed by the same letter are not significantly different ($p \leqslant 0.05$).

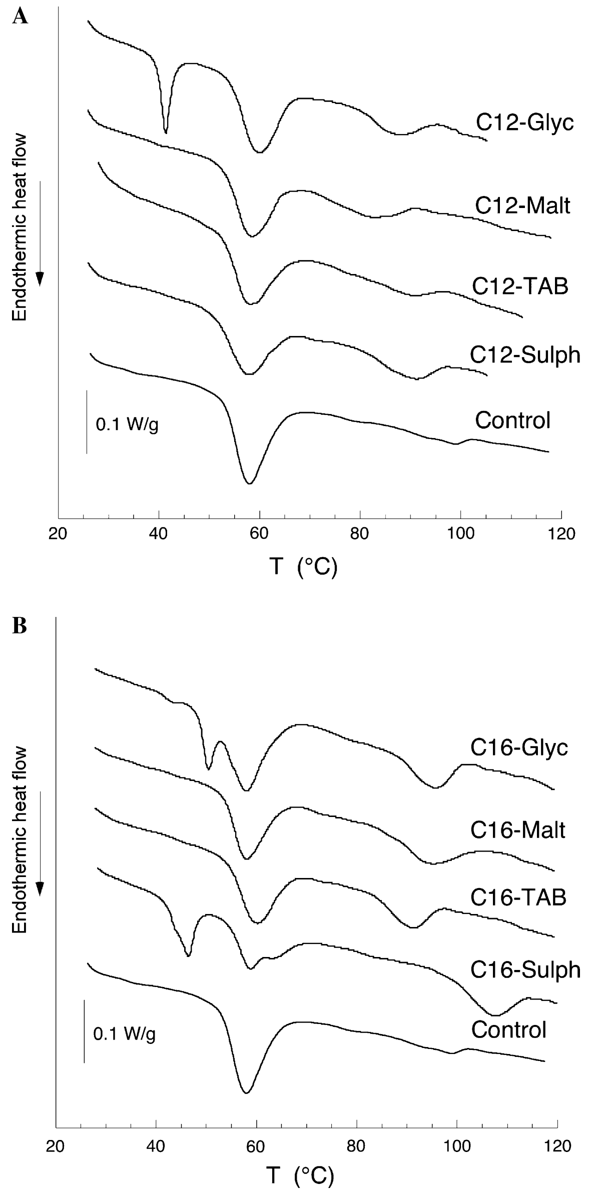

Fig. 3. DSC traces for normal wheat starch (starch:water 1:3) in the presence of (A) short-chain and (B) long-chain surfactants. Heating rate 6.5 °C/min.

