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On the Effects of Surface Active Agents on the Gelatinization of Starch — a Calorimetric Investigation

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SUMMARY

Differential scanning calorimetry (DSC) was used to study how the gelatinization process of starch is affected by the presence of surface active agents. A decrease in gelatinization enthalpy was observed, which was explained by an exothermic formation of amylose–lipid complexes during the gelatinization. It was also found that certain substances (sodium dodecyl sulphate and lysolecithin) made the gelatinization occur earlier, whereas another (sodium stearoyl lactylate) delayed the gelatinization. The results showed further that the phase behaviour of the surface active agent greatly affected the amount of complex formed, and also that the source of starch affected this amount. It was found that the complex formation occurred more easily in wheat starch than in potato starch.

INTRODUCTION

It is well known that polar lipids, added as well as native, greatly affect the rheological behaviour of starch (Chichester & Sterling, 1957; Osman & Dix, 1960; Krog, 1973; Melvin, 1979; Ghiasi *et al.* 1982*a*). It has also been observed that the swelling of starch granules (Collison *et al.*, 1960; Gray & Schoch, 1962; Ghiasi *et al.*, 1982*b*; Eliasson, 1985*a*), the amylose leaching during gelatinization (Gray & Schoch, 1962; Ghiasi *et al.*, 1982*b*; Eliasson, 1985*a*) and the retrogradation of starch (Krog & Nybo Jensen, 1970; Lagendijk &

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Pennings, 1970; Russell, 1983) are all affected by the presence of polar lipids. These effects are usually attributed to the formation of the amylose–lipid complex, although it is not known if the course of gelatinization is affected by the complex formation. The gelatinization process is basically an order–disorder transition, which could be regarded as a water-mediated melting of the crystalline regions in the starch granule (Donovan, 1979). This melting results in the disappearance of the birefringence of starch granules observed in the polarizing microscope and in the disappearance of the X-ray diffraction pattern. The gelatinization has been thoroughly studied by differential scanning calorimetry (DSC) where the gelatinization is observed as an endothermic transition, and the gelatinization temperature range and enthalpy have been reported for several starches (Stevens & Elton, 1971; Donovan, 1979; Wootton & Bamunuarachchi, 1979; Biliaderis *et al.*, 1980; Eliasson, 1980; Evans & Haisman, 1982). In a few investigations DSC has been used to study the gelatinization of starch in the presence of added surface active agents, and the gelatinization ethalpy has been reported to increase (Hoover & Hadziyev, 1981), decrease (Kugimiya & Donovan, 1981; Gough *et al.*, 1985) or to be unaffected (Eliasson *et al.*, 1981).

The presence of the amylose–lipid complex is observed on the DSC thermogram as an endothermic transition at temperatures above the gelatinization temperature range (Kugimiya *et al.*, 1980). It is known that this transition temperature depends on the complexing agent, and it is affected by fatty acid chain length, unsaturation and the nature of the polar head (Stute & Konieczny-Janda, 1983; Biliaderis *et al.*, 1985; Eliasson & Krog, 1985; Kowblansky, 1985; Morrison, 1985). The complex formation ability, i.e. the amount of complex formed under certain conditions, is related to the phase behaviour of the complexing agent (Larsson, 1980; Krog & Riisom, 1984).

In one single DSC experiment it is thus possible to obtain information concerning both the gelatinization of the starch and the presence of the amylose–lipid complex. Although a great deal of work has been done in the field an unambiguous explanation of how surface active agents affect the starch gelatinization has not emerged. One reason for this might be that different studies are difficult to compare due to the various experimental conditions used. For example, the complex forming ability (i.e. during the heating in the DSC) of different starches is not known. It is well known that different surface active agents differ

in their ability to form complexes with amylose in solution (Krog, 1971), although the complex formation ability during the conditions in the DSC is not systematically investigated. In the present investigation DSC was used in order to obtain more information concerning the effects of added surface active agents on the gelatinization of starch. Also, the significance of such parameters as type of starch, and type of surface active agent and its phase behaviour was looked into. Wheat starch and potato starch were compared as these starches differ in their native lipid content. Wheat starch contains about 1% lipids, mainly lysolecithin, whereas potato starch is essentially lipid free (Acker & Schmitz, 1967). The surface active agents used were selected to represent different phase behaviours and they also included anionic as well as cationic substances.