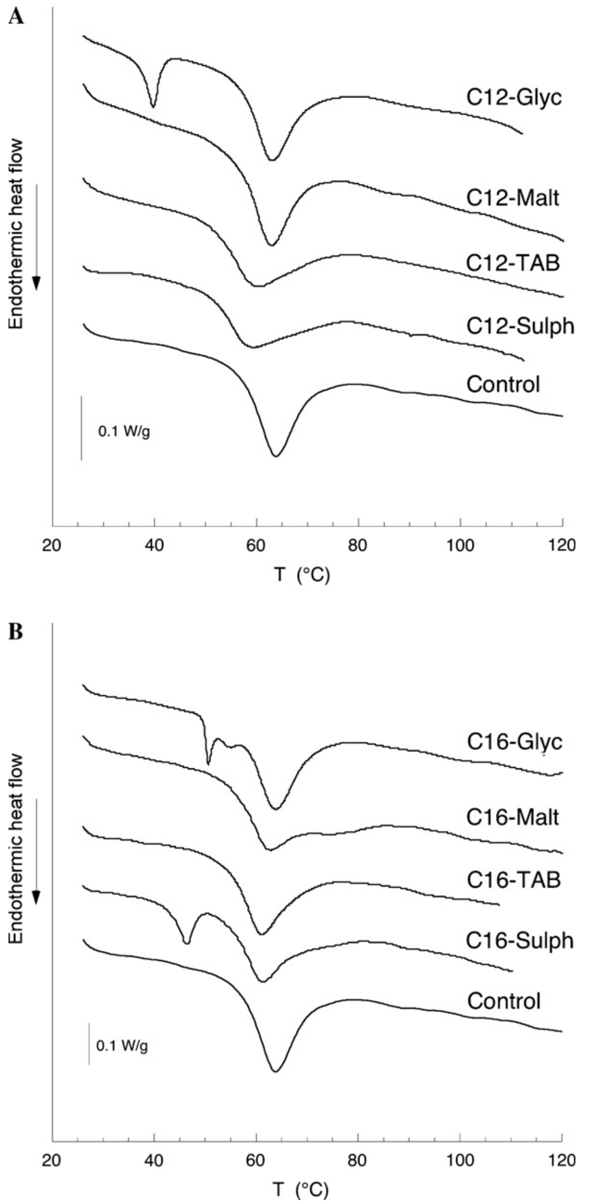

Fig. 4. DSC traces for waxy wheat starch (starch:water 1:3) in the presence of (A) short-chain and (B) long-chain surfactants. Heating rate 6.5 °C/min.

starch. The third transition, a smaller and sharper endotherm occurring at $T < 50$ °C in the thermograms of normal and waxy wheat starches in the presence of some surfactants (C_{16}Sulph, C_{12}, and C_{16}Glyc), is associated to the melting of surfactant crystals (i.e., the crossing of the Krafft boundary in the surfactant phase diagram). This transition it is known to occur at or below 20 °C for C_{12}Sulph, C_{12}TAB, C_{16}TAB and C_{12}Malt (Boyd, Drummond, Krodkiewska, & Grieser, 2000; Gu & Sjoblom, 1992; Laughlin, 1990) which is why it is not observed in the thermograms. As confirmed by DSC thermograms of the surfactants alone (results not shown), the thermal transition associated to the melting of the surfactant crystals is the only surfactant-related transition that can be observed at these levels of addition. As discussed elsewhere (Eliasson, 1985b; Eliasson & Krog, 1985), other phase transitions like the ones occurring typically in monoglycerides, involve much lower enthalpy values and will thus not show in the thermogram. The melting endotherm of the C_{16}Glyc crystals is found to take place at temperatures of ca. 50 °C. This transition coincides with the initial part of the main starch gelatinization endotherm in both normal and waxy wheat starch, thus making it impossible to determine the actual onset temperature of the gelatinization endotherm in these cases.

3.2.1. The gelatinization transition: Onset temperature (T_{OGEL})

The temperatures and enthalpies of the gelatinization transition of normal and waxy wheat starch in the presence of surfactants are summarized in Tables 6 and 7, respectively. Regarding the effect of surfactants on T_{OGEL}, compared to their non-ionic counterparts, short-chain ionic

Table 6
Characteristic temperatures [onset ($T_{O\,GEL}$), peak ($T_{PEAK\,GEL}$)] and enthalpies (ΔH_{GEL}) of the gelatinization endotherm of normal wheat starch (starch to water ratio: 1:3) in the presence of surfactants

Surfactant	$T_{O\,GEL}$ (°C)	$\Delta T_{O\,GEL}$	$T_{PEAK\,GEL}$ (°C)	$\Delta T_{PEAK\,GEL}$	ΔH_{GEL} (J/g)	$\Delta (\Delta H_{GEL})$
–	52.42 ± 0.08^{a}	—	57.35 ± 0.05^{ab}	–	10.05 ± 0.20^{a}	—
C_{12}Sulph	50.30 ± 0.25^{b}	−2.11	57.10 ± 0.17^{ab}	−0.25	7.05 ± 0.42^{bh}	−3.00
C_{12}TAB	50.10 ± 0.14^{bc}	−2.31	55.31 ± 0.11^{b}	−2.04	8.97 ± 0.30^{ceg}	−1.08
C_{12}Malt	52.72 ± 0.12^{ag}	0.30	57.76 ± 0.16^{ab}	0.41	7.82 ± 0.12^{dgh}	−2.23
C_{12}Glyc	53.85 ± 0.07^{def}	1.44	59.30 ± 0.24^{ac}	1.95	8.59 ± 0.09^{eg}	−1.46
C_{16}Sulph	53.54 ± 0.05^{ef}	1.12	57.58 ± 0.05^{ab}	0.23	5.45 ± 0.16^{f}	−4.60
C_{16}TAB	53.62 ± 0.11^{f}	1.20	59.36 ± 0.36^{ad}	2.00	8.32 ± 0.37^{gh}	−1.73
C_{16}Malt	52.93 ± 0.02^{g}	0.51	55.94 ± 2.60^{be}	−1.41	7.67 ± 0.13^{h}	−2.38
C_{16}Glyc	—		—		—	

Heating rate 6.5 °C/min.
See Table 1 for the abbreviations used to refer to the different surfactants.
$\Delta T_{O\,GEL}$, $\Delta T_{PEAK\,GEL}$, and $\Delta (\Delta H_{GEL})$ denote the difference between the respective calorimetric parameter in the presence and absence (control) of surfactant.
Reported values are means ± standard deviation of triplicates. Values within the same column followed by the same letter are not significantly different ($p \leqslant 0.05$).
—, Not measurable.

Table 7
Characteristic temperatures [onset ($T_{O\,GEL}$), peak ($T_{PEAK\,GEL}$)] and enthalpies (ΔH_{GEL}) of the gelatinization endotherm of waxy wheat starch (starch to water ratio: 1:3) in the presence of surfactants

Surfactant	$T_{O\,GEL}$ (°C)	$\Delta T_{O\,GEL}$	$T_{PEAK\,GEL}$ (°C)	$\Delta T_{PEAK\,GEL}$	ΔH_{GEL} (J/g)	$\Delta (\Delta H_{GEL})$
–	56.60 ± 0.08^{a}	—	63.19 ± 0.08^{a}	–	12.45 ± 0.10^{ab}	—
C_{12}Sulph	51.12 ± 0.21^{b}	−5.48	58.35 ± 0.25^{b}	−4.84	9.95 ± 0.07^{ab}	−2.50
C_{12}TAB	51.20 ± 0.01^{bc}	−5.40	59.65 ± 0.10^{c}	−3.54	10.77 ± 0.95^{ab}	−1.68
C_{12}Malt	55.92 ± 0.08^{ad}	−0.68	62.07 ± 0.01^{d}	−1.12	11.58 ± 0.84^{ab}	−0.87
C_{12}Glyc	56.67 ± 0.19^{a}	0.07	62.63 ± 0.01^{e}	−0.56	9.64 ± 1.77^{ab}	−2.81
C_{16}Sulph	54.79 ± 0.32^{def}	−1.81	60.66 ± 0.06^{fg}	−2.53	8.85 ± 1.62^{ab}	−3.60
C_{16}TAB	54.28 ± 0.20^{ef}	−2.32	60.37 ± 0.09^{g}	−2.82	10.69 ± 0.08^{bd}	−1.76
C_{16}Malt	54.40 ± 0.52^{f}	−2.20	61.54 ± 0.16^{h}	−1.65	13.17 ± 0.42^{ae}	0.72
C_{16}Glyc	—		—		—	

Heating rate 6.5 °C/min.
See Table 1 for the abbreviations used to refer to the different surfactants.
$\Delta T_{O\,GEL}$, $\Delta T_{PEAK\,GEL}$, and $\Delta (\Delta H_{GEL})$ denote the difference between the respective calorimetric parameter in the presence and absence (control) of surfactant.
Reported values are means ± standard deviation of triplicates. Values within the same column followed by the same letter are not significantly different ($p \leqslant 0.05$).
—, Not measurable.

surfactants are found to have a special ability to depress the $T_{O\,GEL}$ (i.e., have a granule destabilizing effect) in both normal and waxy wheat starch, although the reductions induced in waxy wheat starch are larger. On the other hand, the longer chain surfactants have very different effects on the $T_{O\,GEL}$ of the two type of starches. These surfactants, regardless of their head group charge, are found to delay the onset of the gelatinization endotherm in normal wheat starch while they produce the opposite effect on waxy starch. In general, these results are in good agreement with the previously reported effects of some short- and long-chain anionic surfactants on the $T_{O\,GEL}$ of normal (Biliaderis & Tonogai, 1991; Eliasson, 1986b; Villwock et al., 1999) and waxy cereal starches (Eliasson, Finstad, & Ljunger, 1988; Evans, 1986).