MATERIALS AND METHODS

Materials

The starches investigated were potato starch (a commercial sample, Stärkelsen, Sweden) and wheat starch (prepared from the Swedish spring wheat Amy according to the method of Meredith *et al.* (1978)). The emulsifiers and surfactants used were sodium dodecyl sulphate (SDS) (BDH Chemicals Ltd, England), cetyltrimethyl ammonium bromide (CTAB) (BDH Chemicals Ltd, England), sodium stearoyl-2-lactylate (SSL) (Artodan SP50; Grindsted Products, Denmark), saturated monoglycerides (SMG) (Dimodan PVP, fatty acid composition: 55% palmitic acid and 45% stearic acid; Grindsted Products, Denmark), lysolecithin (L-α-lysophosphatidylcholine from egg yolk, primarily palmitic and stearic acids; Sigma, USA), and lecithin (Epicuron 200; Lucas Meyer, Federal Republic of Germany). The water used was distilled and deionized.

Addition of surface active agents to the starch

SDS, CTAB and lysolecithin were used as micellar solutions. SSL and SMG were mixed with water (1:10), heated to 70°C to obtain the lamellar liquid crystalline phase, then allowed to cool before the addition to starch (i.e. the gel state was added). Lecithin was shaken with

water (1:20) at room temperature until a homogeneous dispersion of the lamellar liquid crystalline phase was obtained.

One hundred milligrams of starch were weighed into a test tube and the proper amount of the lipid preparations described above was added to give 5% lipids calculated on starch dry weight. CTAB was also added at 1, 10 and 20% levels. When necessary, extra water was added to give the starch:water ratio of 1:3. The content of the test tube was mixed with a spatula and the sample was allowed to equilibrate overnight.

DSC

An aliquot of the starch suspensions described above was transferred to a preweighed DSC pan (coated aluminium sample pans, Du Pont, Wilmington, USA) which was sealed and reweighed. The amount of sample was usually in the range 8–10 mg. The dry matter content was determined in each individual pan after the DSC scan by puncturing and drying the pan at 105°C for 16 h. The sample pan was put in the DSC (a Perkin-Elmer DSC-2) at 22°C with an empty sample pan as a reference. The heating rate used was 10°C min^{-1} and the upper temperature limit was usually 112°C. The transition temperatures and enthalpies were calculated by a computer program constructed for evaluating DSC measurements. The baseline under the peak was fitted to the baseline before and after the peak with an exponential equation, and the curve was recalculated to this new baseline. The transition temperatures were determined as the intersection between the baseline and the low temperature side of the endotherm (T_0), and as the temperature at peak maximum (T_G or T_{CX}). Each reported value is the mean and standard deviation of five measurements.

RESULTS AND DISCUSSION

Examples of the DSC thermograms obtained for wheat starch in the presence of the different surface active agents are given in Fig. 1, and the corresponding thermograms for potato starch are given in Fig. 2. The gelatinization endotherm was observed around 60°C, and the transition due to the amylose–lipid complex somewhere between 80 and 115°C, depending on the additive. In case of SSL and SMG a

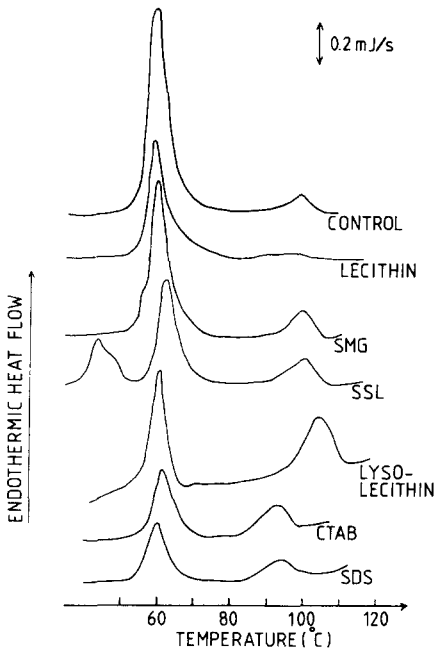

Fig. 1. DSC thermograms of wheat starch in the presence of certain surface active agents (the thermograms are the original recorder traces).