Although it is known that both the molecular and crystalline order are disrupted concurrently during gelatinization (Cooke & Gidley, 1992; Jenkins & Donald, 1998), recent experimental evidence suggests that the enthalpy of gelatinization primarily reflects the loss of molecular (double helical) order (Cooke & Gidley, 1992). Moreover, *in situ* studies of starch gelatinization in excess water (Jenkins & Donald, 1998) have conclusively shown that water enters and swells the amorphous growth rings before any crystallites become destabilized. Thus, the onset of the DSC gelatinization transition is expected to depend on a complex interplay of factors, among which water transport into the granules can be considered to play a very important role. Molecules like surfactants could be thought to affect this process in many possible ways depending on their relative affinity for the starch polysaccharides. In consequence it is perhaps not surprising to find that surfactants can have so different effects on the $T_{O\,GEL}$ as the ones found in this study. Despite no clear trends can be recognized in this respect, the results presented here show clearly that, for a given type of starch, such effects are not entirely governed by the surfactant chain length nor by the presence of a charged head group.

3.2.2. The gelatinization transition: Enthalpy (ΔH_{GEL})

As reported in Table 6, all surfactants lower (in 10–45%) the enthalpy of gelatinization of normal wheat starch, the largest reduction being produced by C_{16}Sulph (see $\Delta\Delta H_{GEL}$) in (Table 6). Similar trends are found in the waxy starch samples (Table 7), in which case most surfactants lower the ΔH_{GEL}. However, compared to normal wheat starch samples, the enthalpy values of the gelatinization transition in waxy wheat starch samples exhibited poorer reproducibility. In consequence, the reductions induced by most surfactants in the ΔH_{GEL} of waxy wheat starch are not statistically significant, although they are of the same magnitude as the ones induced in normal wheat starch.

Gelatinization studies of wheat and other normal cereal starches in the presence of different surfactants have invariably found lower gelatinization enthalpies than the one in the absence of any additives (Biliaderis & Tonogai, 1991; Eliasson, 1986b; Eliasson et al., 1988; Svensson et al., 1998; Villwock et al., 1999). A similar effect has even been reported for normal tuber (Evans, 1986; Svensson et al., 1998), legume (Biliaderis & Tonogai, 1991) and even waxy cereal starches (Evans, 1986; Villwock et al., 1999). The magnitude of the reductions in ΔH_{GEL} has been found to depend on the surfactant concentration (Evans, 1986; Villwock et al., 1999) and the type of surfactant. As for the relative ability of different surfactants to depress the ΔH_{GEL} of common cereal starches, no consistent trends have been reported (Biliaderis & Tonogai, 1991; Villwock et al., 1999). However, a general feature that most of these studies seem to agree with, is the special ability of C_{12}Sulph to reduce ΔH_{GEL}. A finding which agrees well with the trends found in the present study.

Upon heating past their gelatinization temperature, most starches in the presence of surfactants would exhibit an endotherm (usually at $T > 80$ °C) which corresponds to the disordering transition of complexes formed between surfactants and the AM fraction. As it has been found to be the case for various surfactants, this transition is comparable in magnitude to the reductions that surfactants induce on the ΔH_{GEL} of starches. (Eliasson, 1986b; Evans, 1986; Kugimiya & Donovan, 1981). The decreasing effect of surfactants on ΔH_{GEL} has therefore been suggested to be the result of an exothermic effect associated to the formation of starch–surfactant complexes occurring simultaneously as the starch granule gelatinizes. No evidence of such DSC transition is found in waxy (i.e., AM-free) starches. This has been attributed not to the incapability of AMP to form complexes with surfactants but to the non-cooperativity of the association (or dissociation) process between these two molecules (Evans, 1986).

All the surfactants included in this investigation were found to produce significant reductions in the ΔH_{GEL} of normal wheat starch. On the other hand, the data obtained from the waxy starch samples does not provide any conclusive evidence on whether the surfactants induce or not similar reductions in the gelatinization transition of this type of starch. Consequently, if the reductions in ΔH_{GEL} induced by surfactants are to be taken as due to the occurrence of a simultaneous, exothermic surfactant–starch complex formation, the results presented here do not provide any evidence to support the hypothesis that surfactants have the ability to complex to a similar extent with the AM and the AMP fraction. Surface tension studies have provided evidence suggesting that is indeed the case, showing that surfactants such as C_{12}Sulph and C_{16}TAB can bind to AMP and AM in aqueous solution to a somewhat similar extent (Lundqvist, Eliasson, & Olofsson, 2002; Svensson, Gudmundsson, & Eliasson, 1996). In this case, the binding is thought to proceed through the formation of inclusion complexes with the AMP outer chains. Despite being considered as a plausible explanation for the reductions in ΔH_{GEL} produced by surfactants, it has been acknowledged that it is not possible (specially from DSC measurements alone) to rule out other possibilities. Destabilizing effects towards the crystalline regions in the starch granule and lower degrees of gelatinization due to an inhibited AM leaching, have been mentioned as other possible ways in which surfactants could lower the energy required to complete gelatinization (Eliasson, 1986b). The reductions brought about by surfactants in the ΔH_{GEL} of normal (and perhaps waxy) wheat starch likely involve, to a different extent, not only one but all of these mechanisms at the same time.

3.2.3. The amylose–surfactant/lipid complex transition

As most cereal starches do, normal wheat starch contains small amounts of integral and surface polar lipids in the form of lysophospholipids and free fatty acids (Soulaka & Morrison, 1985). The DSC trace of lipid-containing starches usually exhibits an endothermic transition near 100 °C. This endotherm, which can be recognized in the DSC trace of the normal wheat starch presented in Fig. 3, has been shown to be associated with the dissociation transition of small amounts of AM-complexed lipids (Bulpin, Welsh, & Morris, 1982; Kugimiya, Donovan, & Wong, 1980). Complexes formed between added surfactants and the AM fraction in starch will also undergo a similar type of endothermic dissociation transition. This endothermic event is attributed to the disordering of the complexes (V-helix → coil transition) rather than to the melting of the crystallites (Biliaderis & Seneviratne, 1990; Raphaelides & Karkalas, 1988; Seneviratne & Biliaderis, 1991). Furthermore, it has been claimed (Karkalas, Ma, Morrison, & Pethrick, 1995) that such disordering involves the actual dissociation of the complex into free ligand and AM.

The dissociation transition of the complex formed between surfactants and the AM fraction in normal wheat starch is seen to occur at different temperatures and temperature ranges depending on the type of surfactant (Fig. 3). The enthalpies and characteristic temperatures of the thermal transition of these complexes (presented in Table 8) are consistent with those of form I complexes reported elsewhere (Tufvesson, Wahlgren, & Eliasson, 2003a; Tufvesson, Wahlgren, & Eliasson, 2003b).

Table 8
Characteristic temperatures [onset ($T_{\mathrm{O\,CX}}$), peak ($T_{\mathrm{PEAK\,CX}}$), endset ($T_{\mathrm{E\,CX}}$)], and enthalpies (ΔH_{CX}) of the transition endotherm of the surfactant(lipid)/AM complex in normal wheat starch (starch to water ratio: 1:3) in the presence of surfactants

Surfactant	$T_{\mathrm{O\,CX}}$ (°C)	$T_{\mathrm{PEAK\,CX}}$ (°C)	$T_{\mathrm{E\,CX}}$ (°C)	ΔH_{CX} (J/g)
–	88.30 ± 1.41^{a}	97.45 ± 0.67^{a}	101.95 ± 0.57^{a}	1.02 ± 0.09^{a}
C_{12}Sulph	80.01 ± 0.81^{bceg}	90.51 ± 0.59^{bg}	97.11 ± 0.96^{bg}	3.36 ± 0.64^{bcdefh}
C_{12}TAB	79.38 ± 1.96^{ce}	86.45 ± 0.81^{ce}	93.21 ± 0.56^{c}	1.27 ± 0.04^{a}
C_{12}Malt	71.06 ± 1.04^{d}	81.06 ± 0.77^{d}	90.32 ± 0.62^{d}	2.80 ± 0.23^{cf}
C_{12}Glyc	80.86 ± 2.03^{eg}	86.78 ± 0.35^{e}	93.63 ± 0.29^{e}	2.92 ± 0.75^{defh}
C_{16}Sulph	97.35 ± 0.48^{f}	105.69 ± 0.07^{f}	112.21 ± 0.02^{f}	3.54 ± 0.19^{efgh}
C_{16}TAB	83.34 ± 0.48^{gh}	90.36 ± 0.45^{g}	96.32 ± 0.70^{g}	3.34 ± 0.11^{fh}
C_{16}Malt	85.79 ± 0.24^{ah}	94.21 ± 0.66^{hi}	102.53 ± 0.63^{a}	4.73 ± 0.27^{gh}
C_{16}Glyc	86.90 ± 0.34^{ah}	95.00 ± 0.36^{i}	100.77 ± 0.69^{a}	4.18 ± 0.30^{h}

Heating rate 6.5 °C/min.
See Table 1 for the abbreviations used to refer to the different surfactants.
Reported values are means ± standard deviation of triplicates. Values within the same column followed by the same letter are not significantly different ($p \leqslant 0.05$).