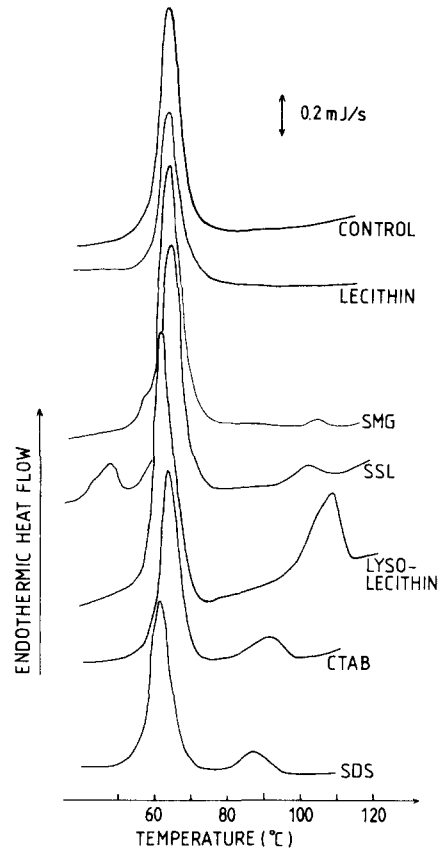

Fig. 2. DSC thermograms of potato starch in the presence of certain surface active agents in excess water (the thermograms are the original recorder traces).

peak due to the chain melting (Krog & Lauridsen, 1976) of these additives was also obtained at the low temperature side of the gelatinization endotherm (Figs 1 and 2). This means that the endotherm for gelatinization of starch in the presence of SMG could not be separated from the endotherm related to the lipid, whereas in the case of SSL these peaks seemed to be separated well enough to make it possible to calculate the gelatinization enthalpy. The phase behaviour of the surface active agent must thus be known (e.g. from phase diagrams) in

order to make a correct interpretation of the DSC thermogram. When the phase transition involves a chain melting, as in the case of SSL and SMG discussed above, the enthalpy involved is high enough to contribute significantly to the ΔH_G value calculated, even at low levels of addition. For the transition β-crystals → lamellar phase in the glycerol–monostearin–water system a ΔH value of 194 J g^{-1} lipid has been reported (Eliasson & Krog, 1985). Transitions between different liquid-crystalline phases represent much lower enthalpy values (1 J g^{-1} lipid for the transition hexagonal II → L2 according to Eliasson & Krog (1985)), and might thus not influence the ΔH_G value at low levels of addition. Before the gelatinization process is discussed, the presence of the amylose–lipid complex, as observed from the DSC thermogram, will be discussed.

The presence of amylose–lipid complexes

The presence of the amylose–lipid complex after gelatinization was observed on the DSC thermogram as an endothermic transition in the temperature range 80–115°C (Figs 1 and 2). The corresponding temperatures (T_{CX}) and enthalpies (ΔH_{CX}) are given in Table 1. When the native starches were compared it was observed that the wheat starch gave the complex transition whereas potato starch did not (Table 1). This is to be expected as wheat starch contains lipids, whereas potato starch does not (Acker & Schmitz, 1967).

The transition temperature (T_{CX}) of the amylose–lipid complex was found to depend on the surface active agent with SDS and CTAB giving the lowest value and lysolecithin giving the highest T_{CX} value. The results in Table 1 are consistent with results obtained in other investigations (Biliaderis *et al.*, 1985; Eliasson & Krog, 1985; Kowblansky, 1985; Morrison, 1985), and show that T_{CX} increased with increasing chain length (e.g. SDS and lysolecithin), and by the presence of a charged group (for example, SMG compared with lysolecithin). Further, the T_{CX} values seemed also to be related to the starch as the T_{CX} value obtained for the SDS complex was lower in potato starch than in wheat starch, whereas SMG and lysolecithin gave higher values in potato starch than in wheat starch. CTAB and SSL gave similar T_{CX} values in both wheat and potato starch. The T_{CX} values observed for wheat starch in the presence of additives were thus closer to the T_{CX} value in the native starch. It could also be

observed that the diacyl-lipid included in the investigation, lecithin, apparently affected the complex in wheat starch, as T_{CX} was lowered in the presence of lecithin. In the case of potato starch no complex formation seemed to occur between the lecithin and the amylose. This might be expected as the complex formation ability of diacyl-lipids is poor (Osman & Dix, 1960; Krog, 1971). However, if another type of complex is present, as the lysolecithin complex in wheat starch, lecithin evidently has some effect.

TABLE 1

Transition Temperatures (T_{CX}) and Enthalpies (ΔH_{CX}) of the Transition of the Amylose–Lipid Complex when Wheat and Potato Starches are Heated in the Presence of Certain Surface Active Agents (Starch : Water Ratio is 1 : 3)

Additive[a]	*Wheat starch*		*Potato starch*	
	T_{CX} (°C)	ΔH_{CX} (J g^{-1} dry matter)	T_{CX} (°C)	ΔH_{CX} (J g^{-1} dry matter)
—	100·5 ± 0·6	1·33 ± 0·21	—	—
SDS	94·2 ± 0·5	4·40 ± 0·59	88·6 ± 1·7	1·84 ± 0·13
CTAB	92·8 ± 0·5	4·41 ± 0·15	91·9 ± 0·5	2·05 ± 0·15
SSL	100·3 ± 1·4	2·72 ± 0·50	101·9 ± 0·3	0·42 ± 0·46
SMG	100·2 ± 0·5	2·26 ± 0·17	104·8 ± 0·8	0·34 ± 0·04
Lysolecithin	104·6 ± 0·3	6·36 ± 0·56	109·7 ± 0·5	5·91 ± 0·28
Lecithin	96·9 ± 1·9	0·88 ± 0·13	—	—

[a] 5% calculated on starch dry weight.

The ΔH_{CX} values given in Table 1 are of course proportional to the amount of complex present. However, it is not possible to simply compare the different ΔH_{CX} values in order to obtain the complex formation ability of the different surface active agents, as the ΔH_{CX} values depend both on the complexing agent (Eliasson & Krog, 1985; Kowblansky, 1985; Morrison, 1985) and on the conditions during the complex formation (Stute & Konieczny-Janda, 1983; Björck *et al.*, 1984). In the present investigation, where the complexes presumably have formed during the heating in the DSC, it might be expected that all complexes have been formed during similar conditions, and it should thus be possible to compare the same additive in wheat starch and in potato starch. The conclusion might then be drawn that the complex formation occurred to a greater extent in wheat starch than in

potato starch, as the ΔH_{CX} values measured for wheat starch were greater than the corresponding ΔH_{CX} values for potato starch even when the ΔH_{CX} of the native wheat starch was compensated for. The amount of surface active agent used was chosen to give as much complex as possible without giving an excess of free, uncomplexed lipid, as this might influence the thermal behaviour of the complex (Eliasson, 1985*b*; Eliasson & Krog, 1985). For the potato starch–lysolecithin complex it has been observed that if ΔH is plotted versus the ratio lysolecithin/starch a plateau value is reached at about 0·07 (Kugimiya & Donovan, 1981). As an excess of lipid had to be avoided, 5% (w/w) of the additives were used. The degree of complex formation at this level of addition was checked for CTAB which was added also at other levels, and the curve of ΔH_{CX} against the level of CTAB is given in Fig. 3. It is observed that 5% CTAB complexed completely with the available amylose in wheat starch, as an increased addition of CTAB did not increase the ΔH_{CX} value. In the case of potato starch about 10% of CTAB had to be added to complete the complex formation.

The ΔH_{CX} values obtained for different starches in excess of lysolecithin have been compared with the ΔH_{CX} value of the amylose–lysolecithin complex in order to obtain the percentage of amylose in the starch (Kugimiya & Donovan, 1981). Similar calculations were made for the present results with ΔH_{CX} values for the com-

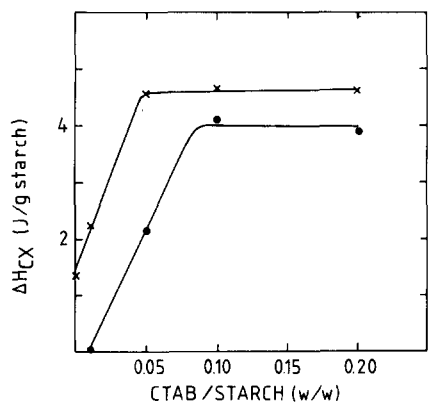

Fig. 3. The enthalpy of the starch–CTAB transition at different levels of CTAB added to starch at a water-to-starch ratio of 3:1: ×——× wheat starch; ●——● potato starch.