The complexes formed between AM and the long-chain surfactants included in this study are found to have greater thermal stabilities (i.e., higher $T_{\mathrm{O\,CX}}$) and, in half of the cases, significantly higher dissociation enthalpies (ΔH_{CX}) than the complexes formed by their shorter-chain counterparts. This finding generalizes previously reported trends on the effect of the surfactant chain length on the $T_{\mathrm{O\,CX}}$ (Eliasson, 1986b; Tufvesson et al., 2003a) and the ΔH_{CX} (Hoover & Hadziyev, 1981; Tufvesson et al., 2003a) of AM/*n*-alkyl-monoglyceride complexes formed under similar experimental conditions to the ones used in the present study.

The dissociation enthalpy of the AM–surfactant complexes (ΔH_{CX}) has usually been taken to be a measure of the amount of complex present (Kowblansky, 1985; Tufvesson et al., 2003a; Tufvesson et al., 2003b). However, the available experimental evidence on the subject suggests that, at least under the experimental conditions imposed by a DSC program as the one used here, a higher ΔH_{CX} cannot be unambiguously ascribed to higher amounts of complexes. Complexes formed between AM and fatty acids with different chain lengths have been reported to have different molar stoichiometries and, in consequence, perhaps different structures (e.g., number of turns per helix) (Karkalas & Raphaelides, 1986). Differences of such nature would result in different numbers of intrahelical hydrogen bonds and van der Waals contacts per glucosyl residues, and thus in different ΔH_{CX}. Therefore, it appears more prudent to interpret differences in ΔH_{CX} as due to differences in the ability (extent and/or characteristics of the association) of surfactants to interact with the AM fraction.

Some researches have attributed the higher ΔH_{CX} obtained in the presence of some surfactants (e.g., C_{16}TAB in comparison to C_{16}–C_{18} monoglycerides) to a higher monomer concentration of the amphiphile (Eliasson, 1986b; Larsson, 1980). In this respect, the present results seem to provide evidence against this hypothesis. At the surfactant concentrations used in this study (34 mM in DSC studies), long- and short-chain alkyl sulphates, maltosides and trimethyl ammonium bromides exist as micellar solutions. The critical micelle concentration, cmc, (i.e., the monomer concentration in equilibrium with micelles) of these surfactants decreases in the order C_{12}TAB > C_{12}Sulph > C_{16}TAB > C_{16}Sulph > C_{12}Malt > C_{16}Malt (see Table 1). The surfactant C_{12}TAB is in fact the one that gives the lowest ΔH_{CX}, while the rest of the surfactants yield very similar complex enthalpy values. Thus, a higher cmc does not result in a higher ΔH_{CX}. Monoglycerides, on the other hand, exist as diluted surfactant–water blends above their Krafft temperature (<50 °C for C_{12} and ~70 °C for C_{16}Glyc) (Krog, Riisom, & Larsson, 1983). The two monoglycerides C_{12} and C_{16}Glyc, give ΔH_{CX} values which are not significantly different from the ones obtained in the presence of most of the "micelle-forming" surfactants. Consequently, the results found in this study seem to suggest that different ΔH_{CX} values cannot be ascribed to differences in the monomer concentration (cmc) or phase behaviour of the surfactants. Moreover, the experimental evidence presented in this investigation indicates that the surfactant chain length is, to an important extent, the factor that determines the characteristics and/or extent of complex formation. The existence of such differences between the complexes formed between long- and short-chain surfactants is further stressed by the higher thermal stabilities ($T_{\mathrm{O\,CX}}$) of the complexes between AM and the long-chain surfactants, as found in this study and reported by others (Eliasson, 1986b; Godet, Bulleón, Tran, & Colonna, 1993; Raphaelides & Karkalas, 1988; Tufvesson et al., 2003a; Tufvesson et al., 2003b).