TABLE 2
The Percentage of Complexed Starch after Gelatinization in the Presence of Certain Surface Active Agents

Additive[a]	ΔH *of complex* ($J\ g^{-1}$ *complex*)	ΔH_{CX}[b] *wheat starch* ($J\ g^{-1}$ *starch*)	ΔH_{CX}[b] *potato starch* ($J\ g^{-1}$ *starch*)	*% Complexed starch*	
				Wheat	*Potato*
—	24·7[c]	1·33	0	5	0
Lysolecithin	24·7[c]	6·68	6·21	27	25
SMG	32·7[d]	2·37	0·36	7	1
CTAB, 5%	19·5[e]	4·63	2·15	24	11
CTAB, 10%		4·64	4·08	24	21
CTAB, 20%		4·57	3·88	23	20

[a] The amount of additive is 5% calculated on starch weight unless otherwise specified.
[b] ΔH_{CX} values from Table 1 are compensated for the weight of surface active agent present.
[c] Lysolecithin from Kugimiya & Donovan (1981).
[d] Dimodan PM from Eliasson & Krog (1985).
[e] CTAB–amylose complex.

plexes taken from the literature, and the results are given in Table 2. These results indicate that in wheat starch the complex formation is more or less complete in the presence of CTAB and lysolecithin, whereas SMG gave a very low complex formation during the present conditions. These results illustrate the importance of the phase behaviour of the additive. SMG gives liquid-crystalline phases at the actual temperatures, and due to the low monomer concentration (about 10^{-6} M according to Krog *et al.* (1985)) a very low amount of complex was formed. The additives forming micelles, where the monomer concentration is much higher, gave a larger amount of complex. The results in Table 2 show that it is possible to detect 1% of complexed starch by DSC. In order to obtain this amount, more of the surface active agent had to be added to potato starch than to wheat starch, as 1% CTAB gave an increase in ΔH_{CX} observed for wheat starch whereas no transition could be observed for potato starch at this level of addition (Fig. 3). With the values obtained for CTAB (Fig. 3 and Table 2) the amylose content of wheat starch could be calculated to 24%, and that of potato starch to 20%. These values are lower

TABLE 3
Gelatinization Enthalpies (ΔH_G) and Temperatures (T_0 and T_G) for Wheat and Potato Starches in the Presence of Certain Surface Active Agents (Starch : Water Ratio is 1 : 3)

Additive[a]	*Wheat starch*			*Potato starch*		
	T_0 *(°C)*	T_G *(°C)*	ΔH_G *(J g^{-1} dry matter)*	T_0 *(°C)*	T_G *(°C)*	ΔH_G *(J g^{-1} dry matter)*
—	57·0 ± 0·2	61·3 ± 0·5	12·7 ± 0·3	58·2 ± 0·3	63·7 ± 0·2	17·0 ± 0·4
SDS	54·7 ± 0·2	60·1 ± 0·3	9·51 ± 1·17	55·4 ± 0·1	60·8 ± 0·4	13·9 ± 0·8
CTAB	57·6 ± 0·2	61·7 ± 0·2	8·55 ± 0·25	58·6 ± 0·3	63·9 ± 0·3	14·1 ± 0·1
SSL	58·4 ± 0·4	62·3 ± 0·5	10·3 ± 0·63	59·5 ± 0·6	64·2 ± 0·9	17·9 ± 0·4
SMG	56·7 ± 0·5	60·5 ± 1·0	12·8 ± 2·2	58·8 ± 0·2	63·3 ± 0·3	17·8 ± 0·3
Lysolecithin	55·7 ± 0·2	60·6 ± 0·3	7·50 ± 0·25	57·8 ± 0·5	63·4 ± 0·3	15·8 ± 0·7
Lecithin	56·7 ± 0·4	60·8 ± 0·2	12·2 ± 0·3	59·1 ± 0·1	63·7 ± 0·2	18·1 ± 0·1

[a] 5% calculated on starch dry weight.

than the corresponding results obtained for lysolecithin. These discrepancies might be related to the nature of the endothermic transition (see below) and further investigations are needed in order to elucidate if it is possible to use this method for determination of the amylose content in starch.

The gelatinization process

The gelatinization enthalpies (ΔH_G) and temperatures (T_0 and T_G) for wheat and potato starches in the presence of surface active agents are given in Table 3. When the gelatinization temperatures were compared the additives seemed to fall into three groups depending on their effects: SDS and lysolecithin decreased both T_0 and T_G, SSL increased the gelatinization temperature whereas the effects of lecithin and CTAB were very minor. SMG was not included in this comparison as ΔH_G calculated in this case would also include the phase transition of the surface active agent. These results are in agreement with earlier findings from microscopy studies (Collison *et al.*, 1960; Ghiasi *et al.*, 1982*b*; Eliasson, 1985*a*).

The effect of the additives on the gelatinization enthalpy (ΔH_G) was to decrease these values, except in the case of lecithin which seemed not to affect ΔH_G (Table 3). The decreasing effect was greatest in wheat starch, paralleling the greater amount of complex formed in this starch (Table 2). When the level of additive was increased, as in the case of CTAB, ΔH_G reached a plateau value (Fig. 4).

The most obvious explanation for the decrease in ΔH_G values is perhaps an exothermic complex formation occurring during the gelatinization. If the enthalpy of the transition of the amylose–lipid complex (ΔH_{CX}) is supposed to equal the enthalpy of the exothermic complex formation, the sum of ΔH_G and ΔH_{CX} should be equal in all cases. Such a result was obtained by Kugimiya & Donovan (1981), and this is also what is obtained if the ΔH_{CX} values from Table 1 are added to the ΔH_G values in Table 2, except in the case of potato starch and lysolecithin. However, it is not completely clear what the transition represents (Kugimiya *et al.*, 1980; Stute & Konieczny-Janda, 1983; Eliasson, 1985*b*), and ΔH_{CX} need not equal the exothermic complex formation. It is thus not possible from the DSC measurements alone to rule out other possibilities which could cause a decrease in ΔH_G, such as, for example, a lower degree of gelatiniza-

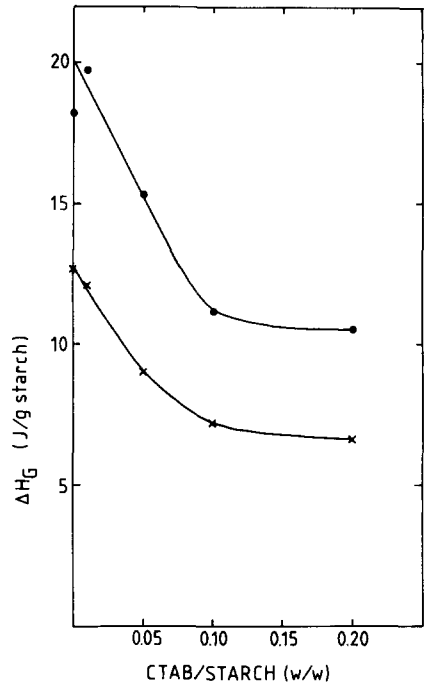

Fig. 4. The gelatinization enthalpy of starch in the presence of different levels of CTAB at a water-to-starch ratio of 3:1: ×——× wheat starch; ●——● potato starch.

tion due to an inhibited amylose leaching (Lindqvist, 1979; Larsson, 1980). Further, if the surface active agent destabilizes (Gough *et al.*, 1985) the crystalline regions in the starch granule, less energy might be needed during the heating to complete the gelatinization. These possibilities might be investigated by the X-ray diffraction technique as might also the exact temperature range for the complex formation, i.e. the formation of V-amylose might be followed during a heating sequence. However, it is only possible to study the complex formation by the X-ray diffraction technique if the complexes formed are arranged in crystalline arrays. In such a case the exothermic complex transition discussed above must also result from the crystallization of the complex. From the shape of the peaks on the DSC thermogram it can be concluded that the complex formation (and crystallization) must occur during a broad temperature interval coinciding with the gelatinization interval, as there were no signs of exothermic peaks

except in the case of lysolecithin (Figs 1 and 2). An exothermic peak after the gelatinization endotherm was observed also in the case of potato starch at higher levels of CTAB.

Any changes in ΔH_G observed in the presence of surface active agents must thus be interpreted with caution. When increased ΔH_G values are observed this might be due to phase transitions of the surface active agent present, whereas an unaffected ΔH_G value might be due to the fact that the level of addition is too low to be detected by the DSC (see Fig. 3). As discussed above a decrease in gelatinization enthalpy seems to be explained by the exothermic complex formation occurring during the gelatinization. However, certain substances seem to have the ability to delay the gelatinization, whereas others make the gelatinization occur earlier. These results are consistent with a model which relates the gelatinization not only to the total water content of the system but to the water content inside the starch granules (Evans & Haisman, 1982). The effects on the gelatinization temperature observed for the different surface active agents might thus be explained from their effects on the water transport into the granule.

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