3.3. Pasting vs. calorimetric studies

Fig. 5 summarises the temperature intervals over which the gelatinization (ΔH_{GEL}) and the AM–surfactant complex transition (ΔH_{CX}) take place in normal and waxy wheat starch in the absence and presence of surfactants. Triangles indicate the pasting temperatures obtained with the RVA under the same heating rate conditions as those used for the DSC experiments. Despite the use of similar heating rates and surfactant/starch ratios, direct

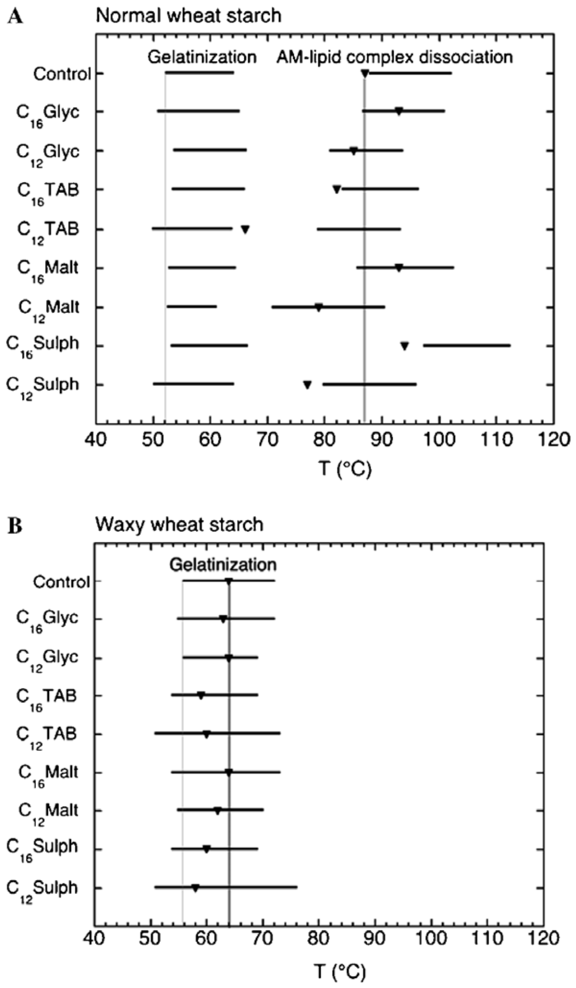

Fig. 5. Temperature ranges for the gelatinization and AM–surfactant complex transitions in the presence of surfactants in (A) normal and (B) waxy wheat starch. Triangles indicate the onset of the pasting (PT) at the same heating rate (6.5 °C/min). The thin and bold grey lines highlight the onset of the gelatinization endotherm (T_{OGEL} from DSC) and the onset of pasting (PT from RVA), for the control sample, respectively.

comparisons of the temperature intervals of the events detected by the two techniques should be used with caution as differences inherent to the actual experimental techniques (sample size, mechanical shear, and starch concentration) are expected to have an effect. In spite of this, by comparing results from DSC and RVA experiments, a good overview can be obtained on the temperature range within which important thermal events take place during the temperature-induced pasting.

As shown in Fig. 5, the gelatinization transition of normal wheat starch takes place at temperatures well below those at which any dramatic changes in viscosity occur. On the other hand, the rapid, unrestricted swelling of the waxy starch granules which leads to a dramatic increase in viscosity, takes place within the temperature interval of the gelatinization transition. Despite such differences, for both normal and waxy wheat starch it can be observed that a lower (or higher) PT with respect to the control sample does not coincide with the occurrence of a lower (respectively higher) T_{OGEL} with respect to the control sample. This seems to indicate that no direct connection exists between the effect of different surfactants on the onset of the gelatinization transition (T_{OGEL}) and their effects on the onset of the pasting (PT).

For normal wheat starch the PT in the presence of most surfactants is found to occur either within or very close to the temperature interval of the dissociation transition of the AM–surfactant complex. Only in the presence of C_{12}TAB the PT is found to occur at much lower temperatures. Moreover, the same as for the PT of normal starch in the presence of all surfactants but the alkyl-TABs, the thermal properties of the AM–surfactant complexes (both T_{OCX} and ΔH_{CX}) exhibit a clear dependence on the surfactant chain length. These findings seem to suggest that the effect of most surfactants on the PT of normal wheat starch is linked to the nature of their interactions with AM (in particular, the dissociation temperature of the AM–surfactant complexes), and how these may affect the granule swelling and AM-leaching processes. The conformational changes that the AM fraction undergoes upon formation of complexes inside and/or at the granule surface may increase the internal bonding of the granules thereby restricting the swelling. Thus, once the AM–surfactant complexes begin to dissociate such constraints would disappear and the granule would swell unrestrained.

In waxy wheat starch, only charged surfactants tend to induce significant changes in the PT. Moreover, in contrast to what was observed in normal wheat starch, surfactant effects on the PT were rather small and no significant influence of the surfactant chain length was found. Under the premise that surfactants form complexes both with AM and AMP, such differences could be understood on the basis of the differences existing between the two types of complexes. In the case of AMP, only the outer branches of the clusters would have the possibility to form helical complexes with surfactants. Given the highly branched nature of the AMP molecule, the structural and/or conformational changes that surfactants would induce upon complexation could be expected to be minor compared to the ones that would take place in AM. Additionally, in AMP many of the characteristics of the complex would be fixed by the length of the AMP outer chains thereby perhaps dampening any possible influence of the surfactant chain length. While the surfactant chain length may not exert a strong influence on the characteristics the AMP-surfactant complex, an important effect could be expected to arise from the presence of charged head groups. Like-charge repulsions between the head groups that project from the ends of the AMP short chains could destabilize granules by expanding AMP crystallites thereby enhancing the swelling of the starch granule (Villwock et al., 1999).

It should at this point be mentioned that surfactants like SDS (i.e., C_{12}Sulph, according to the notation used in this study) have been found to be very effective in removing starch granule surface proteins and lipids (Debet & Gidley, 2006; Nierle, El Baya, Kersting, & Meyer, 1990b; Seguchi, 1995; Seguchi & Yamada, 1989). Partial removal of surface protein and lipids (by means of SDS-treatments and other extraction methods) has in turn been found to result in an enhanced rate and extent of granule swelling (Debet & Gidley, 2006; Han, Campanella, Guan, Keeling, & Hamaker, 2002; Maningat & Juliano, 1980; Melvin, 1979; Nierle et al., 1990b; Tester & Morrison, 1990). It is not known whether the ability to solubilise surface proteins and lipids is specific for a surfactant such as SDS. Moreover, the available experimental evidence does not allow to assess the extent to which a surfactant like SDS can remove surface proteins and lipids at the levels of surfactant concentration used in the present study or under the conditions imposed by RVA pasting experiments. In consequence, it cannot be ruled out whether the ability to solubilise surface granule proteins and lipids contributes to the effects found to be produced by different surfactants on the swelling properties of wheat starch. Moreover, a special ability to interact and solubilise surface proteins and lipids may explain the puzzling effect that both the C_{12}TAB and the C_{16}TAB had in normal wheat starch. These surfactants were found to have a strong swelling/AM-leaching-enhancing effect that neither correlates with the dissociation transition of the AM–surfactant complex nor seems to be linked to a particularly strong granule-destabilizing effect (as judged by the results provided by the calorimetric experiments). Systematic studies of the effect of surfactant structure on their ability to interact with and solubilise surface proteins and lipids would be required to clarify this.

4. Conclusions

Pasting studies revealed that the effect of most of surfactants on the onset of pasting (PT) of normal wheat starch suspensions is determined to a great extent by the surfactant chain length. On the contrary, the presence of a charged head group is the factor that seemed to play the most important role in the case of waxy wheat starch. Regardless of their chain length, all charged surfactants lowered the PT of waxy wheat starch while non-charged surfactants had small, in some cases negligible, effects on PT. Calorimetric studies showed that for a given type of starch, no general trends exist regarding the influence of the surfactant chain length or the presence of a charged head group on the overall effect of surfactants on the onset of the gelatinization transition (T_{OGEL}). Moreover, no direct correlation was found to exist between the effect of surfactants on T_{OGEL} and PT.

The PT of normal wheat starch in the presence of all the studied surfactants, except the alkyl ammonium bromides, fell either within or very close to the temperature range within which the thermal transition associated to the dissociation of the AM–surfactant complex takes place. Consequently, the effect of surfactants on the PT of normal wheat starch is suggested to be linked to the dissociation of the AM–surfactant complexes. We cannot rule out the occurrence of interactions between surfactants and starch granule components other than AM and AMP (e.g., surface proteins and lipids) which could contribute to the effects induced on the pasting behaviour of starch. Interactions of such nature may be behind the puzzling swelling-enhancing effect produced by both the short- and long-chain alkyl ammonium bromides in normal wheat starch.

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